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Electrochemical evaluation of inhibition efficiency of ciprofloxacin on the corrosion of copper in acid media

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HIGHLIGHTS

- The inhibitor efficiency increases with increase in ciprofloxacin concentration.
- Polarization measurements show that ciprofloxacin acts as a mixed type inhibitor.
- The adsorption of the inhibitor on copper surface follows Langmuir adsorption isotherm.
- The negative values of ΔG_{ads} indicates that the adsorption is spontaneous and exothermic.

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ABSTRACT

The inhibition efficiency of ciprofloxacin on the corrosion of copper was studied in 1.0MHNO_3 and 0.5MH_2SO_4 solutions by electrochemical impedance spectroscopy and potentiodynamic polarization techniques. The corrosion inhibition action of ciprofloxacin was observed to be of mixed type in both the acid media, but with more of a cathodic nature. The experimental data were found to fit well with the Langmuir adsorption isotherm. The thermodynamic parameters such as adsorption equilibrium constant(K_{ads}), free energy of adsorption(ΔG_{ads}), activation energy(E_a) and potential of zero charge(PZC) showed that the adsorption of ciprofloxacin onto copper surface involves both physisorption and chemisorption.

1. Introduction

Copper and copper-based alloys are widely used in a great variety of applications, such as industrial equipments, building construction, electricity, electronics, coinages, ornamental parts, water treatment, etc. [1]. Though copper is relatively a noble metal, it is susceptible to corrosion in acids and in strongly alkaline solutions, especially in the presence of oxygen or oxidants. The behavior of Cu in acidic media was extensively investigated, and several schemes have been presented for its dissolution process [2–6]. Chemical dissolution and electrolytic plating are the main processes in the fabrication of electronic devices [7] involving copper. Nitric acid is one of the most widely used corrosive medium for copper that attracted a great deal of research [8,9] and sulfuric acid is widely used in acid copper plating baths. One of the most important methods of protection of metals from corrosion in acid media is the use of organic inhibitors [10–14] containing hetero atoms such as N, O, S, P etc., and/or multiple bonds and aromatic rings. They inhibit corrosion by adsorption onto the metal surface through these structural features [15–22]. The interactions between inhibitor molecules and a metal surface are principally physical adsorption and/or chemisorption [23]. Among the organic compounds, sulfur and/or nitrogen containing heterocyclic compounds are considered to be effective corrosion inhibitors [23].

Fluoroquinolones, belonging to a class of hetero-quinolone cyclic aromatic compounds, containing basic structure (I) and a fluorine substitution at position 6 leading to structure (II), fulfilling

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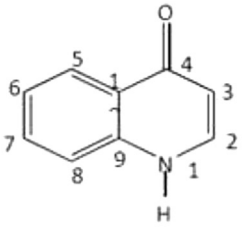
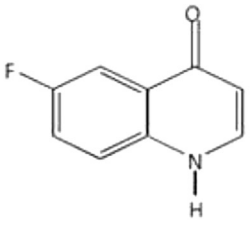
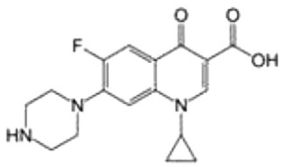
the necessary structural requirements of a corrosion inhibitor, can be used to control the corrosion of metals in acid media. The mechanistic aspect of corrosion inhibitive action of fluoroquinilones [24–26] could be understood from a review of literature on their complexing ability in general and ciprofloxacin (structure III) in particular. Ciprofloxacin is the most widely used drug among fluoroquinolones. An attempt has been made in the present work to describe the corrosion inhibition mechanism and efficiency of ciprofloxacin for corrosion of copper in 1.0 M HNO_3 and 0.5 M H_2SO_4 acid solutions.



Quinolone (I)



Fluoroquinolone (II)



Ciprofloxacin (III)

2. Experiments

2.1. Materials

A Teflon coated cylindrical copper electrode of exposed area 0.2826 cm^2 having a composition of 99.5 wt.% Cu, 0.003wt.% Ni, 0.019 wt.% Al, 0.002 wt.% Mn and 0.116 wt.% Si was used for polarization and electrochemical impedance studies. Prior to these measurements, the surface was polished to mirror finish, using emery papers of various grades in the increasing order (1/0,2/0,3/0,4/0 and 5/0), degreased with acetone and blown dry with nitrogen. Perfectly uniform wettability with water after this treatment was considered as a good indication for surface cleanliness. All experiments were carried out at room temperature 27 ± 1 °C. All purchased chemicals were of analytical reagent grade (Sigma Aldrich), E Merck (India) and were used without further purification and double-distilled water was used throughout. Inhibitor stock solutions were prepared in 2.5 M solution of respective acids.

2.2. Electrochemical impedance measurements

A conventional three electrode setup was used for electrochemical studies, in which a Pt foil served as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The Teflon coated copper electrode served as the working electrode. Prior to the impedance measurement, a stabilization period of 45 min was allowed after immersion of the specimen in the corrosive media, which proved sufficient for E_{ocp}/Vs (SCE) to attain a stable value. Electrochemical Impedance measurements were carried out at the open circuit potential (E_{ocp}/Vs(SCE)), using a potentiostat (GAMRY REFERENCE 600) and the data were analyzed using GamryEchem Analyst Software. The AC frequency range was scanned from 100 kHz to 10 mHz, with 10 mV peak-to-peak sine wave being the excitation signal. The data processing was based on a non-linear leastsquares fitting procedure as described elsewhere [27–29]. Inhibition efficiencies (IE%) in this case were calculated using the expression [12].

$$IE\% = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100 \quad (1)$$

Where R_{ct} and R'_{ct} are the charge transfer resistance values in the uninhibited and inhibited solutions respectively.

2.3. Polarization measurements

Potentiodynamic polarization curves were recorded, using the same cell setup employed in the impedance studies, at a sweep rate of 1.6 mV^{-1}, primarily from more negative potential than OCP to the more positive potential than OCP through corrosion potential. The inhibition efficiencies were calculated using the relationship [30].

$$IE\% = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \quad (2)$$

where i_{corr} and i'_{corr} are the corrosion current densities in the absence and in the presence of inhibitor respectively.

2.4. Measurement of the potential of zero charge (PZC)

The electrochemical impedance spectra were recorded, imposing various applied DC potentials at 20 kHz AC frequency. The double layer capacitance values obtained were plotted against applied potentials to determine the potential of zero charge.

2.5. Determination of activation energy

In order to determine the activation energy and understand the mechanism of adsorption of the inhibitor onto copper surface, potentiodynamic polarization studies were carried out in the temperature range 30–55 °C in the presence and in the absence of the inhibitor in both the solutions. The dependence of corrosion rate on temperature is calculated using the Arrhenius equation

$$i_{corr} = A\, e^{-E_a/RT} \quad (3)$$

where i_{corr} is corrosion current density, A is the Arrhenius pre-exponential constant, R is the universal gas constant, E_a is the energy of activation and T is the absolute temperature.

2.6. Study of synergistic effect

The synergistic effect of halide ions with the inhibitor on the corrosion inhibition was studied by potentiodynamic polarization studies. The synergism parameter was evaluated using the equation initially proposed by Aramki and Hackermann and reported elsewhere [31–34].

$$S_{I=}\frac{1 - I_{1+2}}{1 - I'_{1+2}} \quad (4)$$

where $I_{1+2} = (I_1 + I_2)$; I_1 is the inhibition efficiency of the halide, I_2, the inhibition efficiency of ciprofloxacin and $I'_{(1+2)}$the inhibition efficiency for ciprofloxacin in combination with halide ion.