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Nicotinonitriles as green corrosion inhibitors for mild steel in hydrochloric acid: Electrochemical, computational and surface morphological studies

Priyanka Singh [a], M. Makowska-Janusik [b], P. Slovensky [b], M.A. Quraishi [a,*]

[a] Department of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi 221005, India
[b] Institute of Physics, Faculty of Mathematics and Natural Science, Jan Dlugosz University in Czestochowa, Al. Armii Krajowej 13/15, 42-200 Czestochowa, Poland

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ABSTRACT

The corrosion inhibition effect of two nicotinonitriles namely, 2-amino-6-phenyl-4-(*p*-tolyl)nicotinonitriles (ATN) and 2-amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile (AMN), has been investigated for mild steel in 1 M HCl solution by using weight loss, electrochemical impedance spectroscopy and potentiodynamic polarization methods. The experimental results show that the inhibition efficiency increases (80–97%), with increase in the ATN and AMN concentration from 0.08–0.33 mM. The maximum inhibition efficiency 97.14% and 95.23% was obtained for AMN and ATN respectively at 0.33 mM. Both the inhibitors efficiently inhibit corrosion via adsorption on the metal surface and found to obey the Langmuir adsorption isotherm. Electrochemical impedance spectroscopy analysis reveals an increase in the charge transfer resistance due to the adsorption of inhibitors molecules on metal surface. Potentiodynamic polarization data reveals that, both ATN and AMN predominantly act as cathodic inhibitors. The SEM and AFM, study confirms that the surface of inhibited metal surface is better than without inhibitor. The density function theory and Monte Carlo simulation have also been used to determine the relationship between molecular configuration and inhibition efficiencies. The experimental and theoretical results are in good agreement with each other.

1. Introduction

Organic compounds are widely used as acid corrosion inhibitors for various industrial processes like acid cleaning, pickling, descaling of boilers and oil well acidification [1–4]. These compounds are readily adsorbed on the metal surface by replacing water molecules and inhibit metallic corrosion [5–8]. Most of the commercially used inhibitors are costly and hazardous to the environment and human being. Therefore, in the recent year the researches are being focused on the development of cost effective and green corrosion inhibitors. In view of these facts, we have synthesized two new inhibitors namely 2-amino-6-phenyl-4-(*p*-tolyl) nicotinonitriles (ATN) and 2-amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile (AMN) to investigate their corrosion inhibition performance in 1 M HCl. The selection of these compounds is based on following considerations: (i) These compounds contain electron rich hetero atoms (S, N and O) as well as possessing, π electrons inside their skeleton, through which they are likely to adsorb easily on the metal surface (ii) $-CH_3$, $-OCH_3$ electron donating groups facilitates absorption on metal surface. The literature survey reveals that some pyridine derivatives have been reported as corrosion inhibitor in acid medium showing inhibition 93–97% in the concentration range 0.90–50.0 mM [9–12]. The present study is designed towards those compounds that are capable of providing higher inhibition efficiencies at relatively lower concentrations (97.14%, 95.23% for AMN, ATN at 0.33 mM).

So, the present investigation deals to study the corrosion inhibition performance of the two nicotinonitriles having different substituent, by using weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. Surface analyses were carried out by using scanning electron microscopy (SEM) and atomic force microscopy (AFM). To explain the adsorption mechanism and the interaction between selected nicotinonitriles and iron surface, the presented study were completed by computer simulations. The computational studies were carried out to establish the correlation between theoretical and experimental results.

2. Experimental

2.1. Materials and solutions

The MS coupons having the following composition (wt%): C 0.17%; Mn 0.46%; Si 0.026%; Cr 0.050%; P 0.012%; Cu 0.135%; Al 0.023%; Ni 0.05%; and balance Fe, were used for the experimental work. The MS coupons having dimension 2.5 cm × 2 cm × 0.025 cm were used for weight loss studies and 8 cm × 1 cm × 0.025 cm for electrochemical

* Corresponding author.
E-mail addresses: maquraishi@rediffmail.com, maquraishi.apc@itbhu.ac.in (M.A. Quraishi).

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studies with an exposed surface area of 1 cm^2. The surface of MS coupons was abraded with emery papers (grades ranges from 600 to 1200) and washed. The test solution of 1 M HCl was prepared by diluting analytical grade 37% HCl with double distilled water.

2.2. Inhibitors

The ATN and AMN were synthesized according to previously reported literature [13]. The synthetic route is shown in Scheme 1.The compounds were recrystallized from ethanol. The molecular structures of the studied nicotinonitriles are given in Table 1.

2.3. Weight loss measurements

The weight loss experiments were performed to optimise the inhibitor concentration. The reliability of weight loss method gives a baseline method to perform other corrosion techniques. The weight loss experiments were performed by immersing abraded MS coupons in 1 M HCl in the absence and presence of ATN and AMN at different concentrations (0.08–0.33 mM) at 308 K. The MS coupons were taken out after 3 h of immersion, and then they were washed, dried and weighted accurately. The corrosion rate (C_R), was determined by using the equation,

$$CR(\mathrm{mm/y}) = \frac{87.6W}{atD} \quad (1)$$

where W is the weight loss of MS specimens, a is total surface area of MS specimen, t is the immersion time (3 h) and D is the density of MS in (g cm^{-3}).

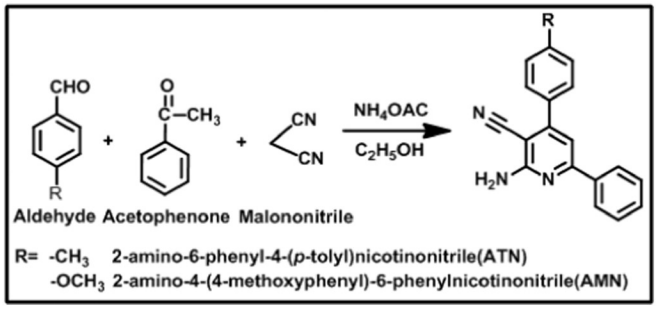
2.4. Electrochemical measurements

The electrochemical experiments were performed by using a three-electrode cell system connected to the Potentiostat/Galvanostat G300-45050 (Gamry Instruments Inc., USA). Gamry Echem Analyst 5.50 software package was used for data analyses. The cell assembly contains MS, platinum and saturated calomel electrodes (SCE) as working, auxiliary, and reference electrode, respectively. All experiments were carried out at 308 K. The EIS measurements were conducted in a frequency range from 100 kHz to 0.01 Hz, with amplitude of 10 mV AC signal. Tafel curves were obtained by sweeping the electrode potential from −0.25 V to +0.25 V versus open circuit potential at 1.0 mVs^{-1} scan rate. The experiments were performed after 30 min of MS immersion in the respective aggressive solutions.

2.5. Surface characterization

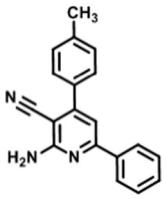
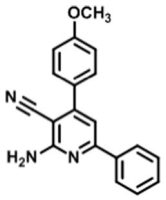
2.5.1. Scanning electron microscopy

Surface morphology studies were carried out on MS coupons after immersion in 1 M HCl solution without and with optimum concentration of ATN and AMN molecules. The scanning electron microscope



Scheme 1. Synthetic route for the preparation of nicotinonitriles.

Table 1
Molecular structures of nicotinonitriles.

Inhibitors	Molecular structures
2-Amino-6-phenyl-4-(*p*-tolyl)nicotinonitrile (ATN)	
2-Amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile (AMN)	

Supra 40, Carl Zeiss, Germany was used for the surface analyses and the images were taken at 500× magnification.

2.5.2. Atomic force microscopy

AFM images of MS surface immersed in 1 M HCl solution without and with optimum concentration of ATN and AMN were taken using Bruker Dimension Icon SPM with tapping mode in Air, RTESPA probe; k = 40 N/m and fo = 302 kHz, at 10um.

2.6. Quantum chemical calculations

Starting an analysis of the electronic properties of the ATN and AMN molecules in neutral and protonated state, first of all their geometry was optimised applying the ab initio formalism implemented in GAMESS program package [14,15]. The procedure was performed for isolated molecule in vacuum. The initial geometry was built up using the ACD/ChemSketch, an integrated software package from Advanced Chemistry Development, Inc. The minimum of the potential energy surface was calculated at restricted Hartree-Fock (RHF) level [16] for neural molecules and at unrestricted Hartree-Fock (UHF) level for protonated ones with the 6-311G basis set in C_1 symmetry. The quadratic approximation (QA) optimisation algorithm [17] based on augmented Hessian techniques was used to reach the geometry of the investigated molecules possessing the minimum of the total energy. The gradient convergence tolerance was equal to 10^{-4} Hartree/Bohr. At the end of geometry search the Hessian evaluation was performed to exclude the structures giving negative modes and ensure the thermodynamic equilibrium of the molecule.

To predict electronic properties of the investigated molecules the single point quantum chemical calculations were performed using the structures with optimised geometry. The electronic properties were computed for the isolated molecules in neutral and protonated state. The calculations were also carried out applying density functional theory (DFT) with B3LYP [18–20] potential using GAMESS program package. The single point calculations were performed with 6-311G basis set augmented by polarization and diffusion functions (6-311++G**) [21–23] The RHF and UHF SCF energy convergence criterion was chosen to be 10^{-12} Hartree.

2.7. Monte Carlo simulation

Adsorption of the ATN and AMN molecules at the (110) surface of Fe single crystal was also investigated using Adsorption Locator module developed in BIOVIA Materials Studio program package. The simulations were performed to find the preferential adsorption sites and their adsorption energy modelling selected nicotinonitriles situated at