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Organic synthesis and inhibition action of novel hydrazide derivative for mild steel corrosion in acid solutions

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HIGHLIGHTS

- One-pot synthesis of novel hydrazinyl hydrazide (HDOP) derivative is described.
- Both spectral and elemental analyses are used for characterization of the HDOP.
- EIS, Tafel plots, SEM and EDX are used in the corrosion study in HCl and H_2SO_4.

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ABSTRACT

A new derivative of hydrazide family, 2-(2-hydrazinyl-1,6-dihydro-6-oxopyrimidin-4-yl) acetohydrazide (HDOP) is synthesized and used as a corrosion inhibitor for mild steel both in 1 M HCl and 0.5 M H_2SO_4 solutions. A facial synthesis of a novel hydrazinyl hydrazide derivative is accomplished via a one-pot synthesis. Reaction of *ethyl 2-(1,2,3,6-tetrahydro-6-oxo-2-thiopyrimidin-4-yl)acetate* (**1**) with hydrazine hydrate in an ethanol refluxing produces the target hydrazinyl hydrazide derivative in a good yield. Different techniques such as IR, NMR and mass spectroscopy are used for characterization of the obtained products. The inhibition of mild steel corrosion using HDOP in different concentrations is studied by electrochemical impedance spectroscopy and polarization measurements. The inhibition efficiency (*IE*) of HDOP is found to be higher in HCl than that in H_2SO_4 solution. This is attributed to the stronger adsorption of Cl^- on the iron surface which enables better synergism between Cl^- and the protonated inhibitor. The HDOP acts mainly as a cathodic inhibitor (in both acid solutions) and an inhibition efficiency of ~89% was obtained in the HCl solution. The free energy of adsorption obtained by applying Langmuir adsorption isotherm predicts physisorption of HDOP on the iron surface in the HCl solution.

1. Introduction

Hydrazides are a class of organic compounds that have been demonstrated as promising materials for applications in biological activities such as anti-inflamtory [1–3], anticonvulsant [4–6], antibacterial [7–9] and antitubercular agents [10–12]. Moreover, they have been used as effective corrosion inhibitors for different metals [13–15]. In this context, a great fraction of the used corrosion inhibitors is organic compounds containing nitrogen, sulfur, oxygen and phosphorus in their molecular structures and are simultaneously bearing aromatic and heterocyclic rings [16–24]. The inhibition action of such organic compounds is imparted by adsorption on the metal surface providing a barrier between the metal and the corroding solution. The extent of the inhibition action depends on the nature and surface charge of the metal, composition of the solution and the molecular structure of the inhibitor. The latter factor comprises functional groups, aromaticity, π-electrons characteristics of π-bonding orbitals, steric factor, and electron density at the donor atoms [25–30].

Organic compounds of different structures have been known of their inhibition actions for acid corrosion of different metals. The choice of an organic inhibitor relies on the nature of the metal surface and on the molecular structure of the inhibitor [31–34]. Pickling of metals, chemical cleaning and descaling in acid solution can be made efficient and economically accepted in presence of corrosion inhibitors. This can offer a protection for the underlying metal and less consumption of the used acid. Many categories of

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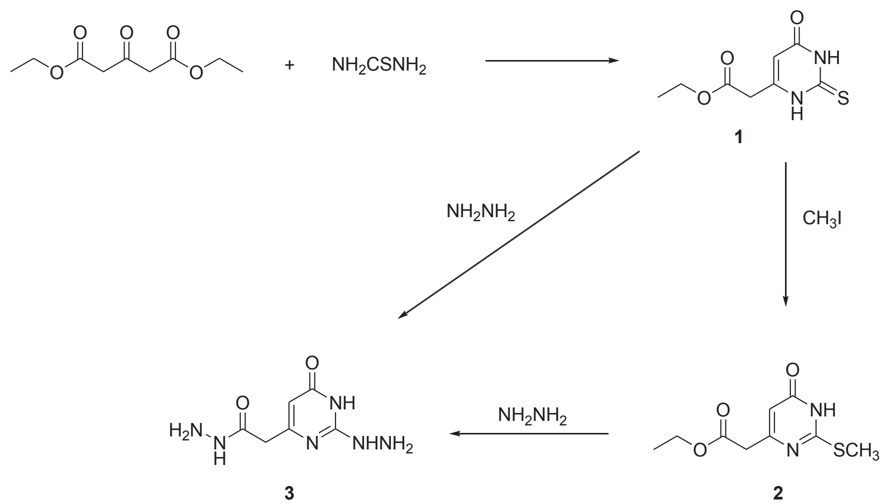

Fig. 1. Synthesis of hydrazinyl hydrazide 3 (HDOP).

organic compounds have been used as corrosion inhibitors for mild steel [35–41]. However, toxicity of such organic compounds has been a concern and yet there is a great demand for nontoxic corrosion inhibitors. Of these categories, hydrazides represent an important category [42,43]. This can be explained in the light of the fact that hydrazides are considered to be less toxic or relatively ecofriendly than other categories [44,45]. Also, this category of organic compounds gives reasonable inhibition action towards mild steel corrosion in acid solution [46,47].

In this article, a new organic inhibitor belong to hydrazide family is synthesized using one-pot organic synthetic route. The compound is evaluated as a corrosion inhibitor for mild steel in 1 M HCl and 0.5 M H_2SO_4 solutions. The study of corrosion inhibition was achieved using electrochemical impedance spectroscopy (EIS) and polarizations measurements.

2. Experimental

2.1. Organic synthesis

2.1.1. Materials

Diethyl 1,3-acetonedicaboxylate (CAS number 165123), iodomethane (CAS number 67692), thiourea (CAS number T8656), potassium hydroxide (CAS number 221473), hydrazine (CAS number 215155) and ethanol were all purchased from Aldrich (USA) and were used without further purification. The progress of the reaction was monitored by thin layer chromatography (TLC) which was purchased from Aldrich (USA).

2.1.2. Measurements

The melting points were measured using Gallenkamp apparatus and were uncorrected. IR spectra were recorded in potassium bromide using Perkin–Elmer FT-IR 1650 and Pye-Unicam SP300 infrared spectrophotometers. ^{1}H NMR spectra were recorded in deuterated DMSO using Varian Gemini 300 NMR spectrometer. Mass spectra were recorded on a GCMS-QP 1000 EX Shimadzu and GCMS 5988-A HP spectrometer. Elemental analyses were carried out at the Microanalytical Laboratory of Cairo University, Giza, Egypt.

2.2. Electrochemical measurements

The iron sample had a chemical composition of 0.19% C, 0.59% Mn, 0.19% Si, 0.03% Ni, 0.02% B, 0.06% P and the remaining iron. The molecular structure and synthesis scheme of the used organic compounds is shown in Fig. 1. Stock solution of the organic compound was prepared either in 1 M HCl or 0.5 M H_2SO_4 and the desired concentrations were obtained by appropriate dilutions. Bidistilled water was used in preparation of the solutions. The temperature was adjusted at 30 ± 0.2 °C using a water thermostat.

Electrochemical measurements were performed using Gamry potentiostat/galvanostat supported with Gamry electrochemical analysis technique. Electrochemical measurements were carried out in a conventional three-electrode cell. The iron electrode was fitted into a glass tube of proper internal diameter by using epoxy resins. The exposed surface area of the working electrode is 0.50 cm^2. The iron electrode was polished gradually with emery paper down to mirror-like surface. It was then washed with bidistilled water and finally degreased by rinsing with acetone and then dried.

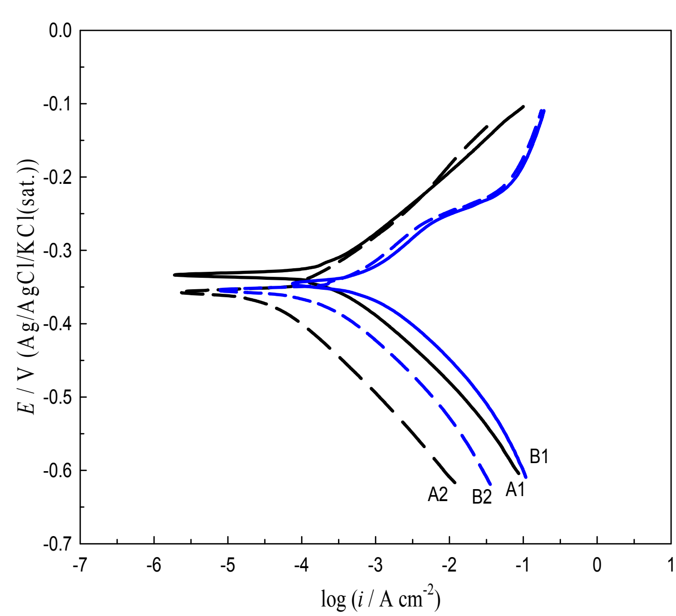

Fig. 2. Tafel Plots of mild steel in 1 M HCl (A1) and 1 M HCl containing 1 × 10^{-2} M HDOP (A2) and 0.5 M H_2SO_4 (B1) and H_2SO_4 containing 1 × 10^{-2} M HDOP (B2).