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Potent inhibition of copper corrosion in neutral chloride media by novel non-toxic thiadiazole derivatives

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ABSTRACT

Inhibiting effect of two novel non-toxic thiadiazole derivatives on copper were investigated in 3.5% NaCl solution using weight loss and electrochemical measurements. Presence of inhibitors and increase of concentration greatly decrease corrosion rate, parameters determined from polarization curves and EIS plots show that inhibitors decrease both cathodic and anodic current densities, suppressing charge transfer process by adsorption on copper surface. Thermodynamic calculation indicates chemisorption obeys Langmuir isotherm. Surface layers were characterized by SEM coupled with EDX. Raman micro-spectroscopy reveals that inhibitor molecules suppress copper corrosion via formation of thiadiazole–Cu complex. Relationships between inhibition efficiency and molecular orbital were also evaluated.

1. Introduction

Copper is known for plenty of favourable properties such as electrical and thermal conductivity, mechanical workability, corrosion resistance, making them suitable for a wide range of applications in marine engineering [1,2]. Hence, it is used in a great variety of seawater systems, for production of shipbuilding, seawater desalination, pipelines and heat exchanger [3,4].

In spite of the fact that copper can form an insoluble layer of cuprous chloride at lower Cl^- concentrations [5], which can suppress the dissolution of substrate and the diffusion of oxygen from bulk solution to metal surface, However, the passivity and stability of this layer are greatly affected by the aggressive Cl^- in seawater [6,7], which could easily cause a serious corrosion. Therefore, the protection of copper, when the concentration of Cl^- is high, is a fundamental academic and industrial concern that received a considerable amount of attention [8–11].

Employment of inhibitors is one of the most significant strategies for protecting copper against corrosion [12–19]. N-heterocyclic compounds are considered to be the most effective corrosion inhibitors on copper in chloride media [20–24]. They exert inhibition action through adsorption on the copper surface blocking the active sites by forming a compact barrier film to decrease corrosion rate. The adsorption of N-heterocyclic inhibitor takes place through heteroatom, as well as those with conjugated double bonds or aromatic rings in their molecular structures [25–28]. By considering increasing the strength of bonding between copper and the organic molecule, various derivatives were investigated, changing the number or position of substituent groups and nitrogen atoms on the azole ring, or adding another heteroatom like sulphur [29–31]. For instance, triazole and its amino derivatives, tetrazole, pyrazole and imidazole have been suggested [32–35]. Furthermore, the research in the field of eco-friendly corrosion inhibitors has been addressed toward the goal of using cheap, effective molecules at low or zero environment impact. In latest trend many alternative inhibitors including thiazole derivatives, cysteine and substituted uracil were studied [36–39]. In our previous work five green triazole fungicides have been studied as good inhibitors for copper in synthetic seawater [40–42].

As another important N-heterocyclic compound, thiadiazole derivatives could be deemed as good potential inhibitors owing to containing electronegative N,S-heteroatom and aromatic systems. In addition, they are non-toxic and biodegradable; this makes the investigation of their inhibiting properties significant in the context of the current priority to produce inhibitors with low environment impact [43–51]. Nevertheless, data regarding the use of thiadiazole-type compounds as potent inhibitors for copper corrosion appears to be very poor.

The aim of this paper is to present the remarkable inhibiting properties of two novel inhibitors synthesized in our laboratory (5-phenyl-1,3,4-thiadiazole-2-thiol (PTT) and 2-(5-mercapto-1,3,4-thiadiazole-2-yl)-phenol (MTP)), which consist of only the basic units of thiadiazole structure including one aromatic ring and one thiadiazole ring. They have many advantages such as low cost, non-toxic and easy production. In order to extend PTT and MTP as corrosion inhibitors for copper in neutral chloride media, weight loss, potentiodynamic polarization curves and EIS

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methods were employed to evaluate corrosion rate of freshly polished copper and inhibition efficiencies of the inhibitors in 3.5% NaCl solution. Meanwhile, the copper surface was examined by SEM, EDX and Raman spectra. In addition, the adsorption isotherm of inhibitors on copper surface is obtained. Quantum chemical parameters are calculated and discussed in detail. It is expected to provide useful information on the adsorption and inhibition effect of thiadiazole derivatives on copper in seawater.

2. Experimental details

In the present study, the same experiment was generally performed for 8–10 groups (as a batch) every time in the same experimental condition, and we carried out for 5 batches. The experiments could be reproduced perfectly in our studies.

2.1. Materials and sample preparation

The molecular structures of the studied compounds, namely 5-phenyl-1,3,4-thiadiazole-2-thiol (PTT) and 2-(5-mercapto-1,3,4-thiadiazole-2-yl)-phenol (MTP) were shown in Fig. 1. The compounds were synthesized in our laboratory, which were purified and characterized by ^{1}H NMR, IR and MS. The solution was prepared from the micro-emulsion of 2% PTT or MTP. This was achieved by first mixing 2 g inhibitor with the solvent of 44 g cyclohexanone and 44 g emulsifier OP-10 (Tianjin DaMao Energizing Chemistry) was then added into this mixture. The accurately-weighted mixture was finally transferred into 3.5% NaCl solution to fill a 250 mL beaker. In the concentration studies, the concentration range of the inhibitor in 3.5% NaCl solution was from 10 to 100 mg/L (pH 7.5, 303 K). The solution in the absence of inhibitors was taken as blank for comparison.

The copper specimens (99.999%) for weight loss experiments were mechanically cut into 3.00 cm × 1.50 cm × 1.50 cm dimensions. For electrochemical experiments, the specimens were embedded in epoxy resin with a geometrical surface area of 1 cm^2 exposed to the electrolyte. Prior to all measurements, the samples were abraded with emery paper from 1000 to 2000 grit, respectively, degreased ultrasonically in ethanol and acetone, and dried at room temperature.

2.2. Weight loss experiment

Copper specimens in triplicate were immersed in 3.5% NaCl solution with different concentrations of PTT or MTP (10–100 mg/L) for 20 days. After that, the specimens were removed from the solution, rinsed in 0.1 mol/L HCl, water and acetone, finally dried and weighted. Weight loss experiments are used to calculate the mean corrosion rate (W, g m^{-2} h^{-1}). The obtained inhibition efficiency ($\eta_e\%$) was evaluated by

$$\eta_{eW}\% = \frac{W^0 - W}{W^0} \times 100 \quad (1)$$

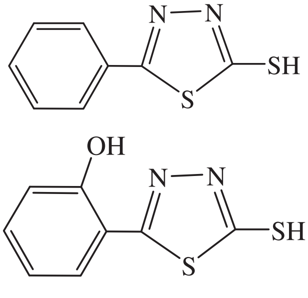

Fig. 1. Molecular structure of PTT and MTP.

where W^0 and W are the corrosion rate of copper in the solution without and with the inhibitor, respectively.

2.3. Electrochemical experiment

The electrochemical measurements were conducted with PARSTAT 2273 Potentiostat/Galvanostat (Princeton Applied Research) in a conventional three-electrode cell system. A copper specimen and a platinum electrode were used as working electrode and counter electrode, respectively. A saturated calomel electrode (SCE) with a Luggin capillary was used as reference electrode. All potentials were measured versus SCE and all tests were performed in non-deaerated solutions at 303 K.

The polarization curves are obtained from −250 to +250 mV (versus open circuit potential (OCP)) with 0.5 mV/s scan rate, and the data were collected and analyzed by electrochemical software PowerSuite ver. 2.58. The obtained inhibition efficiency was calculated by

$$\eta_{ei}\% = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \quad (2)$$

where i_{corr} and i^0_{corr} are the corrosion current density of copper with and without the inhibitor in 3.5% NaCl solution, respectively.

EIS measurements were carried out at the OCP. The ac frequency range extended from 100 kHz to 10 mHz with a 10 mV peak-to-peak sine wave as the excitation signal. Then the impedance data were analyzed and fitted. The inhibition efficiency obtained from EIS measurements was calculated by

$$\eta_{eR}\% = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100 \quad (3)$$

where R_{ct} and R^0_{ct} represent the resistance of charge transfer in the presence and absence of the inhibitor, respectively.

2.4. Surface analysis

The surface morphology of the specimens after immersed in 3.5% NaCl solution with and without inhibitors are performed on scanning electron microscope JEOL-JSM-5600 equipped with an energy dispersive X-ray spectrometer OXFORD Link-ISIS-300.

The contact angles of 4 μL water droplet on bare and filmed copper were measured with contact angle metre (JC2000C1, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd.) at ambient temperature.

2.5. Electrochemical quartz crystal microbalance (EQCM) analysis

This study was based on methods and patents obtained by Kern et al. [52,53]. The mechanical parts of the experimental devices were prepared and fabricated by Lanxess Energizing Chemistry in Germany and CH Electrochemical Instruments in China. A Zahner potentiostat (IM6 Germany) was used, and a platinum wire served as the counter electrode while a SCE as the reference. EQCM electrode and its characterization were described elsewhere in detail [52,53]. The 10 MHz AT cut quartz crystals with a sensitivity factor of 0.217 Hz cm^2 ng^{-1} were contained in exchangeable holders mounted on a rotating shaft [54,55]. The 650 nm thick Cu electrodes were prepared by electro-deposition on a 190 nm thick sputter deposited Au film with an adhesion layer of 50 nm Cr.

The electrodes were immersed in 0.1 mol/L NaClO$_4$ (pH 7.5, 303 K) and a cathodic polarization at −0.9 V was applied and maintained throughout the sequential inhibitor addition process. It should be noticeable a plateau in the EQCM signal appeared after an initial mass loss indicated the complete removal of the oxide. Perchlorate used as the supporting electrolyte showed no specific