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2-Aminobenzene-1,3-dicarbonitriles as green corrosion inhibitor for mild steel in 1 M HCl: Electrochemical, thermodynamic, surface and quantum chemical investigation

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ABSTRACT

The three 2-aminobenzene-1,3-dicarbonitriles derivatives (ABDNs) namely 5′-amino-2,4-dihydroxy-4″-methyl-1,1′:3′,1″-terphenyl-4′,6-dicarbonitrile (ABDN-1), 5′-amino-2,2″,4-trihydroxy-1,1′:3′,1″-terphenyl-4′,6′-dicarbonitrile (ABDN-2) and 5′-amino-2,3″,4-trihydroxy-1,3-methoxy,1′:3′,1″-terphenyl-4′,6′-dicarbonitrile (ABDN-3) were synthesized and their corrosion inhibition properties on mild steel in 1 M HCl were investigated using weight loss and electrochemical techniques. Among the compounds investigated, ABDN-3 exhibited the best inhibition efficiency of 97.83% at 100 mg/L. Scanning electron microscopy (SEM) and dispersive X-ray spectroscopy (EDX) examinations was performed on inhibited and uninhibited mild steel samples to show the presence of ABDNs on mild steel surface. The potentiodynamic polarization studies reveal that all three studied inhibitors were of mixed type and their adsorption on the mild steel surface in 1 M HCl follows the Langmuir adsorption isotherm. Quantum chemical calculations studied were also performed to support weight loss and electrochemical experimental observations.

1. Introduction

Mild steel and its alloys are commonly used for construction material in the petroleum, food, power production, chemical and electrochemical industries. However, mild steel is a reactive material and very sensitive to corrosion in acid media [1]. Because of the destructive and corrosive nature of acid solutions, the use of inhibitors to control the destructive attack of acid environment was found to have widespread applications in many industries [2]. Most of the well known inhibitors are organic compounds containing heteroatoms including nitrogen, sulfur, and/or oxygen atoms and heterocyclic compounds in polar groups such as carbonyl, sulfur, nitrogen, amino, nitrile group and conjugated double bonds [3–5]. The selection of such compounds based on the fact that these compounds contain a better π electron conjugation and heteroatoms (N, O), responsible for effective adsorption properties. The adsorb inhibitor film blocks the active sites present on mild steel surface, thereby isolates the mild steel from corrosive attack. The literature survey revealed that only few carbonitriles and similar compounds [6–9] were utilized as corrosion inhibitors.

Recently quantum chemical calculations based on DFT theory have been developed to study the structural properties of inhibitor molecules and their reactivity toward metal surface [10]. The structural parameters, such as the frontier molecular orbital, the energy of highest occupied molecular orbital (E_{HOMO}), the energy of lowest unoccupied molecular orbital (E_{LUMO}), energy gap ΔE (E_{HOMO} − E_{LUMO}) and dipole moment (μ) are the common parameters which affect the molecular (electronic) interaction between inhibitor and metal surface.

The microwave irradiation has gained a powerful rapid tool for transformation of verities of compounds including etherification, hydrolysis, addition, and rearrangement [11]. The application of microwave irradiation has several advantages over convention synthesis such as: uniform heating occurs throughout the material, reaction rate is increased, high reaction yield, higher atom economy, higher purity of product, improve reproducibility, environmental heat loss can be reduced, reduce wastage of heating reaction vessel and low operating cost [12]. We herein describe the synthesis of three novel 2-aminobenzene-1,3-dicarbonitrile derivatives namely 5′-amino-2,4-dihydroxy-4″-methyl-1,1′:3′,1″-terphenyl-4′,6′-dicarbonitrile (ABDN-1), 5′-amino-2,2″,4-trihydroxy-1,1′:3′,1″-terphenyl-4′,6′-dicarbonitrile (ABDN-2) and 5′-amino-2, 3″,

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4-trihydroxy-1, 3-methoxy, 1′:3′, 1″-terphenyl-4′, 6′-dicarbonitrile (ABDN-3) by microwave irradiation and investigate their corrosion inhibition property on mild steel in 1 M HCl. The choice of these compounds as corrosion inhibitors is based on the considerations that these compounds: (a) can be easily synthesized from relatively cheap and commercially available materials, (b) contain various functional groups including $-NH_2$, –CN, –OH, electronegative oxygen and nitrogen atoms as well as aromatic ring as active centers (c) and have high solubility in test medium. The study was conducted by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy. The surface morphologies of mild steel were examined by high resolution scanning electron microscopy (SEM), and the elements present on the mild steel surface were examined by energy dispersive X-ray spectroscopy (EDX).

2. Experimental

2.1. Material

All the weight loss and the electrochemical corrosion tests were performed on mild steel specimens having composition: (wt%): C = 0.076, Mn = 0.192, P = 0.012, Si = 0.026, Cr = 0.050, Al = 0.023, and remainder Fe. Prior to all experiments the mild steel specimens were successively cleaned with SiC abrasive papers (600, 800, 1000, and 1200 grade), washed with acetone, ultrasonically cleaned in absolute ethanol and finally dried at ambient temperature. The test solution of 1 M HCl was prepared by analytical-reagent- (AR-) grade HCl in double distilled water.

2.2. Synthesis of corrosion inhibitors

The 2-aminobenzene-1,3-dicarbonitriles derivatives (ABDNs) were synthesized according to Scheme 1 as described earlier in literature [13]. Purity of the synthesized compounds was confirmed by thin layer chromatography using the SiliaPlate TLC Plates – aluminum (Al) silica. Melting point of the synthesized compounds was determined by open capillary method. The products were characterized by infrared (IR) spectra recorded on KBr discs using a Perkin-Elmer (Spectrum100) Fourier transform (FT-IR) spectrophotometer and ^{1}H NMR (300 MHz) spectra using a JEOL AL 300 FT-NMR spectrometer in $CDCl_3$ having TMS as internal reference. IUPAC name, chemical structure and molecular formula, melting point, analytical data and chemical abbreviation of synthesized compounds are given in Table 1.

2.3. Gravimetric experiment

The gravimetric or weight loss measurements were performed by immersing accurately weighed mild steel specimens of dimension 2.5 cm × 2.0 cm × 0.025 cm in 1 M HCl with and without ABDNs for 3 h. After the elapsed time the mild steel specimens were taken out and then washed, dried and weighed accurately. Inhibition efficiency (η) was calculated using the following relation [14].

$$\eta\,(\%) = \frac{w_0 - w_i}{w_0} \times 100 \tag{1}$$

where w_0 and w_i are the values of weight loss of mild steel in absence and presence of ABDNs, respectively. The mild steel corrosion rates (C_R) in absence and presence of ABDNs were calculated using following equation:

$$C_R = \frac{87.6w}{AtD} \tag{2}$$

where w is the weight loss of mild steel (mg), A is the area of the working electrode (cm^2), T is the exposure time (h) and D is the density of working electrode (7.85 g/cm^3).

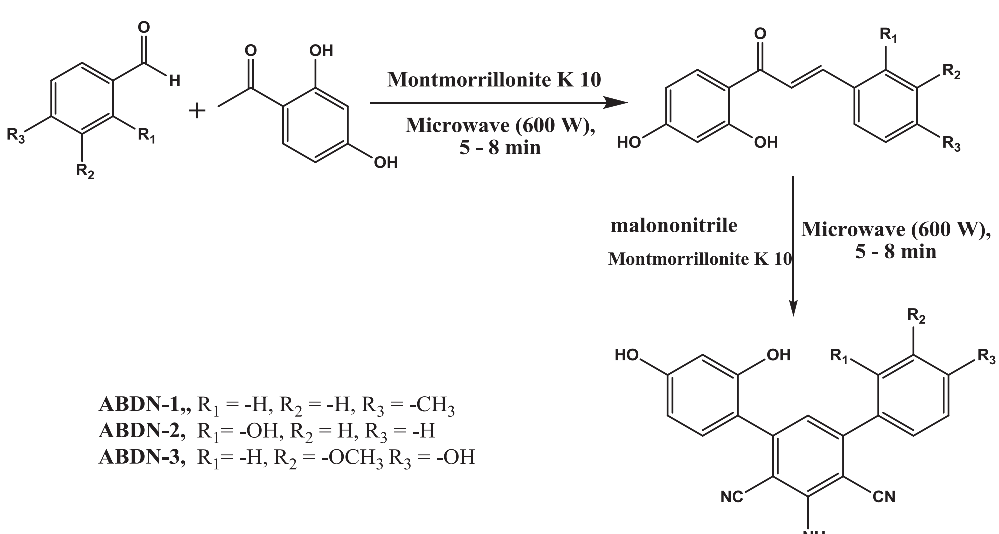
2.4. Electrochemical measurements

Conventional three electrode cell consisting of mild steel as working electrode, a high purity platinum foil as counter electrode and saturated calomel as reference electrode, was used to perform the all electrochemical experiments. Gamry Potentiostat/Galvanostat containing Mode G-300 and software Gamry Echem Analyst 5.0 was used to collect and analyzed all the electrochemical data. The working electrodes were immersed in test solution in absence and presence of different concentration of ABDNs for stabilization of steady state potential.

The impedance measurements were performed over frequency range between 100 kHz and 0.01 Hz having AC-amplitude signal voltage of 10 mV at open circuit potential and scan rate of 0.1 mV/s. The values of charge transfer resistance (R_{ct}) were calculated from the diameter of the Nyquist plots. The percentage inhibition efficiency was derived from R_{ct} value using following relation [15]:

$$\eta\,(\%) = \frac{R^i_{ct} - R^0_{ct}}{R^i_{ct}} \times 100 \tag{3}$$

where, R^0_{ct} and R^i_{ct} are the charge transfer resistance in without and with ABDNs, respectively.



Scheme 1. Synthetic routes of inhibitors ABDN-1, ABDN-2 and ABDN-3.

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