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A new corrosion inhibitor for copper protection

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ABSTRACT

Methyl 3-((2-mercaptophenyl)imino)butanoate (MMPB) was synthesized as inhibitor compound for copper protection. The molecule was designed with azole, thiol functional groups and carboxylate tail group. The inhibition efficiency was examined in acidic chloride media, by means of various electrochemical and spectroscopy techniques. Electrochemical study results showed that high efficiency of MMPB was mainly related with its capability of complex formation with Cu(I) at the surface. The thiol group also improves the adsorptive interaction with the surface, as the carboxylate groups provide extra intermolecular attraction.

1. Introduction

Protection of copper is of particular interest, especially in acidic media which also includes chloride ions [1–16]. Copper is vulnerable against corrosion in such severe environment, although it is highly resistant in nearly neutral or slightly alkaline aqueous environment [2,17–36]. The use of an appropriate inhibitor is necessary, taking into account the specific corrosion mechanism of copper in acidic chloride environment. Especially, in heat exchangers, cooling water system pipelines copper surface is exposed to locally attack of various aggressive species [21]. Local defects and pitting are highly important risks to be handled for copper protection in chloride solution [37–40]. Generally, film assembling inhibitors based on the green chemicals are preferred for this purpose [41–44].

The use of nitrogen and sulfur containing organic compounds as corrosion inhibitor for copper has been widely investigated [1,2,45–51]. Azole compounds tailored with hydrophobic end groups are very popular. The azole group is able to form coordinative covalent bond with vacant d orbitals of copper atoms. Also rings containing conjugated bonds (π electrons) positively affect the interactions between copper and inhibitor compound. There are many reports about various azole group organic inhibitors forming complexes with copper ions and generating highly protective film chemisorbed on the surface. The film built over Cu(I) complex which is inert, insoluble and long lasting polymer like structure [1,2,52].

Also, mercapto group (–SH) containing inhibitors are able to form stable complex with copper ions via the thiolate bond. Most of these inhibitors are modified with an aromatic ring which has certain substituents, in order to increase hydrophobicity on top of protective layer. The inhibition mechanism is based on chemisorption of complex between inhibitor and copper ions, on the surface. The inhibition efficiency is governed by the position of –SH group on the ring (ortho > meta > para) [41,43,53–56].

Methyl 3-((2-mercaptophenyl)imino)butanoate was synthesized as inhibitor compound, the molecule is functionalized with both azole and thiol groups. These groups generate strong adsorptive interaction with metals/alloys, especially in acidic environment. Also, the carboxylate end group has significant dipole character and results with important intermolecular interaction between the molecules adsorbed on the metal surface. Once the adsorbed molecules interact with each other along the carboxylate tails, a film like adsorption layer could be formed on the surface. The inhibition efficiency of this organic compound was investigated against copper corrosion, in 0.1 M HCl solution. The effect of temperature, concentration and extending exposure periods were investigated.

2. Experimental

2.1. Synthesis of inhibitor

Methyl 3-((2-mercaptophenyl)imino)butanoate (MMPB) was synthesized in our laboratory. For synthesis of the inhibitor a mixture of 2-aminobenzenethiol (1.25 g, 10 mmol) and methylacetoacetate (1.26 g, 10 mmol) and %10 mol of trifloroaceticacid (TFA) in 5 ml ethanol in a round bottom flask was stirred at 80 °C

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in an oil bath. Thin layer chromatography (TLC) of the reaction mixture after 150 min showed the completion of the reaction. Then, the mixture reaction was filtered, and the solid was washed with ethyl acetate. The filtrate was then evaporated under reduced pressure to give the crude product. The pure product was crystallized from ethanol. A general reaction of the synthesized inhibitor was given in Fig. 1.

2.2. Characterization of MMPB

We have synthesized methyl 3-((2-mercaptophenyl)imino)butanoate (MMPB) which is an imine compound [57,58]. The reaction was a facile reaction due to the good electrophilic and nucleophilic properties of β-ketoester compound and amine compound, respectively. The condensation of 2-aminobenzenthiol with methylacetoacetate afforded 85% yield in 150 min at 80 °C, with catalysis of TFA. The yellow colored product was recrystallized from ethanol solution. The characterization of the inhibitor was realized with NMR spectroscopic analysis. The NMR data of inhibitor was given below.

^{1}H NMR (600 MHz, $DMSO_4$-d_6) δ ppm: 6.97 (d, J = 7.8 Hz, 1H), 6.82 (d, J = 7.2 Hz, 1H), 6.57–6.50 (m, 2H), 3.61 (s, 3H), 3.33 (s, 1H), 3.01–2.92 (m, 2H), 1.70 (s, 3H) ^{13}C NMR (150 MHz, $DMSO_4$-d_6) δ ppm: 170.58, 146.57, 125.59, 121.75, 118.99, 109.54, 75.16, 51.93, 48.06, 29.57.

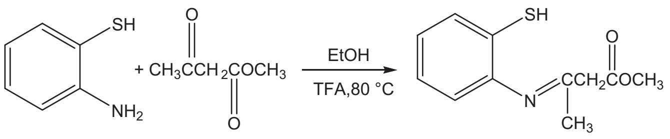
The stability of MMBP against hydrolysis was examined in acidic corrosive environment. The synthesized molecule is an imine compound and these species may undergo hydrolysis in order to yield amine and carbonyl compounds, in highly acidic media. For this purpose, 10 mM inhibitor containing test solution (0.10 M HCl) was stirred continuously for an hour, under 45 °C temperature. Then, samples were taken from this solution and analyzed with help of FTIR (Fourier transformed infrared). The solution was mixed KBr and pellets were prepared. The obtained spectra revealed that there was not any amine group, since there was not any absorption peak between 3443 and 3357 cm^{-1}. Also, there was no evidence for any other possible hydrolysis product.

2.3. Electrochemical studies

Electrochemical studies were realized in 0.1 M HCl test solution, employing three electrodes setup in one compartment cell. A platinum sheet was utilized as the counter electrode and Ag/AgCl (3 M KCl) was the reference. The working electrode was copper (99.99% purity) cylindrical rod embedded in resin, with one bottom surface (0.283 cm^2) open to exposure. Before each experiment, the specimens were mechanically abraded with silicon carbide papers (from grades 500 to 1000), degreased with acetone, washed with distilled water and dried.

For studies aiming to determine corrosion rate with quantitative analysis of immersion test solutions, square shaped (10 × 10 × 1 mm) copper (99.99% purity) coupons were utilized. The surface of these samples was prepared with the same route as described above.

CHI 660C model electrochemical workstation was employed for potentiodynamic, ac impedance measurements. Before each electrochemical test, the potential of the electrode was monitored with time until the steady state conditions set on the electrode surface. Then, the measured stable electrode potential was handled as the corrosion potential (E_{corr}). It was seen that approximately 30 min was sufficient for reaching the said steady state, in presence and absence of inhibitor in test solution. Potentiodynamic method was used to obtain anodic polarization plots, starting from E_{corr} value and employing 1 mV/s scan rate. EIS measurements were realized at E_{corr} value, with 5 mV perturbation voltage in a frequency range of 10^{+4}–10^{-2} Hz.



MMPB

Fig. 1. The synthesis reaction of inhibitor compound.

In order to clarify the inhibition mechanism, the effect of concentration and temperature were studied separately. The temperature range was between 25 and 55 °C, which was valid for many open cooling water systems. The concentration range was selected in between 0.5 and 10 mM inhibitor, for the purpose of less chemical consumption in practical applications.

In order to investigate the morphology and structural composition of the surface, Zeiss/Supra 55 model FE-SEM (field emission scanning electron microscope) equipped with EDX was utilized. Copper coupons were immersed in blank and 10 mM inhibitor containing solutions, for 7 days.

3. Results and discussion

3.1. Corrosion inhibition studies

Before realization of potentiodynamic and electrochemical measurements, steady state conditions must be provided on the electrode surface. In Fig. 2, the corrosion potential (E_{corr}) of copper electrodes are plotted against immersion time. It is clear that stable corrosion potential value is reached in about 30 min, for both inhibitor free and 10 mM inhibitor containing solutions. Then before each electrochemical measurement, 30 min immersion time was employed for each electrode.

In Fig. 3, potentiodynamic measurement results are given for copper in the absence and presence of 10 mM MMPB, in 0.1 M HCl. In inhibitor free solution, copper dissolution leads to formation of sparingly soluble copper (I) chloride (K_{sp}: 1.72×10^{-7}) on the surface [41,59]. None of the copper oxides are stable under studied pH conditions and anodic dissolution rate is directly related to barrier effect of CuCl deposit on the surface. This event is observed as a wide peak in the potential range of −0.02 and +0.08 V (vs. Ag/AgCl). Once the surface is covered with CuCl, this deposit exhibits a physical barrier between the solution and metal. Then the anodic dissolution rate (thus the current density) was controlled by the stability of this CuCl layer and limitation of mass transfer. The anodic dissolution of copper has been extensively discussed in the literature, considering various mechanism steps in order to explain the kinetics of dissolution properly [10,24]. In our case, the following steps are considered to explain the potentiodynamic measurement results. The first irreversible reaction (Eq. (1)) defined the general pattern observed at earlier potential region of anodic plots, at which the film formation is completed and a maximum peak current density is observed. Then the charge transfer becomes controlled with the mass transfer limitation of protective layer. The Eqs. (2) and (3) explain the current density increase due to formation of Cu(II) species, under high potentials.

$$Cu + Cl^- \rightarrow CuCl_{(ads)} + e \qquad (1)$$

$$CuCl_{(ads)} + Cl^- \leftrightarrow CuCl^-_{2(ads)} \qquad (2)$$

$$CuCl^-_{2(ads)} \leftrightarrow Cu^{2+} + 2Cl^- + e \qquad (3)$$

In the case of 10 mM MMPB containing solution, the current density value was quite lower than inhibitor free conditions. Also, the peak attributed to Cu(I) chloride formation disappeared. This