



An investigation of copper corrosion inhibition in chloride solutions by benzo-hydroxamic acids

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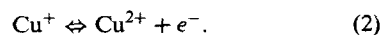
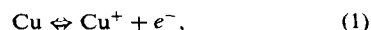
Abstract—Benzo-hydroxamic acids (BHA) are investigated as potential copper corrosion inhibitors in chloride solution. The BHAs investigated were: *p*-chloro-benzo-hydroxamic (*p*-Cl-BHA), *o*-chloro-benzo-hydroxamic acid (*o*-Cl-BHA), *p*-nitro-benzo-hydroxamic acid (*p*-N-BHA) and *o*-methyl-benzo-hydroxamic acid (*o*-M-BHA). Electrochemical measurements, potentiostatic polarization and *ac* impedance spectroscopy were carried out to evaluate the inhibition effect of the investigated BHAs. An Electrochemical Quartz Crystal Microbalance (ECQM) was used to measure electrode corrosion and inhibitor adsorption or layer formation processes. A poorly soluble layer consisting of the inhibitor and copper corrosion products is proposed to account for the protective effect in chloride solutions. © 1997 Elsevier Science Ltd

Key words: copper corrosion inhibition, quartz crystal microbalance, benzo-hydroxamic acids.

INTRODUCTION

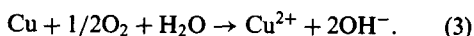
Copper and its alloys are applied extensively in marine environments due to their high corrosion resistance in harsh sea waters. In addition, copper dissolution in chloride solutions is very important in the electropolishing and electromachining industries. Due to those reasons attention has been focused on the behavior of copper in chloride solutions. Even if copper corrosion in near neutral aqueous solutions seems to be low, the damage from the corrosion products such as Cu^{2+} ions could be very harmful. In most cases of copper corrosion, an additive must be added to the environment in order to modify or hinder the reactions involved in the process. Theoretically, there are a great number of materials that could be applied as corrosion inhibitors for copper corrosion but only a few formulations have been thoroughly investigated. Azoles, specifically triazoles, have been intensively investigated as effective copper corrosion inhibitors [1-3]. Stricter environmental restrictions forced the need to develop a more environment friendly replacement to toxic inhibitors. Hydroxamic acids (HAs) are well known

chelating agents for mono-, bi- and trivalent metal ions [4]. Previous investigations showed HA derivatives as potentially effective corrosion inhibitors for copper [5]. Despite all the research devoted to azoles and other additives as copper inhibitors, the exact mechanism by which inhibition takes place on the metal is still not well understood. When considering the copper inhibitors, most researchers had to include surface products, such as oxides and different salt products, in the mechanism of inhibitor actions [1, 2]. This approach makes common sense from both theoretical and practical points of view. In most practical cases, inhibitors have to be applied on more-or-less preexisting oxide or salt layers. This further complicates the corrosion system by involving different processes. In the absence of different complexing agents in the corrosion medium, such as Cl^- ions, anodic dissolution of copper proceeds in two steps [3]:

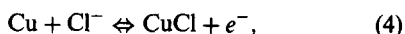


In neutral aqueous solutions, where oxygen is present, the overall reaction of anodic copper dissolution could proceed as follows:

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When complexing agents, such as Cl^- , are present in the corrosive aqueous medium, complex copper ions, such as CuCl_2^- , must be considered. In the near-neutral pH range of oxygen-containing mediums, the anodic reactions (at least at the immersion time) are as follows:



Mass transfer effects have been shown to be significant during the anodic dissolution of copper in chloride media with cuprous chloride complexes as the major product species. At chloride concentrations less than 1 M the copper dissolution reaction rate is of a second order with respect to Cl^- , indicating that in this Cl^- concentration range CuCl_2^- is the dominant cuprous species [2]. Several mechanisms involving reactions (4) and (5) and mass transfer of CuCl_2^- from the electrode surface to the bulk solution have been suggested to explain the kinetics of copper dissolution in the apparent-Tafel region.

The suggested electrochemical mechanism of copper corrosion could be verified by investigations using different electrochemical and electrogravimetric methods. Electrochemical potentiostatic polarization curves and electrochemical impedance spectroscopy measurements (EIS) were performed in order to evaluate the inhibition effect of the investigated benzo-hydroxamic acids (BHA) on copper corrosion in NaCl solution. The application of the electrochemical quartz crystal microbalance technique (ECQM) allows us to determine the corrosion rate and observe the adsorption behavior of the inhibitors on the copper electrode surface. When an alternating voltage is applied between two faces of a quartz crystal blade, the blade oscillates. The frequency of oscillation of a quartz crystal is highly sensitive to the mass supported by the two faces of the device. Ideally a sub-mono-molecular adsorbed layer can be detected. Jope *et al.* [6] utilized the ECQM in corrosion inhibition studies in aqueous solutions. Differences in the inhibitor adsorption or metal dissolution velocities and the film thickness can be monitored simultaneously [6, 7]. It is also possible to study the corrosion of different metal alloys by ECQM [8].

EXPERIMENTAL

Chemicals and solutions

Analytical reagent-grade NaCl was used in this investigation without any further purification. The aqueous solution of NaCl was prepared in doubly distilled water. Benzo-hydroxamic acids, which were synthesized from their appropriate carboxylic acid

chloride and hydroxylamine, were purified by recrystallization [9]. Their purity was checked by elemental analysis and melting point determination. Experiments were performed on copper electrodes in 0.5 M NaCl aqueous solutions without and with the addition of 1 mM of each BHA.

Electrochemical measurements

A three-electrode glass cell was used for the potentiostatic polarization measurements. The counter electrode (*ce*) was a platinum half cylindrical plate with an area of 90 cm². The cell reference was a saturated calomel electrode (*sce*) and the measured potential was referred to this electrode. The working electrode was a copper rod of 99.99% purity and 9.5 mm diameter imbedded into epoxy resin. The electrode was polished successively with 800 and 1200-grade emery papers, washed with acetone, rinsed with distilled water, and immersed immediately into the cell containing the electrolyte solution. The electrode corrosion potential was monitored until the change was less than 5 mV/5 min.

Measurements were performed at room temperature and with continuous stirring. A computer controlled Solartron Electrochemical Interface (Mod. 1286) was utilized to perform the polarization measurements. Starting from the corrosion potential, the applied potential was swept automatically to a value of 500 mV in the anodic region using a scan rate of 15 mV/min.

A rotating disk electrode assembly, with a 250 ml three-electrode cell, and conditions similar to the previous ones, was applied for EIS measurements. The working electrode was a rotating copper disk of 99.99% purity and 0.2 cm² area inserted in a Teflon sample holder. The electrode rotation speed was 500 r.p.m. A computer-driven Solartron ECI-1286 and FRA-1250 instruments were used to perform the measurements. Data were collected at the corrosion potential in a frequency range between 0.01 and 10000 Hz.

Electrogravimetric method

The quartz crystal used was an AT-cut disk of 12 mm diameter and of 10 MHz nominal oscillation frequency. At both sides gold electrode was deposited over a thin layer of chromium for adhesion purposes. Copper was galvanostatically deposited from an acidic copper bath containing 0.5 M CuSO_4 , 0.5 M H_2SO_4 and 1 M $\text{C}_2\text{H}_5\text{OH}$ [6, 7]. The freshly deposited copper electrode was washed thoroughly with distilled water. Then immediately the aggressive solution was added into the cell. Measurements were performed under open circuit potential conditions (*ocp*). An assembly which consisted of a Model PS-205 Potentiostat/Galvanostat and a Model EQCN-700 Electrochemical Quartz Crystal Nanobalance (ELCHEMA) was used for the measurements. The program wave-form was generated by VOLTSCAN Real-Time Data Acquisition System (Intellect

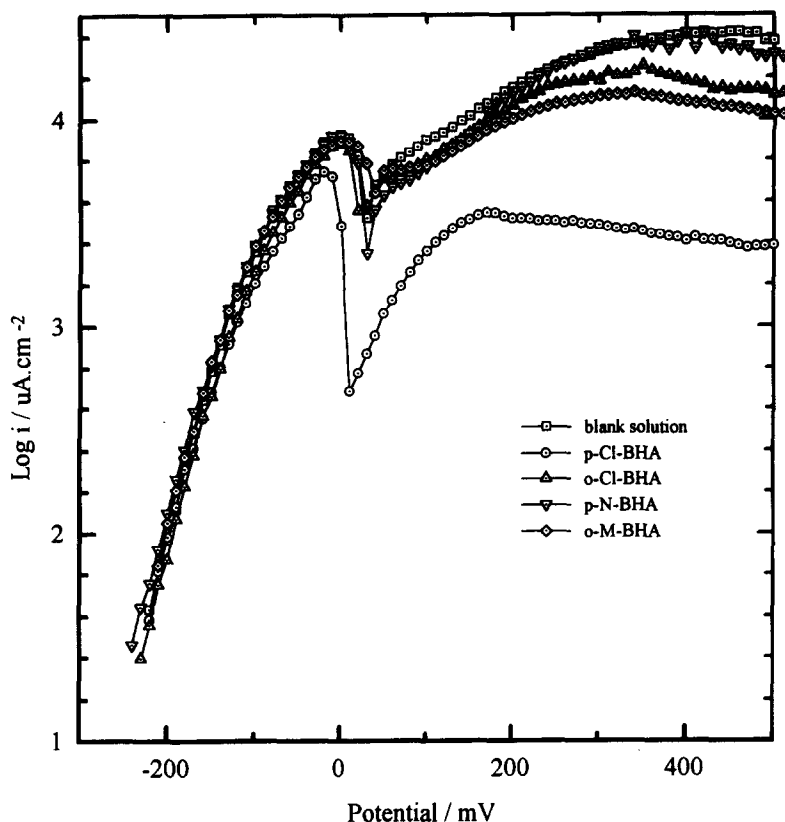


Fig. 1. Anodic polarization curves of copper electrode in 0.5 M NaCl with the addition of 0.001 M inhibitor.

Software). A *sce* and a platinum wire were used as reference and counter electrodes, respectively. Frequency changes which were automatically converted to mass changes on the working quartz electrode surface were registered as a function of time.

RESULTS AND DISCUSSION

Electrochemical results

The anodic polarization behavior of copper determined in 0.5 M NaCl solution without and with the addition of BHAs is illustrated by the curves in Fig. 1. All curves exhibited three distinct regions as previously reported by different researchers [1–3]: the Tafel region at lower over-potentials extending to a peak current density (i_{peak}), then a region of decreasing currents until a minimum value i_{min} is

reached and finally, a region of sudden increase in current density leading to a limiting value (i_{lim}). In the apparent-Tafel region curves deviated slightly from the blank solution. The anodic slope (β_a) and (i_{peak}) values for all curves are listed in Table 1. A Tafel region exists in the absence and in the presence of the added BHAs. However, the addition of the inhibitors to the corrosive medium shifted the polarization curves toward lower i_{lim} , i_{min} and i_{peak} values. The extent of the shift was maximal in the case of *p*-Cl-BHA. The curves almost were superimposed on each other between i_{peak} and i_{min} except for the *p*-Cl-BHA curve which was clearly shifted to a much lower i_{min} value. In the presence of *p*-Cl-BHA i_{min} was much lower than the blank solution (i_{min}). A decrease in current density was also observed at potentials higher than that correspond-

Table 1.
Corrosion inhibition parameters of Cu electrode in 0.5 M NaCl without and with the addition of different BHAs

Inhibitor	β_a (mV/Dec)	(i_{peak}) ($\mu\text{A}/\text{cm}^2$)	(i_{min}) ($\mu\text{A}/\text{cm}^2$)	Polarization res. (R_p) (k ohm cm^2)
Blank	65	8700	3675	3.5
<i>p</i> -Cl-BHA	82	5620	485	17.2
<i>o</i> -Cl-BHA	72	7820	3935	9.7
<i>p</i> -N-BHA	75	7780	2265	13.0
<i>o</i> -M-BHA	72	7940	4345	5.5

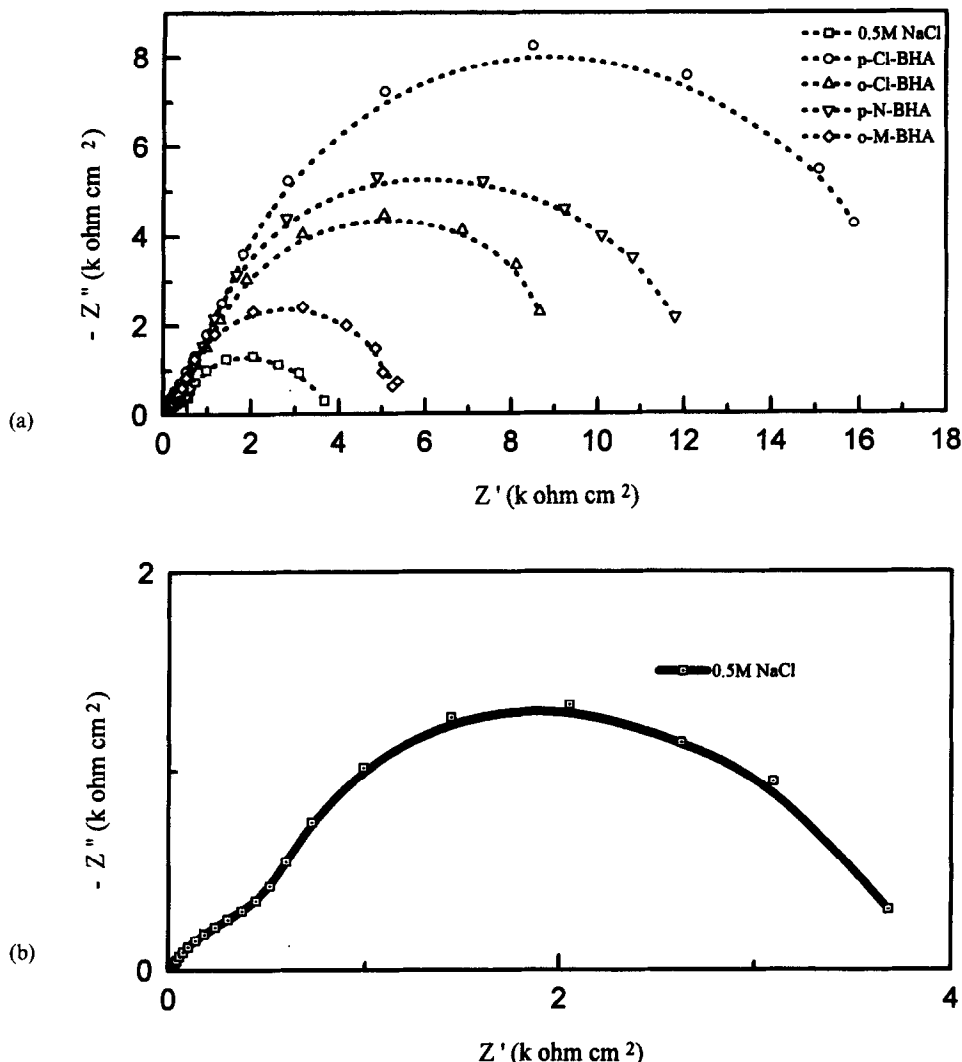


Fig. 2. (a) *ac* impedance Nyquist plots for copper electrode in 0.5 M NaCl with the addition of 0.001 M inhibitor at the corrosion potential. (b) *ac* impedance Nyquist plots for copper electrode in 0.5 M NaCl (an illustration of the high frequency semi-circle).

ing to i_{\min} . The change in i_{\lim} was noticeable for all BHAs tested except for *p*-N-BHA.

The AC impedance results, obtained at the corrosion potential, are depicted as Nyquist plots in Fig. 2(a). As reported by Fiaud [1] and Mansfeld [10], two more-or-less poorly separated semi-circles are obtained and are characteristic of the anodic partial reaction involving mass transfer occurring through the Cu₂O layer. The semi-circle at high frequency is due to the modulation of CuCl adsorbed at the electrode, as indicated by reactions 4 and 5 and illustrated in Fig. 2(b). The low frequency part of the curves represents the diffusion process at the electrode, due to CuCl₂ and other adsorbed materials. Data deviation was noticed at the low frequency region due to the instability of the electrode surface. The radius of the low frequency semi-circle represents the polarization resistance value (R_p).

The R_p values, listed in Table 1, are used to estimate the corrosion inhibition effect. All investigated BHAs produced higher R_p values than the blank solution, indicating the formation of a protective layer on the electrode surface which hinders the anodic reactions. As could be seen from Fig. 2 and Table 1, the order of inhibition effectiveness was *p*-Cl-BHA > *p*-N-BHA > *o*-Cl-BHA > *o*-M-BHA.

Electrogravimetric results

Figure 3 shows the results of ECQM experiments for the BHAs studied in 0.5 M NaCl. The curves represent the change of mass on the electrode surface as a function of time. The decrease of mass, which can be calculated from the frequency increase, represents the material loss due to copper corrosion. The addition of 0.5 M NaCl solution shows the highest mass loss rate indicating a high

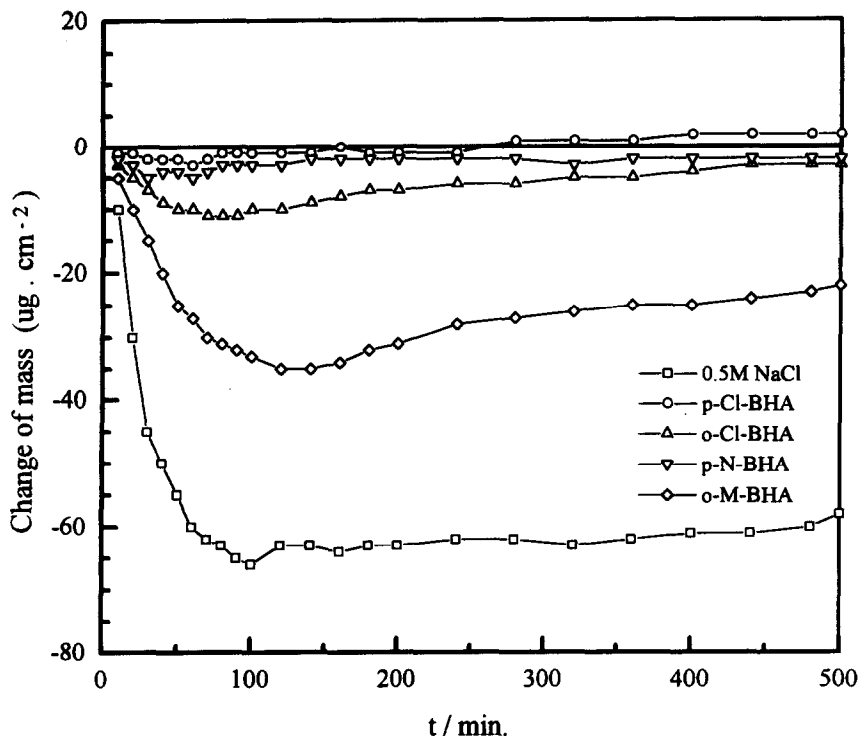


Fig. 3. Mass deviation of copper piezoelectrode in 0.5 M NaCl with the addition of 0.001 M inhibitor at the ocp.

corrosion rate. Curves representing BHAs showed a region of sudden decrease of the electrode mass followed by a relaxed region where the apparent mass loss rate slightly changed. The addition of *p*-Cl-BHA produced the maximum protection against copper corrosion in NaCl. At longer measuring time, when *p*-Cl-BHA was added, the electrode mass increased due to inhibitor adsorption or complex formation processes taking place on the electrode surface. It is difficult to distinguish between the two processes. The addition of *p*-N-BHA also decreased the mass loss noticeably. Figure 3 shows that the order of copper corrosion inhibition is in agreement with the previous electrochemical results. Figure 3 indicates that time is needed for the inhibitors adsorption onto the electrode surface. In most cases this effect took place after an hour of immersion time.

CONCLUSIONS

The inhibition effect of the investigated BHAs on copper corrosion in 0.5 M NaCl solution was studied and the behavior of the copper electrode was discussed. The most affective BHAs, of the investigated series, in controlling copper corrosion were *p*-Cl-BHA and *p*-N-BHA. A complex layer of the inhibitor and copper corrosion products, with low solubility, is proposed to account for the protective effect in chloride solutions. The exact structure of this layer (complex) needs further investigations. The *in-situ* ECQM method could be used to gather quick and vital information on the copper electrode

behavior in near neutral aqueous chloride solutions. Its high sensitivity enables us to investigate even a mono-layer scale. A set back for this method is to distinguish between different processes taking place at the same time on the electrode surface.

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