

Inhibitive properties, adsorption and a theoretical study of 3,5-bis(*n*-pyridyl)-4-amino-1,2,4-triazoles as corrosion inhibitors for mild steel in perchloric acid

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Abstract

Corrosion inhibition of mild steel in molar perchloric acid by 3,5-bis(*n*-pyridyl)-4-amino-1,2,4-triazoles (*n*-PAT, *n* = 2, 3 and 4) was studied at 30 °C using gravimetric and electrochemical impedance spectroscopy techniques. Protection efficiencies of 95% and 92% were obtained with 12×10^{-4} M of 3-PAT and 4-PAT, respectively; while 2-PAT reached only 65%. The inhibiting properties of *n*-PAT were found to depend on the concentration and the order of increasing inhibition efficiency was correlated with the modification of the position of the nitrogen atom in the pyridinium substituent. It was shown that adsorption of 4-aminotriazole derivatives on the steel surface is consistent with the Langmuir adsorption isotherm and the obtained standard free energy of adsorption (ΔG_{ads}^0) values indicate that the corrosion inhibition of the mild steel in 1 M HClO₄ depends on both physic- and chemisorption. A significant correlation is obtained between inhibition efficiency and quantum chemical parameters using semi-empirical quantitative structure-activity relationships (QSAR) approach.

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1. Introduction

The industrial consumption and development of new corrosion inhibitors have continuously increased, because this corrosion control technique is one of the most effective and economic methods to protect metal corrosion in acidic media [1,2]. There are various types of organic inhibitors that tend to decrease the corrosion rate of steel and iron in acidic solutions [3,4]. The major use of inhibitors in acid solution is in pickling processes [5], industrial acid cleaning, oil and gas well acidizing and for removal of rust, scale and corrosion products. These inhibitors contain oxygen, nitrogen, sulphur heteroatoms and multiple bonds, which

allow adsorption on the metal surface [6,7]. This phenomenon is influenced by the nature and surface charge of the metallic surface, testing media and chemical structure of inhibitors [8]. It has been observed that the adsorption of organic inhibitors depends on the electron density of the active part of the molecule such as aromatic rings and heteroatoms [9].

The inhibiting effect is generally explained by the formation of a physical and/or chemical adsorption film on the metal surface [10,11]. The new environmental restrictions have resulted in the use of substitute compounds, acceptable from the environmental point of view (“green inhibitors”) such as triazole derivatives, which have been effectively employed as corrosion inhibitors for different metals in several corrosive systems [12]. Our research was aimed to find new environment friendly inhibitor having

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non-toxicity and good inhibition efficiency against mild steel corrosion [13–16].

In our previous investigations the influence of heterocyclic compounds, namely 3,5-bis(*n*-pyridyl)-4-amino-1,2,4-triazoles ($n = 2, 3$ and 4), have been investigated on the corrosion inhibition of mild steel in 1 M HCl solution [17]. We found that these compounds are good inhibitors in 1 M HCl and the corrosion inhibition is due to their adsorption on the metal surface following the Langmuir's adsorption isotherm. The aim of the present paper is to extend these investigations in the other aggressive medium by studying the inhibitive properties of 3,5-bis(*n*-pyridyl)-4-amino-1,2,4-triazoles (*n*-PAT) on the corrosion of mild steel in 1 M HClO₄ using weight loss measurements and electrochemical impedance spectroscopy method. The effectiveness of *n*-PAT in both acidic media (HCl and HClO₄) are compared and discussed. The experimental results are complemented with theoretical calculations in order to provide an explanation of the differences between the probed inhibitors.

2. Experimental method

2.1. Material preparation

The tested inhibitor, namely 3,5-bis(2-pyridyl)-4-amino-1,2,4-triazole (2-PAT), 3,5-bis(3-pyridyl)-4-amino-1,2,4-triazole (3-PAT) and 3,5-bis(4-pyridyl)-4-amino-1,2,4-triazole (4-PAT) were synthesised according to a previously described experimental procedure [18,19]. The molecular structures of *n*-PAT are shown in Fig. 1. The concentration range of *n*-PAT employed was 2×10^{-4} M– 12×10^{-4} M. Fresh solutions of 1 M HClO₄ were prepared before each experiment from an analytical reagent grade of perchloric acid (65%) and bidistilled water. Mild steel strips composed of (wt%): 0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S, and balance Fe were pre-treated prior to the experiments by grinding with emery paper SiC (grades 600 and 1200), then cleaned in ultrasonic bath with ethanol, rinsed with doubly distilled water and finally dried at room temperature.

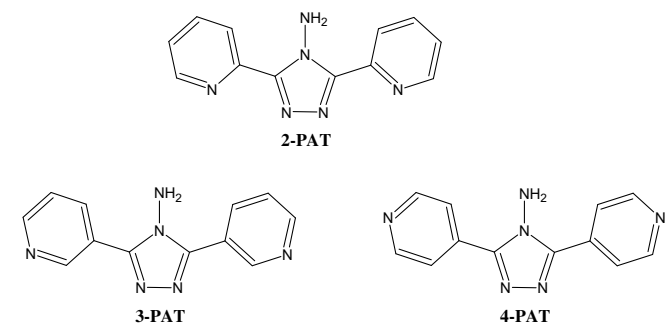


Fig. 1. Molecular structures of the investigated 4-amino-1,2,4-triazoles (*n*-PAT).

2.2. Weight loss method

Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser. The solution volume was 100 ml. The steel specimens used have a rectangular form (length = 2 cm, width = 1 cm, thickness = 0.06 cm). Experiments were performed at 30 °C for 24 h of immersion in non-de-aerated acid solutions. After of the exposure time, the specimens were taken out, carefully rinsing with bidistilled water, ultrasonic cleaning in ethanol and then weighted. The experiments were done by duplicate and the average value of the weight loss was reported. Weight loss allowed calculation of the mean corrosion rate in $\text{mg cm}^{-2} \text{h}^{-1}$.

2.3. The electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was conducted at 30 ± 1 °C using an electrochemical measurement system Tacussel-Radiometer PGZ 301. Ac impedance experiments were carried out in a polymethyl methacrylate (PMMA) cell with a capacity of 1000 ml. A saturated calomel electrode (SCE) was used as the reference; a Pt electrode was used as the counter. All potentials are reported vs. SCE. Ac impedance measurements were performed using Tacussel Radiometer PGZ 301 Frequency Response Analyser in a frequency range of 10^5 Hz– 10^{-2} Hz with ten points per decade. An ac sinusoid ± 10 mV was applied at the corrosion potential (E_{corr}). The experiments were measured after 24 h of immersion in non-de-aerated acid solutions at 30 ± 1 °C. The working electrode was prepared from a square sheet of mild steel such that the area exposed to solution was 7.55 cm². The impedance data were analyzed and fitted using graphing and analyzing impedance software, version Voltmaster 4.

2.4. Computational chemistry

All quantum theoretical calculations were performed with SPARTAN PRO V. 1.05 software package for PC (Irvine Inc.) using ab initio Hartree–Fock 3-21G* basis set at RHF (Restricted Hartree–Fock) level [20], starting without any geometry constraints for full geometry optimizations. 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}), energy band gap, $\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$ and the dipole moment (μ).

3. Results and discussion

Table 1 gives the corrosion rate (W_{corr}) and inhibition efficiency $E(\%)$ obtained by weight loss method, at different concentrations of 2-PAT, 3-PAT and 4-PAT in molar perchloric acid at 30 °C after 24 h immersion. The inhibition efficiency $E(\%)$ was calculated as described previously

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