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Electropolymerization of 2-hydroxybenzothiazole (2-OHBT) in water–methanol media: electrochemical behaviour in NaCl (3%) solution

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A new insulating thin polymer ($<0.1\,\mu$m) formed by the electropolymerization of 2-OHBT is reported. The anodic oxidation of 2-OHBT on copper, iron and platinum in alcohol and alcohol–water solutions are investigated using cyclic polarization and chronoamperometry. Scanning electronic microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) are performed to confirm the presence of the organic layer. Based on the results obtained, a model for the formation mechanism is proposed. The corrosion behaviour of the coated copper is studied in NaCl (3%) solution by impedance spectrometry and anodic polarization. The results of these experiments show a decrease in the dissolution of copper due to the barrier properties of the organic coating.

1. Introduction

Since the 1970s, much work has been directed to the electropolymerization *in situ* of a large number of monomers in either aprotic or aqueous media: in theory, this method might allow preparing, in one step, adherent coatings with low potential differences in comparison with the electrophoretic coating technique. The differences in the physico-chemical and electrochemical properties of polymer films formed by electropolymerization allow a variety of applications. Organic polymer films are either excellent insulators or behave as semiconductors or conductors. Some typical applications for conductive polymers are in antistatic equipment, electrocatalysis [1], electronics (transistors) [2], electrochromic display devices [3] and reversible batteries [4].

Among prospective applications, the anticorrosive properties of organic coatings deposited by electropolymerization have been studied by numerous investigators such as Mengoli [5–9] and Dubois-Lacaze [10–12]. Other aryl-type polymers such as polyaniline, polyxylene and polythiophene have been studied [13, 14]. However, the evaluation of their corrosion resistance has not been made. In most cases studies concern the protection of ferrous metals [6–9, 15]. To date, few papers have referred to the corrosion resistance of electropolymerized copper electrodes even though the relatively good resistance to corrosive agents is well known [6, 17]. Moreover, research concerning the corrosion resistance of copper has focused on heterocyclic organic inhibitors such as benzimidazoles [18], benzotriazoles [19] and benzothiazoles [20].

This paper deals with the feasibility of electro-oxidative polymerization of 2-OHBT metal anodes including iron (Fe), copper (Cu) and platinum (Pt). The corrosion resistance of coated copper in NaCl (3%) solution was investigated using classical electrochemical measurements.

2. Experimental details

2.1. *Chemical reagents*

0.3 M KOH used as supplied was the supporting electrolyte. Methanol was freshly distilled. Water was purified by means of a Millipore system. 2-OHBT (98%) was commercial product (Aldrich). The other compounds were commercially available reagent grade and were used without further purification.

2.2. *Electrodes*

For electrochemical runs, iron, copper and platinum electrodes were embedded in a chemically inert resin with $0.7\,\text{cm}^2$, $0.5\,\text{cm}^2$ and $0.1\,\text{cm}^2$ surface areas, respectively. For scanning electron microscopy (SEM) measurements, Fe and Cu plates with $2 \times 3\,\text{cm}^2$ surface areas were used. For all experiments the electrode was mechanically polished from a grade 400 up to a grade 1200, rinsed in deionized water and air dried.

2.3. *Apparatus and procedure*

The coating was performed at $25 \pm 1\,^\circ$C in a classical three electrode cell. The working electrode was either an embedded electrode (for electrochemical measurements) or a plate (for SEM measurements). The counter electrode was a large surface platinum (Pt) plate ($5\,\text{cm}^2$). A saturated calomel electrode (SCE) was used as a reference. In this work, all potentials were referred to the SCE.

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The polymer films were prepared by linear sweep voltammetry or by chronoamperometry. The experimental setup included a Taccussel (PRT-40-1) potentiostat assisted by a Taccussel (GSTP-3) signal generator. $i = f(E)$ and $i = f(t)$ curves were recorded on a Sefram recorder (X–Y–t). The films formed were rinsed ultrasonically with methanol and deionized water, then air dried.

The ability of solvents of different polarities to remove the passivating material from the electrode surface was tested by cyclic voltammetry using the following procedure:

(i) The clean copper electrode was cycled once in the electrolytic solution between the open circuit potential (E_{oc} −0.30 V vs SCE) and +1.7 V vs SCE. The electrodeposition was carried out until the current approached zero.
(ii) The coated electrode was removed from the cell, rinsed in methanol and air dried.
(iii) It was placed in the selected solvent ($T = 25\,^{\circ}\mathrm{C}$ or T° bp.) and vigorously stirred (30 s) in order to test its ability to remove the material on the electrode.
(iv) The electrode was rinsed in methanol, air dried, replaced in the electrolysis solution and cycled again.

First, it was verified that methanol removed no material from the electrode. The value of the ratio I_{p_2}/I_{p_1} represents the fraction of recovery activity where I_{p_1} and I_{p_2} are the peak current of the first cycle, respectively, before and after the solvent treatment. Scanning electron micrographs of the poly(2-OHBT) were obtained using a Cambridge Stereoscan 120 at an accelerating voltage of 30 kV. The poly(2-OHBT) films deposited on Fe or Cu electrodes were sputter-coated with about 10 nm of gold. The SEM was provided with a Kevex system which allowed energy-dispersive X-ray analysis. For the study of the electrochemical behaviour, the current–potential curves were obtained on bare and protected samples using an EGG potentiostat (model 173). The sweep rate was 0.5 mV s^{-1}. A.c. impedance data were obtained at the open-circuit potential using a Schlumberger 1250/1255 frequency response analyser (FRA) in combination with a 1286 electrochemical interface. The frequency range 10^5 Hz to 5×10^{-3} Hz was applied with an a.c. voltage signal varying by ±10 mV.

3. Results and discussion

3.1. *Preparation of polymer films*

3.1.1. Cyclic voltammetry. Experiments were conducted in a methanol–water (50 vol%) solution with 0.3 M potassium hydroxide before and after adding 2-OHBT (0.1 M). The voltammograms (Figs 1–3) were recorded during a linear potential sweep between the open circuit potential and +0.8, +1.5 and + 1.7 V vs SCE, respectively, on platinum, iron and

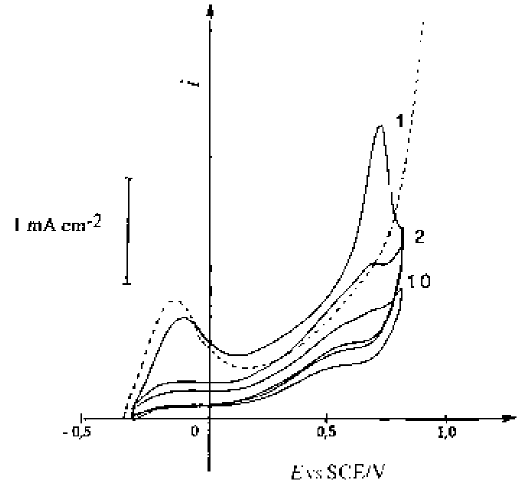


Fig. 1. Voltammetric current–potential curves obtained at a Pt electrode in (- - -) MeOH–H_2O(50–50)+KOH(0.3 M), (——) MeOH–H_2O(50–50)+KOH(0.3 M)+2-OHBT(0.1 M). Scan rate: 50 mV s^{-1}. 1, 2 and 10 refer, respectively, to the 1st, 2nd and 10th cycle.

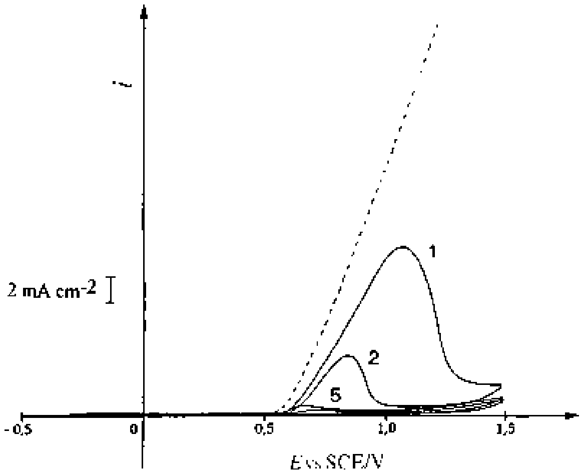


Fig. 2. Voltammetric current–potential curves obtained at a Fe electrode in (- - -) MeOH–H_2O(50–50)+KOH(0.3 M), (——) MeOH–H_2O(50–50)+KOH(0.3 M)+2-OHBT(0.1 M). Scan rate: 50 mV s^{-1}. 1, 2 and 5 refer, respectively, to the 1st, 2nd and 5th cycle.

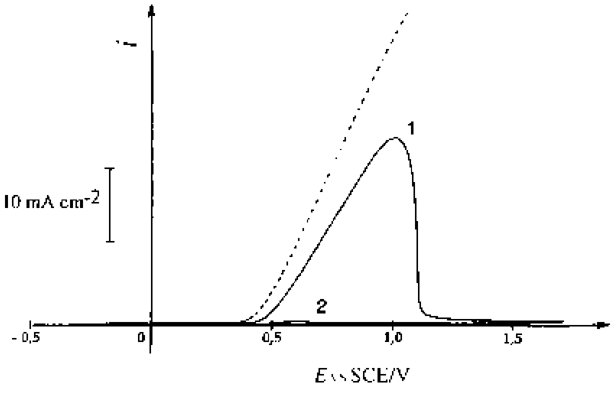


Fig. 3. Voltammetric current–potential curves obtained at a Cu electrode in (- - -) MeOH–H_2O(50–50)+KOH(0.3 M), (——) MeOH–H_2O(50–50)+KOH(0.3 M)+2-OHBT(0.1 M). Scan rate: 50 mV s^{-1}. 1 and 2 refer, respectively, to the 1st and 2nd cycle.

copper at 50 mV s^{-1}. It is worth noting that the same typical current–potential curves were obtained at 5 mV s^{-1}.

On the basis of the electrochemical curves, the following points are clarified:

(i) in the presence of 2-OHBT, a peak appears on Fe and Cu electrodes. This can be attributed to the electrooxidation of the organic compound.

(ii) During the reverse sweep, no cathodic current could be detected. This shows the irreversibility of the above oxidation phenomenon. The passage of a very low current in later cycles indicates partial blockage of the Fe or Cu electrode by an electroinactive film. This passivation phenomenon is characterized by the I_{p_2}/I_{p_1} ratio where I_{p_1} and I_{p_2} correspond to the value of the peak current during the first and the second anodic sweep, respectively. By taking this parameter into account, the passivation of the Cu electrode is by far the most efficient. In fact, during the second anodic sweep, the peak current diminishes by about 98% compared with its value measured in the first sweep.

(iii) for the platinum electrode, the *i*/*E* curve (Fig. 3) displayed two oxidation peaks. The peak located at 0.70 V vs SCE may be attributed to the electrooxidation of the monomer. The first peak potential was situated at −0.1 V vs SCE and was observed even without 2-OHBT. This peak corresponds to the oxidation of methanol [21]. 2-allylphenol is a common phenolic monomer whose oxidation in an alkaline medium is reported to give adherent coatings, especially on iron and copper, by electropolymerization [22]. We decided to compare the cyclic voltammetries recorded respectively on iron and copper with 2-OHBT and 2-allylphenol as the monomer under the same electrolysis conditions (Figs 4 and 5). It may be seen from these figures that the peak potentials are slightly higher for the 2-OHBT solution compared to the 2-allylphenol solution. At the same time, the peak current intensities in the 2-OHBT solution are twice the values measured in the 2-allylphenol solution. The oxidation barrier (E_b) corresponds to the potential beyond which very high anodic currents due to oxygen evolution and/or dissolution of the metal substrate are observed. Beyond the oxidation peak and until the oxidation barrier, the current with the phenolic monomer remains weaker compared to the values with the heterocyclic monomer. On both electrodes, the oxidation barrier is higher for the 2-allylphenol solution. These results suggest that the poly(2-OHBT) coatings have a less insulating character than the poly(2-allylphenol) coating in the electrolysis bath. However, the potential resistance of the Cu electrode coated with a poly(2-OHBT) film is quite satisfactory since no oxygen evolution is visible at potentials as high as +4.0 V vs SCE.

Visual observations of the coating on the Cu, Fe or Pt electrode reveal that the film is transparent and slightly red–brown coloured. The thickness of the film was estimated less than 0.1 μm by the interferometry technique.

The scanning electron micrograph of the poly(2-OHBT) film surface is shown in Fig. 6. The morphology appears to be granular rather than fibrous.

3.1.2. Chronoamperometry. The potentiostatic experiments were carried out on the three electrodes at the

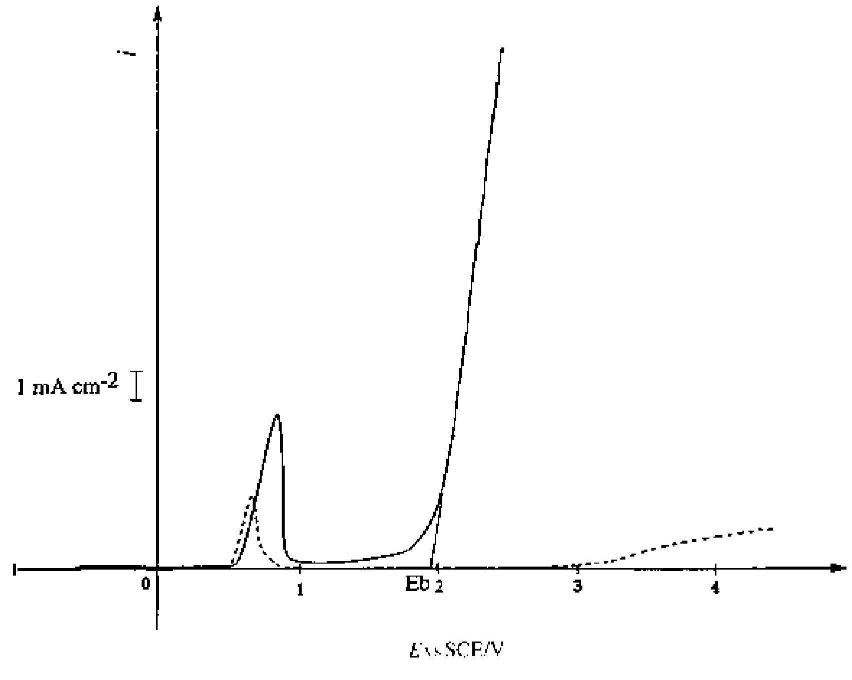


Fig. 4. CV at Fe in MeOH–H_2O(50–50)+KOH (0.3 M) (- - -) + *o*-allylphenol (0.1 M), (——) +2-OHBT (0.1 M). Scan rate: 5 mV s^{-1}.

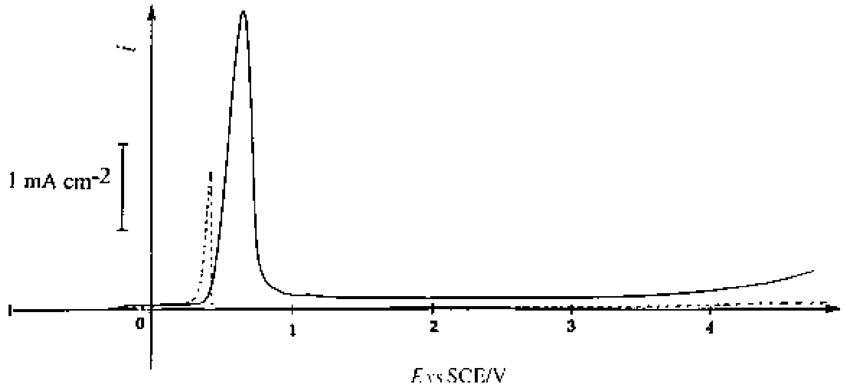


Fig. 5. CV at Cu in MeOH–H_2O(50–50)+KOH(0.3 M) (- - -) + *o*-allylphenol (0.1 M), (——) +2-OHBT (0.1 M). Scan rate: 5 mV s^{-1}.

potential of the oxidative peak attributed to the 2-OHBT, observed when sweeping the potential under the same electrolysis conditions as described in Figure 1 at 5 mV s^{-1}. The water/methanol ratio has been reported to affect the properties of electrosynthesized polymers such as poly(phenylene oxide) (PPO) [5]. We studied the effect of this parameter choosing either a water-methanol solution or a water-free solution. Figures 7, 8 and 9 illustrate the current decrease paralleling the formation of an insulating coating on Cu, Fe and Pt electrodes. From the values of the residual currents observed after 15 min electrolysis in the absence and presence of 2-OHBT namely *i*(a), *i*(b), *i*(c) and *i*(d) (Table 1), we can define the parameters τ_1 and τ_2 which reveal the inhibition efficiency of the coating in the electrolysis medium according to the following equations :

$$\tau_1 = \frac{i(\mathrm{a}) - i(\mathrm{c})}{i(\mathrm{a})} \times 100\ (\%) \text{ in the MeOH}-\mathrm{H_2O}\ (50\text{–}50)\text{solution}$$

and

$$\tau_2 = \frac{i(\mathrm{b}) - i(\mathrm{d})}{i(b)} \times 100\ (\%) \text{ in the MeOH}\ (100\%)\text{ solution}$$

Table 2 shows that the free water solution provides the most efficient passivation for Cu, Fe and Pt. If we consider that polymer precipitation is the main termination step of the electropolymerization mechanism, as with PPO [22], we should obtain higher polymers in methanol, a better solvent than water–methanol (50 vol%) solution, and as a result, a likely stronger passivation of the electrode.

As observed from the voltammetric data, the film formed on the Pt electrode shows relatively poor insulating characteristics particularly in the water–methanol solution compared to the high inhibition efficiency observed both on Fe and Cu electrodes. However, this result is qualified by the fact that in the free monomer solution, the chronoamperometric curve indicates that the platinum electrode is proba-

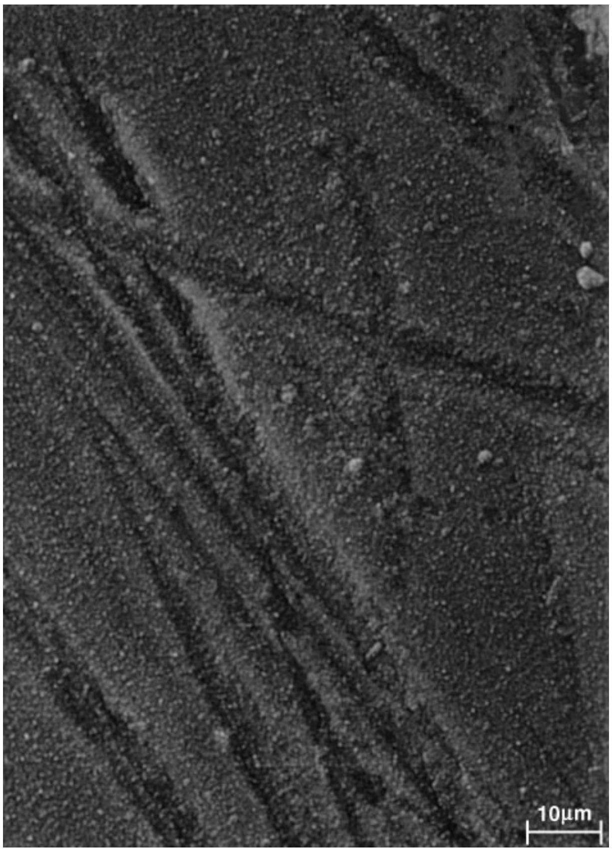


Fig. 6. Scanning electron micrograph of the poly(2-OHBT) film prepared by a potential sweep electrolysis at 50 mV s^{-1} on a Fe electrode. The electrolyte solution is the same as that used in Fig. 1.

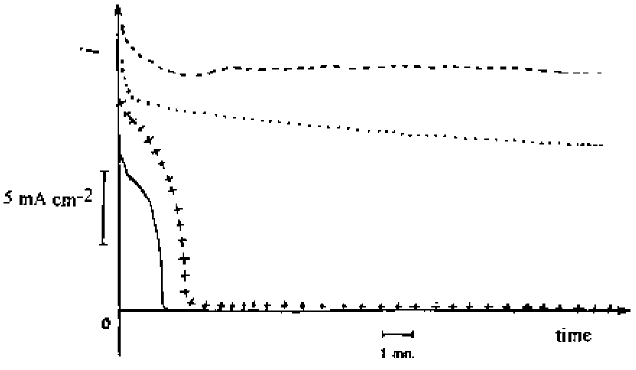


Fig. 7. Current transients at Cu in (- - -) MeOH–H_2O (50–50)+KOH(0.3 M), (······) MeOH+KOH(0.3 M), (+ + +) MeOH–H_2O(50–50) + KOH(0.3 M)+2-OHBT(0.1 M), (——) MeOH +KOH (0.3 M)+2-OHBT(0.1 M). $E = +0.77$ V vs SCE.

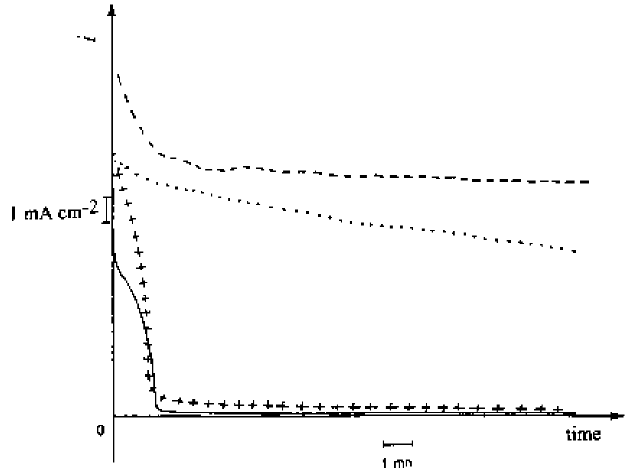


Fig. 8. Current transients at Fe in (- - -) MeOH–H_2O (50–50)+KOH(0.3 M), (·····) MeOH+KOH(0.3 M), (+ + +) MeOH–H_2O(50–50) +KOH(0.3 M)+2-OHBT(0.1 M), (——) MeOH + KOH (0.3 M)+2-OHBT(0.1 M). $E = +0.89$ V vs SCE.

Table 1. Residual currents after 15 min of electrolysis at the fixed peak potential obtained in (a) MeOH–H_2O (50–50)+KOH(0.3 M), (b) MeOH+KOH(0.3 M), (c) MeOH–H_2O(50–50)+KOH(0.3)+2-OHBT(0.1 M), (d) MeOH+KOH(0.3 M)+2-OHBT(0.1 M)

	Residual currents/μA cm^{-2} (*a*)	(*b*)	(*c*)	(*d*)
Cu	17000	11400	74	12
Fe	11200	7700	304	38
Pt	110	100	60	13

bly covered with a platinum oxide layer (PtO and/or PtO_2 according to Pourbaix [23]) which partly inhibits the solvent oxidation and, hence, reduces the contribution of the polymer coating to this inhibition.

3.1.3. Resistance to solvents. The value of the I_{p2}/I_{p1} ratio which is defined in the experimental section is plotted in Fig. 10 as a function of the solvent Hildebrand number [24]. The solvent testing shows that the material deposited on the electrode is best delaminated by a solvent with intermediate polarity (δ_0 12) and that none of the solvents provide a complete removal of the material. The partial insolubility of poly(OHBT) inhibits any molecular weight determination. DMSO is by far the best removal solvent. The effect of temperature is negligible for 'poor' solvents such as water, methanol or acetone but appears significative for 'good' solvents such as DMSO or *m*-cresol. If dissolution is not possible from a thermodynamic point of view, the best diffusion of the solvent into the polymer caused by an increase in temperature (a 'kinetic' factor) is not sufficient to totally remove the coating. The acid resistance was also tested with the same procedure. We observed a complete decomposition of the film in concentrated nitric acid or sulfuric acid, which both have a high oxidation ability, but not in hydrochloric nor hydrofluoric acid.

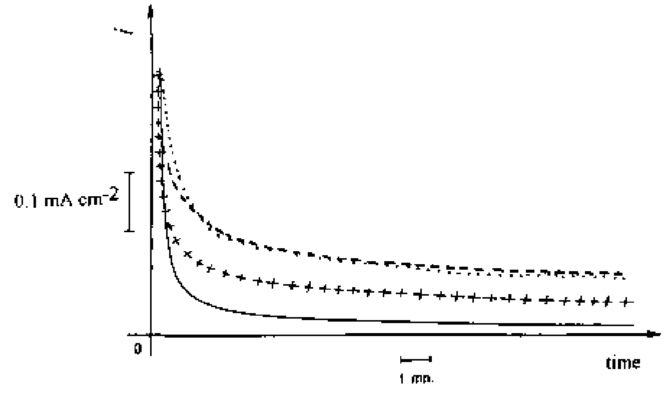


Fig. 9. Current transients at Pt in (- - -) MeOH–H_2O (50–50)+KOH(0.3 M), (····) MeOH+KOH(0.3 M), (+ + +) MeOH–H_2O(50–50)+KOH(0.3 M)+2-OHBT(0.1 M), (——) MeOH+KOH (0.3 M)+2-OHBT(0.1 M). $E = +0.67$ V vs SCE.

3.2. *Mechanism of formation*

The energy dispersive X-ray (EDX) spectrum of the electropolymerized iron and copper electrode exhibits a peak corresponding to sulfur. This result confirms the passivation of the surface by an organic polymer formed from the 2-OHBT monomer. The oxidation peak potentials change depending on the metal substrate, and are higher for non-noble metals. Moreover, the feasibility of the electropolymerization process onto an inert electrode (Pt) proves that metallic ions such as Cu^{2+} or Cu^{+} for the Cu electrode or Fe^{2+} for the Fe electrode do not necessarily intervene in the overall mechanism. On the basis of the above voltammetric data, the oxidation of the monomer during the coating formation competes with both the oxidation of the solvent and/or the metal substrate in the case of the Cu and iron electrodes. A hundred coatings were formed on Cu and Fe electrodes by cyclic voltammetry. The total copper or iron dissolved in the electrolytic bath were quantified by atomic adsorption. Results indicate that only 2–3% of the total current consumption is aimed at oxidizing copper or iron under metal ions in solutions. Moreover, for any organic electrochemical reaction to take place, the first step would be the adsorption of the reacting molecules. Thus, adsorption of 2-OHBT partly inhibits metal oxidation while still allowing other electrode reactions, such as oxygen evolution, owing to the high current consumption involved

Table 2. Inhibition efficiency of poly(2-OHBT) obtained for the electrolysis conditions defined in Table 1

	P_1/% (*in the water–methanolic solution*)	P_2/% (*in the methanolic solution*)
Cu	99.6	99.9
Fe	97.3	99.5
Pt	45.4	87.0

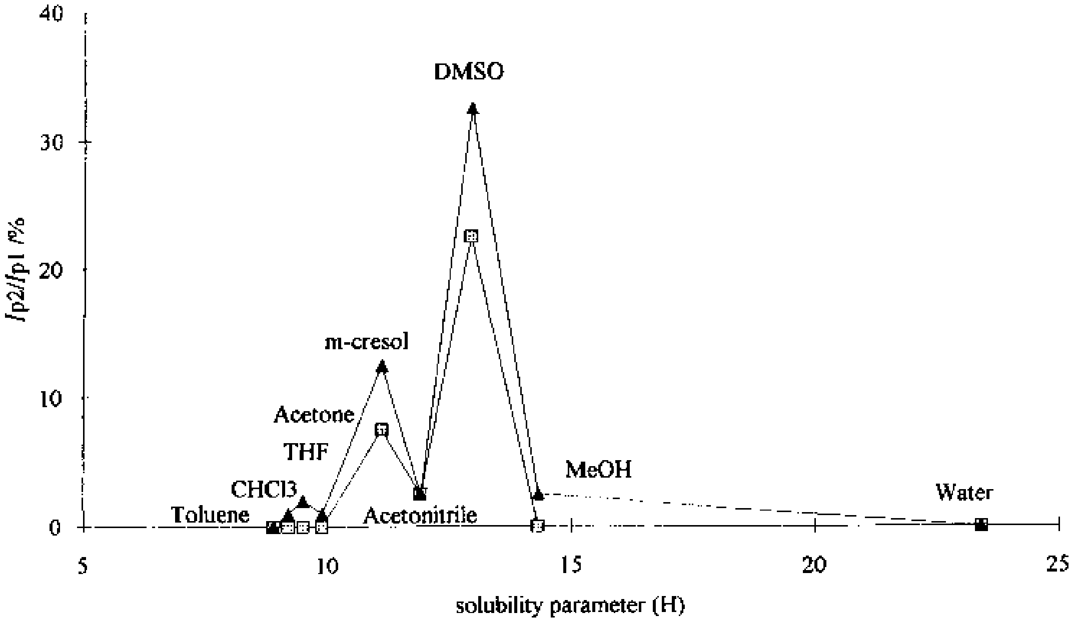


Fig. 10. The ability of various solvents to remove the passivating film. Key: (⊞) room temperature; (▲) boiling temperature.

during the electropolymerization process compared to the low thickness of the resulting coating. Furthermore, the electrolyte in the vicinity of the working electrode progressively developed a light yellowish colour. The relatively high current consumption can also be explained by the formation of soluble oligomers in the electrolysis bath during the electropolymerization process.

Based on the following discussion, scheme 1 has been proposed for the electropolymerization of 2-OHBT in an alkaline solution. When replacing the 2-OHBT monomer with benzothiazole, no insulating coating is formed on the metal substrate (Fig. 11). Thus, the polymerization of 2-OHBT takes place through its –OH group. 2-OHBT is in tautomeric equilibrium with the corresponding imino-(I) and oxo-(II) lines. In neutral solutions, 2-OHBT exists mainly in the Δ-thiazolin-2-one form (II) . It is quite stable and reacts mostly in addition–elimination reactions rather than undergoing ring opening reactions [25]. On the contrary, in alkaline solutions, both the enol type molecule (I) and the keto type (II) can lose a proton. The resulting anion is the same in both cases. Indeed, the enolate type compounds (III) and (IV) are only canonical form. The true structure of the enolate ion is a hybrid of (III) and (IV) but (III) contributes more, since in this form the negative charge is on the more electronegative atom (the O atom is more electronegative than the N atom). The first oxidation step involves the conversion of the deprotonated hydroxy compound (III) into the corresponding radical (V). Owing to the great stability of the thiazole ring [25], we can suppose that no ring-opening reaction follows the polymerization process. Consequently, the following step of the reaction probably consists in the propagation of the polymer building through the coupling reaction between the different canonical forms of the radical species (III). Among those coupling reactions, the O – O coupling leads to the reactive peroxy compound (VI). In contrast, the head to tail type coupling can lead to the building of a polymer. In fact, the dimer (VII) is formed; then, after the elimination of H^+ ion both oxidation and coupling can be repeated at each monomer addition. XPS and infrared analysis are in progress to confirm this proposal mechanism. The values of the inhibition efficiency (τ_1 or τ_2) obtained on Cu electrode, even in the water–methanol solution, confirm the interest in studying the protection against corrosion of a Cu electrode coated with a poly(2-OHBT) film. The poly(2-OHBT) was prepared by potentiostatic experiments in MeOH–H_2O (50–50) + KOH (0.3 M) + 2-OHBT (0.1 M) and was not thermal cured. The behaviour of the protected layer is investigated from the individual anodic polarization curves and a.c. impedance measurements in aerated 3% NaCl solution at room temperature.

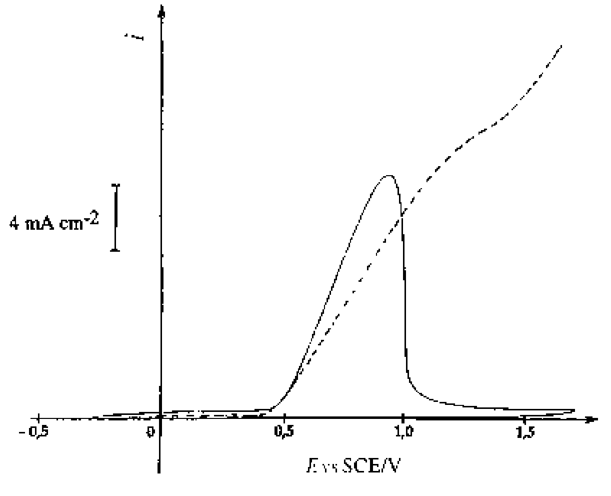
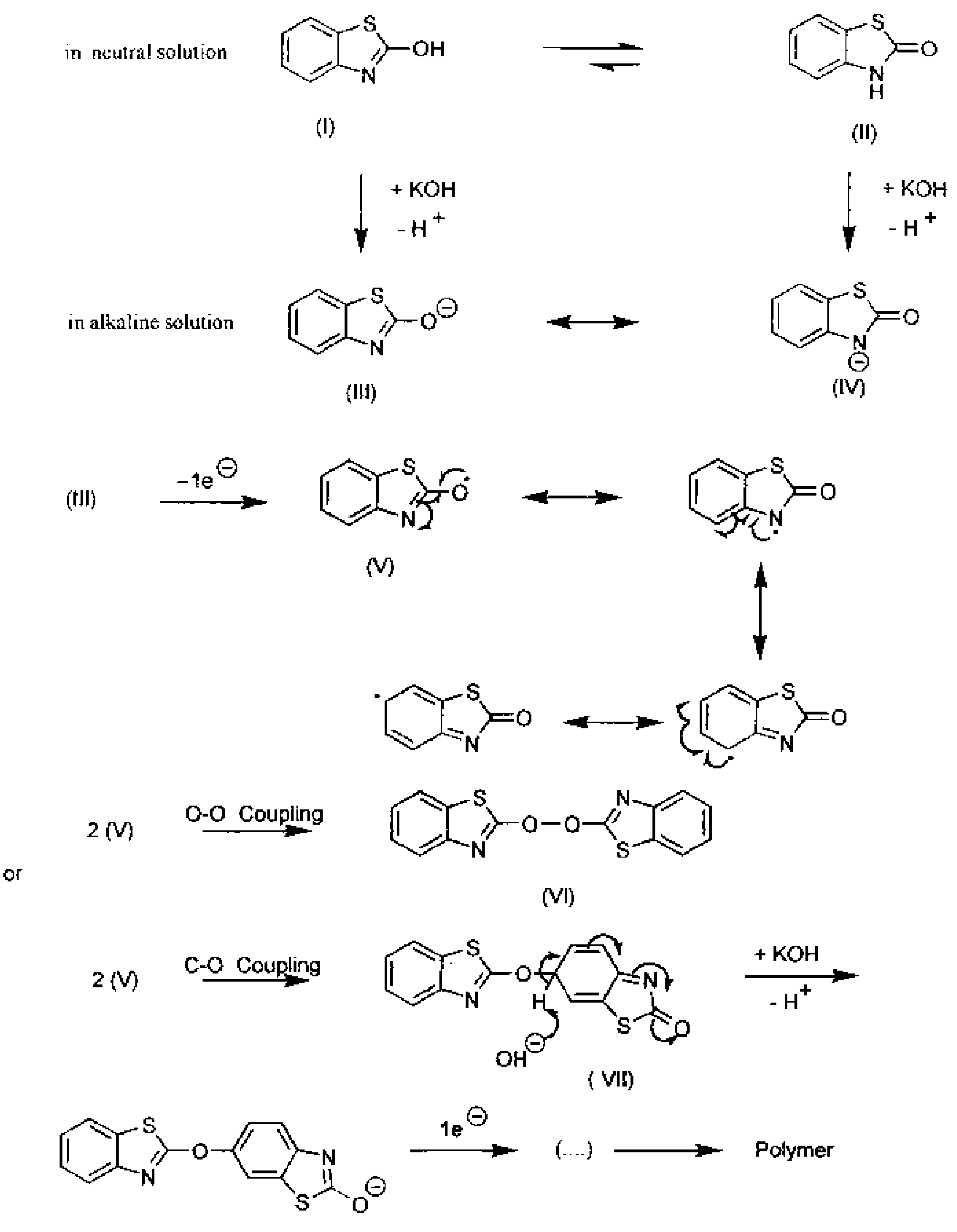


Fig. 11. CV at Cu in MeOH–H_2O (50–50)+KOH (0.3 M) (- - -) + benzothiazole (0.1 M), (——) + 2-OHBT (0.1 M). Scan rate: 50 mV s^{-1}.



Scheme 1

3.3. *Electrochemical measurements*

The corrosion process in the presence and absence of a protective layer is studied using individual anodic polarization curves and a.c. impedance measurements in aerated 3% NaCl solution at room temperature.

3.3.1. *Steady state measurements*

(a)*Anodic curves*

Figure. 12 shows typical anodic polarization curves obtained for film-free copper and coated copper in aerated NaCl media.

● *Uncoated copper*: In the potential range examined, there are four distinct regions for copper. This is in agreement with numerous electrochemical investigations [26–31]: (i) the apparent Tafel region (I), (ii) the peak current appeared at about −0.055 V vs SCE and the current minimum zone (II), (iii) the limiting current region (III), (iv) and the post limiting current region (IV). The Tafel slope d*E*/dlog *i*, on the Cu surface is equal to 2.3 *RT*/*F* and can be readily attributed to a one-electron transfer reaction [26–30]. Thus, if

$$Cu + 2Cl^- \rightarrow CuCl_2^- + e^-$$

is the predominant anodic dissolution reaction in the Tafel region as has been suggested [26], transport of Cl^- to, or of $CuCl_2^-$ away from, the surface is the rate determining step. Structural and composition analyses of the protective layer on the Cu electrode have been conducted by several investigators [32, 33]. It was concluded that the protective film comprises a relatively thick outer layer, mainly $Cu_2(OH)_3Cl$, and an inner thin layer containing appreciable chloride, oxygen and copper.

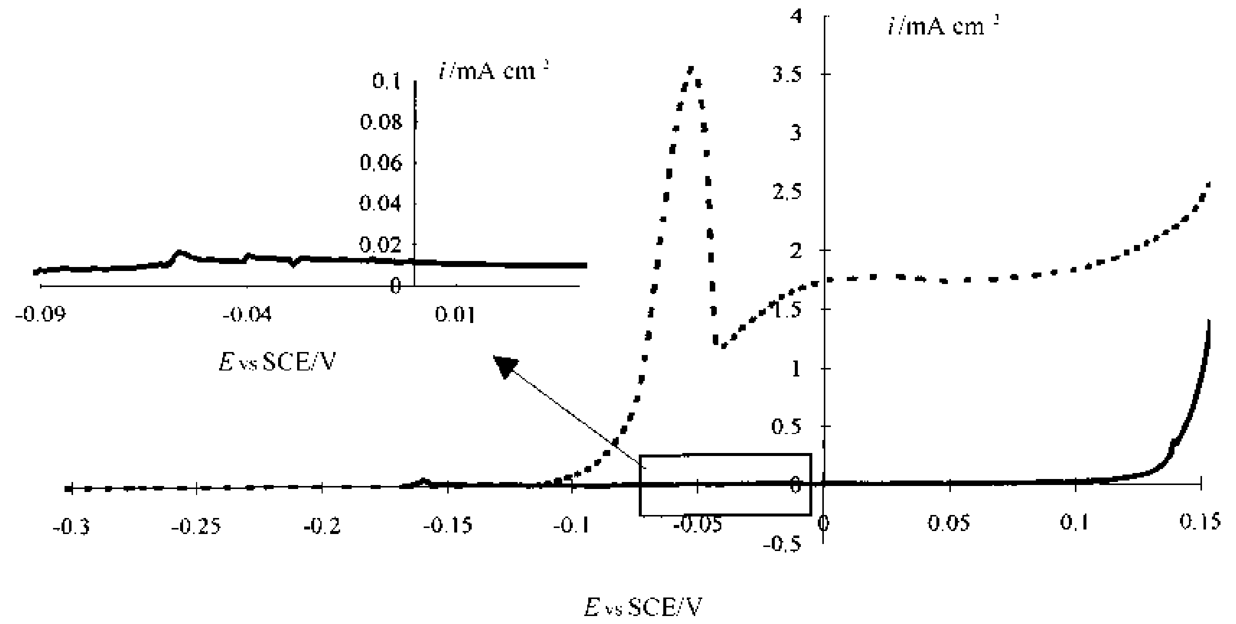


Fig. 12. Comparison of the anodic current–potential curves for (- - -) film-free Cu and (—) polycoated Cu electrodes in aerated NaCl (3%). Scan rate: 0.5 mV s^{-1}. (2-OHBT).

- *Copper coated with* (*poly2-OHBT*): The curve can be divided into only two zones: (i) 'passivation' region extending from −0.180 to 0.125 V vs SCE, (ii) 'transpassive' region extending above 0.125 V vs SCE. Corrosion seems to be suppressed with the poly(2-OHBT) film, thin ohmic barrier, as can be seen by the small current obtained. The current peak observed with Cu samples is strongly reduced with the coated specimens. Indeed, at 0.055 V vs SCE, the density current measured for the free film copper is 3.4 mA cm^{-2} to 14 μA cm^{-2} for the coated copper. The organic film layer restricts the anodic current at any given potential. The decrease is greater the longer the free-corrosion period. The decrease in current is rather large at high anodic potentials. However, the electrodissolution rate is two orders of magnitude smaller with a protective film. The polarization curve also shows that the protective properties of the film decays to higher values (about 0.150 V vs SCE) attributed to deterioration of the film.

(*b*) *Corrosion potential*

The corrosion potential of a Cu electrode in aerated 0.5 M NaCl solutions, after an initial cathodic decay during the first hour (−0.220 to −0.250 V vs SCE), becomes less negative for longer exposure times (−0.240 V vs SCE). The reverse of the trend can be attributed to the protective effect of the corrosion product layer on the limiting corrosion processes. The potential of a film coated Cu electrode is more positive at the beginning of exposure (−0.125 V vs SCE) than the Cu electrode. Then it shifts toward negative potentials after 2 h. For longer times, it oscillates between −0.225 and −0.235 V vs SCE. The low protectiveness shown by the film could be attributed to its thinness ($e < 0.1$ μm).

3.3.2. Unsteady measurements.

To better evaluate film quality, impedance measurements were performed at the free corrosion potential as a function of immersion time. Figures 13 and 14 present respectively typical complex plane plots of the impedance of a polymer coated Cu substrate and an uncoated Cu substrate. In Fig. 13, on initial exposure up to 50 min, the semicircular portion represents the response of the polymer coating consisting of the capacitive contribution from C_c, the capacitance of the coating, and a resistive element ($R_p^\circ + R_e$), at the lowest frequencies. The resistance R_p° due to the penetration of the electrolyte has been called 'pore resistance' [34–36]. The resistance R_e has been attributed to the test electrolyte. With further exposure time, the impedance diagram shape changes and we observed a decrease in R_p° with exposure time due to damage to the coating and the formation of conducting paths. The resistance R_p°, obtained after 10 min of immersion, is equal to $9.3 \times 10^3\ \Omega\,\mathrm{cm}^2$, then decreases to $1.7 \times 10^3\ \Omega\ \mathrm{cm}^2$ after 50 min. It stabilises for longer immersion times. At lower frequencies, a general impedance, Z_f, can be defined by a transfer resistance, R_t, corresponding to corrosion reactions, in series with a Warburg impedance, W, which may result from diffusion. The data demonstrate that the spectra are compressed. It was pointed out [37] that the interpretation of plots of a shape of the flattened semicircle might prove extremely difficult because of various reasons causing such a response. One of them may be surface heterogeneity.

Figure 14 shows that all the impedance curves determined on unprotected Cu from initial exposure to 180 min immersion are predominantly Warburg controlled. The nearest approach to an activation controlled semicircular plot is after 50 min exposure. The charge transfer impedance is estimated as

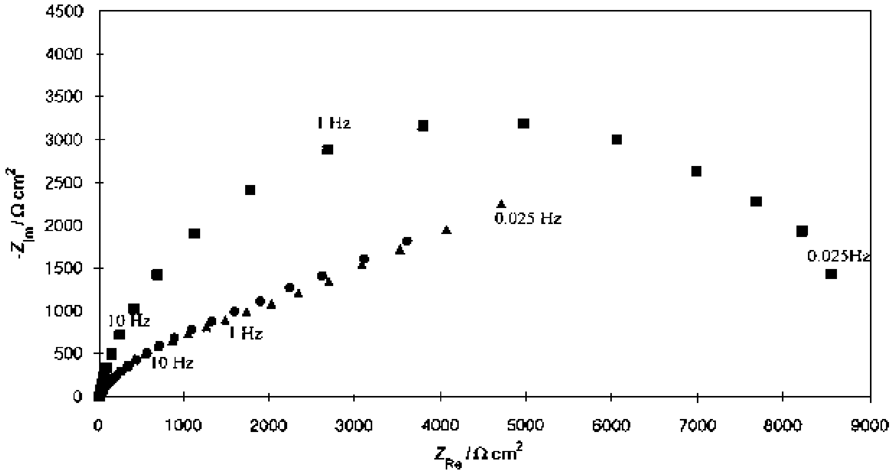


Fig. 13. Impedance spectra (Nyquist plots) of coated Cu samples at different immersion times in NaCl (3%) solution. Times, t: (●) 180, (▲) 50 and (■) 10 min.

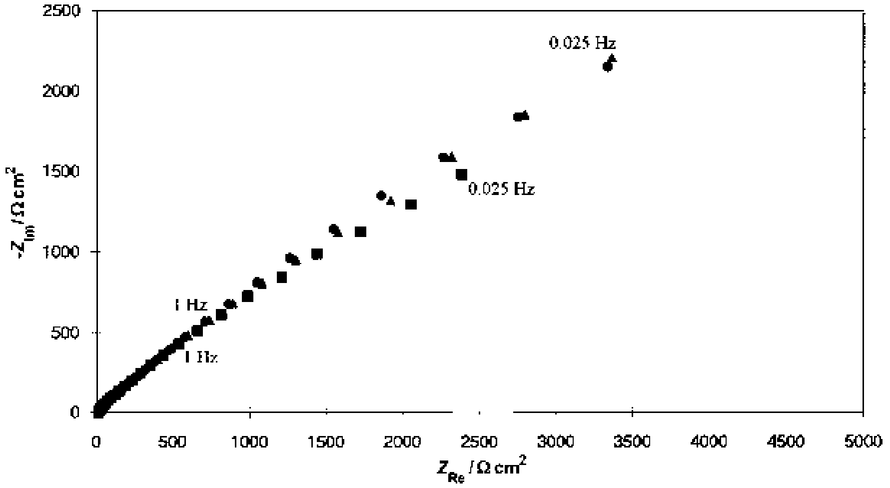


Fig. 14. Impedance spectra (Nyquist plots) of Cu samples at different immersion times in NaCl (3%) solution. Times, t: (●) 180, (▲) 50 and (■) 10 min.

$8 \times 10^2\ \Omega\,\mathrm{cm}^2$. The value of the polarization resistance of the film-coated Cu specimens exceed by more than 10 the impedance value of the uncoated Cu samples. The polarization resistance values obtained for various exposure times under steady conditions corroborate impedance results.

4. Conclusion

The interest of this study consists in the electroformation of a new polymer from (2-OHTB). This monomer has a structure similar to an organic heterocyclic inhibitor, i.e. a strong affinity for the metal. This property can be positively used in the case of the formation of a polymer layer. The proposal mechanism involves C–O coupling which allows the propagation of the polymer chain contrary to O–O coupling. Chemical characterizations of the polymer by classical techniques (FTIR, XPS) will permit confirming the occurrence of this mechanism. The electrochemical behaviour is quite satisfactory owing to (i) the thinness of the film, (ii) the absence of thermal curing and (iii) the absence of any additives such as surfactants in the electrolyte.

It would be interesting to study the influence of the voltage applied during electrolysis and the relative concentrations of 2-OHBT and KOH both on the morphology and the thickness of the coatings. This study provides some ideas for future avenues of investigation into electropolymerization of compounds usually known as organic inhibitors.

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