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2-Amino-5-nitro-4,6-diarylcyclohex-1-ene-1,3,3-tricarbonitriles as new and effective corrosion inhibitors for mild steel in 1 M HCl: Experimental and theoretical studies

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ABSTRACT

The influence of three 2-amino-5-nitro-4,6-diarylcyclohex-2-ene-1,3,3-tricarbonitrile (ANDT) derivatives namely, 2-amino-5-nitro-4,6-diphenylcyclohex-1-ene-1,3,3-tricarbonitrile (ANDT-1), 2-amino-4,6-bis-(4-methoxy-phenyl)-5-nitro-cyclohex-2-ene-1,3,3-tricarbonitrile (ANDT-2) and 2-amino-4,6-bis-(3-hydroxy-4-methoxy-phenyl)-5-nitro-cyclohex-2-ene-1,3,3-tricarbonitrile (ANDT-3) on mild steel corrosion in 1 M HCl has been investigated using experimental and theoretical techniques. Among the all studied inhibitors the ANDT-3 showed maximum inhibition efficiency of 98.96% at 25 mg L^{-1}. Adsorption of the ANDTs on mild steel surface follows the Langmuir adsorption isotherm. Polarization studies show that ANDTs act as mixed type inhibitors. SEM, EDX and AFM techniques were used to confirm the existence of adherent protective film of inhibitors on the mild steel surface. A quantum chemical calculation based on the DFT-theory was used to further corroborate the mechanism of inhibition.

1. Introduction

Mild steel is widely used in the chemical, petrochemical and petroleum industries because of its low cost, and high mechanical and thermal stability [1,2]. However, it undergoes rapid corrosion when it is exposed to acid solutions during acid pickling, industrial cleaning and descaling processes [3–7]. To reduce the attack of acid on metal surfaces, corrosion inhibitors are added in the acid solutions. Use of organic compounds containing heteroatoms (such as N, O, S, and P), aromatic rings and/or π-electrons are considered as one of the most practical and economic methods to prevent metallic corrosion [8]. Previously existing data show that organic compounds act by forming surface film at metal/electrolyte interfaces [9]. Generally, adsorption of these inhibitors is influenced by numerous factors including chemical structure, electronic distribution, and nature of metal and testing medium [10]. Literature survey reveals that heterocyclics containing nitrile groups (carbonitriles) act as efficient corrosion inhibitors for metals in different testing media [11–21].

In view of this, three carbonitrile compounds namely synthesized 2-amino-5-nitro-4,6-diarylcyclohex-2-ene-1,3,3-tricarbonitrile (ANDT) derivatives namely, 2-amino-5-nitro-4,6-diphenylcyclohex-1-ene-1,3,3-tricarbonitrile (ANDT-1), 2-amino-4,6-bis-(4-methoxy-phenyl)-5-nitro-cyclohex-2-ene-1,3,3-tricarbonitrile (ANDT-2) and 2-amino-4,6-bis-(3-hydroxy-4-methoxy-phenyl)-5-nitro-cyclohex-2-ene-1,3,3-tricarbonitrile (ANDT-3) were synthesized to study mild steel corrosion inhibition in 1 M HCl using weight loss, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and atomic force microscopy (AFM). Quantum chemical parameters such as energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE), global hardness (ρ), global softness (σ) and dipole moment (μ) were calculated and discussed [22,23].

2. Experimental

2.1. Materials

Mild steel specimens having percentage elemental composition of 0.076 wt.% C, 0.192 wt.% Mn, 0.012 wt.% P, 0.026 wt.% Si, 0.050 wt.% Cr, 0.023 wt.% Al, and balance with Fe has been used for weight loss electrochemical experiments. Before performing the experiments, the exposed area of these specimens were successively cleaned by abrasive SiC emery papers of different grades, washed with double deionized water, degreased with acetone and finally store in moisture free desiccators. The analytical grade HCl (37%) was purchased from Merck and

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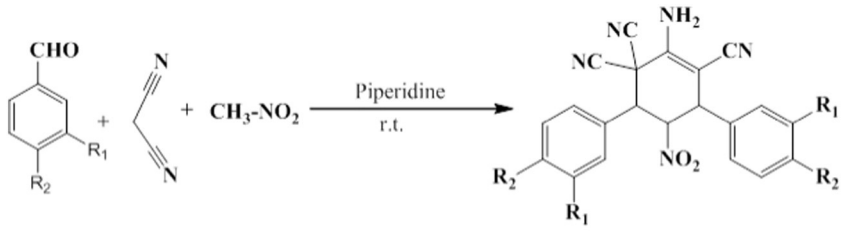


Fig. 1. Synthetic scheme for investigated ANDTs.

was used for preparation of test solution of 1 M HCl. The inhibitors used in the present case were synthesized by previously reported method [24]. The scheme of synthesis of inhibitors is given in Fig. 1. Purity of the synthesized inhibitors was determined by thin layer chromatography (TLC). The characterization data of the synthesized compounds are given in Table 1.

2.2. Methods

2.2.1. Wight loss measurements

The weight loss measurements were carried out by earlier described standard method [25,26]. The corrosion rate (C_R) was calculated by the following equation:

$$C_R = \frac{86.7w}{AtD} \quad (1)$$

where w is the weight loss of mild steel (mg), A the area of the working electrode (cm^2), t is the exposure time (h) and D the density of working electrode (g cm^{-3}). From the evaluated C_R, the inhibition efficiency ($\eta\%$) was calculated using the following equation:

$$\eta\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \quad (2)$$

where $C_{R(i)}$ and C_R are the corrosion rates in the absence and presence of ANDTs, respectively.

2.2.2. Electrochemical measurements

A three electrode glass cell consisting of a platinum counter electrode, a saturated calomel reference and mild steel with exposed area of 1 cm^2 as working electrode, respectively was used to perform all electrochemical measurements. The electrochemical measurements were carried out using a Gamry Potentiostat/Galvanostat (Model G-300) with EIS software Gamry Instruments Inc., USA. Echem Analyst 5.0 software package was used for fitting and analyzing the data. Before, each measurement the specimens were allowed to corrode freely and their OCPs were measured as a function of time (200 s) in order to obtained steady state potential (OCP). The anodic and cathodic Tafel curves were recorded by applying current of ±250 mV with respect to OCP at a sweep rate of 1.0 mV s^{-1}. From the Echem Analyst 5.0 software package installed in the instrument, polarization parameters such as corrosion potential (E_{corr}), corrosion current (i_{corr}) and anodic (β_a)/cathodic (β_c) Tafel slopes were derived by extrapolation method. The inhibition efficiency ($\eta\%$) was calculated with the help of calculated i_{corr} using the following relationship [27]:

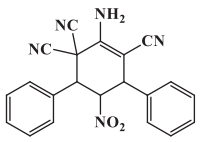
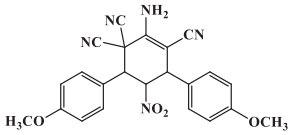
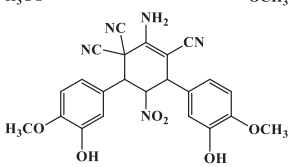
$$\eta\% = \frac{i^0_{corr} - i^i_{corr}}{i^0_{corr}} \times 100 \quad (3)$$

where, i^0_{corr} and i^i_{corr} are the corrosion current densities in the absence and presence of ANDTs, respectively.

Electrochemical impedance spectroscopic (EIS) measurements were carried out using AC voltage of amplitude 10 mV at its open circuit potential (OCP) in the frequency range from 100 kHz to 0.01 Hz. The charge transfer resistances with and without ANDTs were obtained from diameter of the Nyquist plots, utilizing the inhibition efficiency which was calculated using the following equation [27]:

$$\eta\% = \frac{R^i_{ct} - R^0_{ct}}{R^i_{ct}} \times 100 \quad (4)$$

Table 1
Chemical structure, IUPAC name and analytical data of the synthesized ANDTs.

S. no.	IUPAC name	Chemical structure	Analytical data
1	2-Amino-5-nitro-4,6-diphenylcyclohex-1-ene-1,3, 3-tricarbonitrile (ANDT-1)		IR(KBr, 1/cm): 3456, 3360, 3338, 3236, 3220, 2218, 1636, 1778, 1360, 659; ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 4.23, 4.85, 5.12, 5.36, 7.28–7.53
2	2-Amino-4,6-bis-(4-methoxy-phenyl)-5-nitro-cyclohex-2-ene-1,3,3-tricarbonitrile (ANDT-2)		IR(KBr, 1/cm): 3446, 3353, 3216, 3208, 2213, 1649, 1548, 1369, 1150, 836; ^{1}H NMR (300 MHz, DMSO, δ, ppm): 3.79, 4.35, 4.96, 5.77, 7.12–7.51
3	2-Amino-4,6-bis-(3-hydroxy-4-methoxy-phenyl)-5-nitro-cyclohex-2-ene-1,3,3-tricarbonitrile (ANDT-3)		IR(KBr, 1/cm): 3560, 3462, 3323, 3208, 2210, 1643, 1527, 1372, 1254; ^{1}H NMR (300 MHz, DMSO, δ, ppm): 3.73, 3.79, 4.32, 4.85, 6.73–6.97, 9.38,9.87