Results in Physics 8 (2018) 657–670

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Adsorption characteristics of green 5-arylaminomethylene pyrimidine-2,4,6-triones on mild steel surface in acidic medium: Experimental and computational approach

Chandrabhan Verma [a,b,*], Lukman O. Olasunkanmi [a,b,c], Eno E. Ebenso [a,b,*], M.A. Quraishi [d]

[a] Department of Chemistry, School of Mathematical & Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
[b] Material Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
[c] Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife 220005, Nigeria
[d] Center of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

ARTICLE INFO

Article history:
Received 7 November 2017
Received in revised form 19 December 2017
Accepted 4 January 2018
Available online 10 January 2018

Keywords:
Multicomponent reactions
Green corrosion inhibitors
Acid solution
Theoretical studies
Langmuir adsorption isotherm

ABSTRACT

The effect of electron withdrawing nitro (–NO_2) and electron releasing hydroxyl (–OH) groups on corrosion inhibition potentials of 5-arylaminomethylenepyrimidine-2,4,6-trione (AMP) had been studied. Four AMPs tagged AMP-1, AMP-2, AMP-3 and AMP-4 were studied for their ability to inhibit mild steel corrosion in 1 M HCl using experimental and theoretical methods. Gravimetric results showed that inhibition efficiency of the studied inhibitors increases with increasing concentration. The results further revealed that that electron withdrawing nitro (–NO_2) group decreases the inhibition efficiency of AMP, while electron donating hydroxyl (–OH) group increases the inhibition efficiency of AMP. SEM and AFM studies showed that the studied compounds inhibit mild steel corrosion by adsorbing at the metal/electrolyte interface and their adsorption obeyed the Temkin adsorption isotherm. Potentiodynamic polarization study revealed that studied inhibitors act as mixed type inhibitors with predominant effect on cathodic reaction. The inhibitive strength of the compounds might have direct relationship electron donating ability of the molecules as revealed by quantum chemical parameters. The order of interaction energies derived from Monte Carlo simulations is AMP-4 > AMP-3 > AMP-2 > AMP-1, which is in agreement with the order of inhibition efficiencies obtained from experimental measurements.

Introduction

Acid solutions are commonly used in many industries for various purposes such as acid cleaning, acid descaling, oil well cleaning, acid pickling etc [1,2]. However, these industrial processes are accompanied by corrosive dissolution of metals in the acid solutions [2–5]. Several methods have been described in literature for the protection of metals against corrosion in acid solution. The use of organic molecules containing heteroatoms particularly, N, O and S as corrosion inhibitors is one of the most economic, popular and practical methods of strangling corrosion rate [6–9]. Inhibition of metal corrosion by organic molecules has been widely described as a function of the degree of adsorption of the inhibitor molecules on metallic surface. Therefore investigation of inhibitor adsorption at metal/electrolyte interface is an important topic in corrosion studies [7,8,10].

Previous studies have revealed that the adsorption of organic inhibitor molecules on metallic surface mainly depends on physicochemical properties such as the nature of functional groups, chemical and electronic structure, solution temperature, electron density at donor atoms, molecular size as well pi-orbital character of the inhibitor molecule in addition to the nature of electrolyte and the metal/alloy being investigated [8–10]. Barbituric acid and its derivatives have been extensively used for synthesis of compounds having several biological activities such as antibacterial, antihypertensive and so on [11–17]. Since, molecules derived from barbituric acids possess several heteroatoms, polar functional groups and pi-bonds and aromatic rings, corrosion inhibition potentials of barbituric acid derivatives have been extensively studied [18–20].

* Corresponding authors at: Department of Chemistry, School of Mathematical & Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa.
E-mail addresses: chandraverma.rs.apc@itbhu.ac.in (C. Verma), Eno.Ebenso@nwu.ac.za (E.E. Ebenso).

https://doi.org/10.1016/j.rinp.2018.01.008
2211-3797/

Considering the continuous strictness of environmental regulations and increasing ecological awareness, recent researches in all fields of science including corrosion are being directed towards "green" science [21–24]. Multicomponent reactions (MCRs), which combine three or more staring materials (MCRs) in a one-step process have emerged as a potential "green" and sustainable method for the synthesis of variety of organic compounds, particularly biochemically active heterocyclics [25,26]. MCRs are characterized by minimum waste product due to very limited workups, facile automation, simple purification, high chemical selectivity, mild reaction condition, shorter reaction time, high yield, atom economy and ease of operation. These characteristics increase the synthetic efficiency and other green aspects of the multicomponent reactions [27,28]. The use of organic solvents as reaction media in conventional synthesis is often associated with several problems, most of which are due to the toxic nature, hazardous effect, flammability and high cost of the solvent [29–31]. In this regards, the use of water as a reaction medium for organic synthesis has attracted substantial attention because it is free and readily available, it is cheap, non-toxic, non-flammable, non-hazardous and inexpensive. Water also possesses unique redox stability, and it is environmental friendly [32–34].

In view of this, the present study investigated the corrosion inhibition efficiency of four 5-arylaminomethylenepyrimidine-2,4,6-trione (AMPs) namely, 5-(((4-nitrophenyl)amino)methylene)pyrimidine-2,4,6-(1H,3H,5H)-trione (AMP-1), 5-((phenylamino)methylene)pyrimidine-2,4,6-(1H,3H,5H)-trione (AMP-2), 5-(((4-hydroxyphenyl)amino)methylene)pyrimidine-2,4,6-(1H,3H,5H)-trione (AMP-3) and 5-(((2, 4-dihydroxyphenyl) amino)methylene)pyrimidine-2,4,6-(1H,3H,5H)-trione (AMP-4), which were synthesized via three component one step reaction technique in water. The corrosion inhibition tests were carried out on mild steel in 1 M HCl using gravimetric, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, scanning electron microscopy (SEM), atomic force microscopy (AFM). Theoretical quantum chemical calculation and Monte Carlo simulations studies were carried out to corroborate experimental studies. Electron donating (–OH) substituent was found to enhance the inhibition efficiency of AMP, while electron withdrawing ($-NO_2$) substituent reduced the inhibition efficiency.

Experimental

Materials

Electrodes and reagents

Mild steel specimen of chemical compositions (%wt): C (0.076), Mn (0.192), P (0.012), Si (0.026), Cr (0.050), Al (0.023), and balanced with Fe was used as test material for all weight loss and electrochemical experiments. Before starting the experiments, exposed surface area of the specimens were abraded with SiC emery papers of 600, 800, 1000 and 1200 grit sizes, cleaned with double distilled water, degreased with acetone, and finally ultrasonically cleaned with absolute ethanol. Test solution of 1 M HCl was prepared from 30% hydrochloric acid purchased from MERCK India LTD and double deionized water.

Synthesis of 5-arylaminomethylene pyrimidine 2, 4, 6-trione (AMPs)

The AMPs used as corrosion inhibitors in the present study were synthesized by method reported in literature and schematized as shown in Fig. 1 [35]. In a typical procedure, a mixture of aniline and its derivatives (1 mmol), formic acid (4 mmol), barbituric acid (1 mmol) and distilled water (5 mL) were refluxed in round bottom flask (10 mL) at 60 °C for 2–3 h. The progress and completion of the reaction was determined by TLC method. The IUPAC name, chemical structures, molecular formulas, and analytical data of the synthesized 5-arylaminomethylene pyrimidine 2, 4, 6-trione (AMPs) are given in Table 1.

Corrosion tests

Gravimetric measurements

Mild steel with the previously stated chemical compositions was cut into 2.5 cm × 2.5 × 0.025 cm dimension and used for all gravimetric measurements. The specimens were dipped into 1 M HCl for 3 h in the absence and presence of different concentrations of the synthesized corrosion inhibitors. Triplicate measurements were performed both in the absence and presence of the inhibitors, and the mean value was reported in each case. The evaluated weight loss (in mg) was used to calculate the corrosion inhibition efficiency (%) using the equation [36,37]:

$$\eta\% = \frac{w_o - w_i}{w_o} \times 100 \quad (1)$$

where w_0 and w_i are the weight loss values in the absence and presence of different concentrations of AMPs, respectively.

Electrochemical measurements

Gamry Potentiostat/Galvanostat (Model G-300) pre-installed with Gamry Echem Analyst 5.0 software was used for all electrochemical analyses. The experimental setup comprises a three-electrode system with mild steel as working electrode, platinum foil as auxiliary or counter electrode and saturated calomel electrode (SCE) as reference electrode. The working electrode was fabricated to have an exposed surface area of 1 cm^2 (rest part of the specimens was covered with epoxy resin). The working electrode was immersed in 1 M HCl in the absence and presence of different concentrations of AMPs and left unperturbed for 30 min to attain a stable open circuit potential (OCP). Potentiodynamic polarization curves (anodic and cathodic) were plotted by automatically changing the electrode potential from −0.25 V to +0.25 V with respect to the stable OCP. Extrapolation of linear segments of anodic and cathodic Tafel slopes led to the evaluation of corrosion current

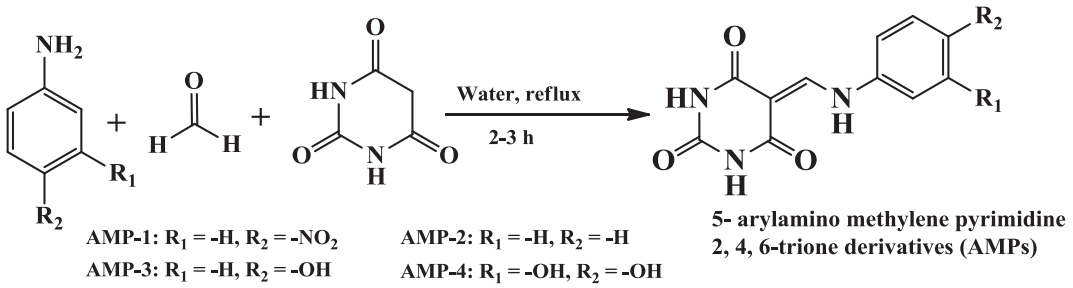

Fig. 1. General scheme for the synthesis of 5-arylaminomethylene pyrimidine 2, 4, 6-triones (AMPs).