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Phenyl-substituted amino thiadiazoles as corrosion inhibitors for copper in 0.5 M H_2SO_4

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ABSTRACT

Three thiadiazole derivatives, namely 5-phenyl-2-amino-1,3,4-thiadiazloe (APT), 5-(4-methoxyphenyl)-2-amino-1,3,4-thiadiazloe (AMPT) and 5-(4-nitrophenyl)-2-amino-1,3,4-thiadiazloe (ANPT), have been synthesized as new inhibitors for the copper corrosion in 0.5 M H_2SO_4. The inhibition properties of the inhibitors were studied by means of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. The results show that the order of inhibition efficiency is AMPT > APT > ANPT. The values of free energies of adsorption, as calculated from the Langmuir adsorption isotherm, indicate that the thiadiazole compounds adsorb on copper by a physisorption mechanism in 0.5 M H_2SO_4. The correlation between inhibition efficiency and quantum chemical parameters has been investigated by PM3 quantum chemical calculation.

1. Introduction

Many heterocyclic compounds containing nitrogen, sulfur, and oxygen atoms are efficient inhibitors of corrosion for copper in acid media [1–7]. Starting with the works of Bastidas and Otero [8,9], there has been much interest in the development of thiadiazole compounds as corrosion inhibitors. The inhibition efficiencies of 2,5-disubstitued 1,3,4-thiadiazoles, in which the substituted groups include pyridyl [10–13], 4-dimethylaminophenyl [13,14], thienyl [13,15], 4-methoxyphenyl [16], phenyl [16], 4-methylphenyl [16], 4-nitrophenyl and 4-chlorophenyl [16], have been studied for carbon steel in acidic media.

The property of corrosion inhibition of organic compounds is related to their molecular structure [17]. Under certain conditions, the electronic structure of the organic inhibitors has a key influence on the corrosion inhibition efficiency of inhibitor. The molecular structure, including the electronic parameters, can be obtained by means of the theoretical calculations by using the computational methodologies of quantum-chemistry [17,18]. Quantum chemical calculation has been used recently to explain the mechanism of corrosion inhibition [19–21], and proved to be a very powerful tool for studying the mechanism [22–24].

In the present work, the inhibition effects of three amino thiadiazoles, namely 2-amino-5-phenyl-1,3,4-thiadiazole (APT), 2-amino-5-(4-methoxyphenyl)-1,3,4-thiadiazole (AMPT) and 2-amino-5-(4-nitrophenyl)-1,3,4-thiadiazole (ANPT) (Scheme 1), on the corrosion of copper in 0.5 M H_2SO_4 have been studied. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were used. Also the relationship between calculated quantum chemical parameters and experimental inhibition efficiencies of the inhibitors was discussed.

2. Experimental

2.1. Synthesis of APT, AMPT and ANPT

APT was prepared by the following process. Phosphorus oxychloride (0.3 mol, A. R.) was slowly added to a mixture of benzoic acid (0.1 mol, A. R.) and thiosemicarbazide (0.1 mol, A. R.) at 0–5 °C. The reaction solution was stirred under reflux for 4 h and then cooled to room temperature. Distilled water (50 mL) was added to the above solution, and its pH value was adjusted to 8.0 using 50% NaOH. The precipitate was collected and re-crystallized from ethanol (yield, 76%). AMPT and ANPT were also prepared by similar procedure using *p*-methoxybenzoic acid and *p*-nitrobenzoic acid instead of benzoic acid, and the yields are 60% and 89%, respectively.

2.2. Electrochemical measurements

A traditional three-electrode cell was used for electrochemical measurements. A platinum sheet electrode was used for the auxiliary electrode, and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary. All potentials were measured with respect to the SCE. The working electrode is 99.9% pure copper rods. The rod specimen was embedded in Teflon holder using epoxy resin with an exposed area of 0.21 cm^2. Before each experiment, the electrode was first mechanically polished with various grades of sandpaper (up to 1200 grit) and then ultrasonic cleaned in acetone for 2 min, followed by a rinse in double-distilled water. Regent-grade H_2SO_4 was used, and the aggressive solution was made up with double-distilled water.

Electrochemical experiments were performed using a ZAHNER IM6ex electrochemical workstation. For potentiodynamic polarization experiments, the potential was scanned at a scan rate of 1 $mV\,s^{-1}$. The electrochemical impedance spectroscopy (EIS) experiments were performed at open-circuit potential over a frequency range

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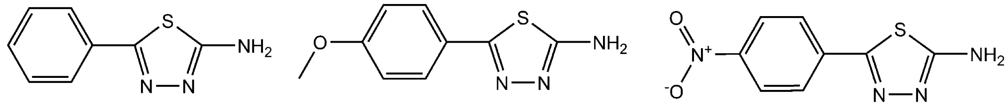

Scheme 1. Structures of APT, AMPT and ANPT.

of 0.1 Hz to 100 kHz. The sinusoidal potential perturbation was 5 mV in amplitude. Electrochemical data were analyzed by a ZAHNER THALES software.

2.3. Methods of calculations

All theoretical computations have been carried out using semi-empirical PM3 method from the program package MOPAC2007. A full optimization of all geometrical variables without any symmetry constraint was performed at the restricted Hartree–Fock (RHF) level. Molecular structures were optimized to a gradient <0.01 in the vacuum phase. The following quantum chemical indices were considered: the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), $\Delta E = E_{HOMO} - E_{LUMO}$ and the dipole moment (μ).

3. Results and discussion

3.1. Potentiodynamic polarization

Potentiodynamic polarization curves for copper in 0.5 M H_2SO_4 at 30 °C in the absence and presence of various concentrations of phenyl-substituted amino thiadiazoles are shown in Fig. 1 (representative examples). Electrochemical kinetic parameters, i.e., corrosion potential (E_{corr}), cathodic and anodic Tafel slope (b_c and b_a) and corrosion current density (i_{corr}), obtained by extrapolation of the Tafel lines, are presented in Table 1. The inhibition efficiencies (E%) of the thiadiazole compounds in 0.5 M H_2SO_4 are also given in Table 1. The inhibition efficiency is defined as:

$$E\% = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \qquad (1)$$

where i^0_{corr} and i_{corr} are the corrosion current density values without and with inhibitor, respectively.

The shifts of E_{corr} values towards negative direction are found in the presence of various concentrations of the thiadiazoles compounds in 0.5 M H_2SO_4, which can be explained by a domination of the cathodic reaction inhibition [25]. However, it is clearly observed from Fig. 1 that the thiadiazole compounds reduce the anodic and cathodic current densities, indicating the inhibiting effects of the compounds. In addition, from Table 1, the slopes of the cathodic

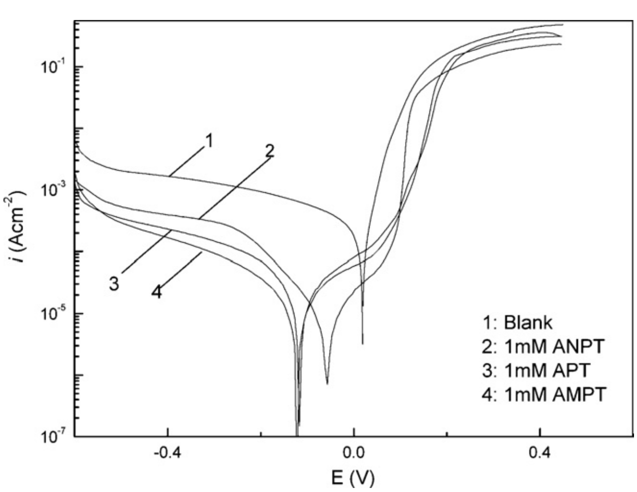

Fig. 1. Potentiodynamic polarization curves for copper in 0.5 M H_2SO_4 in the absence and presence of inhibitors at 30 °C.

Tafel lines (b_c) and anodic Tafel lines (b_a) are observed to change by the addition of the thiadiazole compounds, which indicates the influence of the thiadiaole compounds on the cathodic and anodic reactions, but the cathodic curves are more affected. Thus the compounds act as relatively mixed type inhibitors for copper in 0.5 M H_2SO_4.

The anodic polarization curve shows Tafelian linearity in the absence of inhibitor. However, in the presence of the thiadiazole compounds, flat potential regions are observed from the polarization curves at more positive potentials than corrosion potentials, which are attributed to the desorption of inhibitors from the metal surface [26].

As it can be seen from Table 1, corrosion current densities decrease with the increase of inhibitors concentrations and the inhibition efficiencies increase. But the inhibition abilities of three compounds to copper corrosion in 0.5 M H_2SO_4 are different. With the dosage of 1 mM, for instance, the inhibition efficiencies of APT, AMPT and ANPT are 73.6%, 85.5% and 63.7%, respectively, namely, the percentage inhibition decreases in the order:

AMPT > APT > ANPT

The ability of the inhibitors to inhibit the corrosion of copper is dependent on the group in *para* position in phenyl substituent [16]. Indeed, AMPT and ANPT molecules can be regarded as the replacement of hydrogen atom in *para* position in phenyl substituent of APT molecule by $-OCH_3$ and $-NO_2$. Due to the electron-releasing effect of $-OCH_3$, inhibition ability of AMPT is higher than that of APT. While $-NO_2$ is an electron-withdrawing group, therefore, inhibition ability of ANPT is lower than that of APT. The similar phenomenon for other molecules has been mentioned in Ref. [16].

3.2. Electrochemical impedance spectroscope (EIS)

The corrosion of copper in 0.5 M H_2SO_4 in the presence of the thiadiazole compounds was investigated by the EIS method at 30 °C after 2 h immersion. Nyquist plots of copper in the absence and presence of the thiadiazole compounds are presented in Fig. 2. It is apparent that all Nyquist plots show single capacitive loop, both in uninhibited and inhibited solutions. The impedance diagrams obtained are depressed into the real axis and not perfect semicircles as a result of the roughness and other inhomogeneity of the metal surface, and the phenomena is known "the dispersing effect" [15]. The impedance data of copper in 0.5 M H_2SO_4 are analyzed in term of equivalent circuit of the electrical double layer as described in our previous report [27].

Charge transfer resistance values (R_t) and double layer capacitance values (C_{dl}) were obtained and shown in Table 2. It can be seen from Table 2 that the values of the charge transfer resistance increase with the inhibitor concentration, which is related to the corrosion protection effect of the inhibitor molecules. In the case of the EIS, the inhibition efficiency (E%) is calculated by charge transfer resistance from the equation:

$$E\% = \frac{R'_t - R_t}{R'_t} \times 100 \qquad (2)$$

where R_t and R'_t are the values of the charge transfer resistance in the absence and presence of inhibitor, respectively. The inhibition