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Egyptian Journal of Petroleum

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Full Length Article

Surface protection of mild steel in acidic chloride solution by 5-Nitro-8-Hydroxy Quinoline

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ARTICLE INFO

Article history:

Received 14 September 2016

Revised 5 December 2016

Accepted 24 January 2017

Available online xxx

Keywords:

Acidic chloride solution

MS

NHQ

WL

SEM

FT-IR

ABSTRACT

The effect of commercially available quinoline nucleus based pharmaceutically active compound 5-Nitro-8-Hydroxy Quinoline (NHQ) against the corrosion of mild steel (MS) in 1 M acidic chloride (HCl) solution was investigated by chemical (weight loss – WL) and electrochemical (Tafel polarization, Linear polarization and Electrochemical impedance spectroscopy) techniques. From all the four methods, it is inferred that the percentage of inhibition efficiency increases with increasing the inhibitor concentration from 50 to 300 ppm. The adsorption behavior of inhibitor obeyed through Langmuir isotherm model. Thermodynamic parameters were also calculated and predict that the process of inhibition is a spontaneous reaction. EIS technique exhibits one capacitive loop indicating that, the corrosion reaction is controlled by charge transfer process. Tafel polarization studies revealed that the investigated inhibitor is mixed type and the mode of adsorption is physical in nature. The surface morphologies were examined by FT-IR, SEM and EDX techniques. Theoretical quantum chemical calculations were performed to confirm the ability of NHQ to adsorb onto mild steel surface.

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1. Introduction

Iron is the most abundant element by mass of the earth. Iron and its alloys are widely used in many applications, which have resulted in research into the corrosion resistance in various aggressive environments [1]. The corrosion protection of iron and its alloys especially mild steel in corrosive environments have attracted the attention of many investigators [2–6]. Acid solutions mainly hydrochloric acid is widely used in industry for the removal of corrosion products which in turn accelerates corrosion. Because the cost of hydrochloric acid is very low than other mineral acids. To protect the surface of mild steel and also prevent the further form of corrosion products, the use of inhibitor is one of the important practical methods [7,8]. Most of the heterocyclic organic compounds have been reported in literature as efficient corrosion inhibitors for mild steel in acid medium [9–18].

The corrosion inhibition is a surface process, which involves adsorption of the molecule on the metal/alloy surface. The adsorption is favored by heteroatoms like sulphur, nitrogen, oxygen,

phosphorous and π electrons present in the studied molecule. The adsorption depends mainly on the electronic structure of the molecule [19]. Nowadays several heterocyclic compounds are used as a corrosion inhibitors but, unfortunately some heterocyclic compounds are environmental toxic, high cost, very poor solubility in water and easily unavailable. Therefore, the selection of the inhibitor is mainly based on the availability, low cost, non-toxic, biodegradable, renewable material and the presence of groups or atoms which aid the adsorption of inhibitor to the metal/alloy surface. Moreover, the investigated inhibitor is commercially available, low cost, and soluble in water. Furthermore, it is an environmental friendly inhibitor. Because it acts as an antibiotic and have also been used in an anticancer setting. In the view of these favorable characteristic properties, 5-Nitro-8-Hydroxy Quinoline was chosen for the corrosion studies.

In the present study, NHQ has been investigated for its corrosion inhibition efficiency. Weight loss studies, polarization (Tafel and Linear) studies and impedance studies were employed to investigate the inhibition efficiency of NHQ on MS in acidic chloride solution. FT-IR, SEM and EDX studies were employed to confirm the nature of the adsorbed (protective) film. The results of quantum chemical methods were correlated with experimental results.

Peer review under responsibility of Egyptian Petroleum Research Institute.

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<http://dx.doi.org/10.1016/j.ejpe.2017.01.008>

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Please cite this article in press as: R. Ganapathi Sundaram, M. Sundaravadivelu, Surface protection of mild steel in acidic chloride solution by 5-Nitro-8-Hydroxy Quinoline, Egypt. J. Petrol. (2017), <http://dx.doi.org/10.1016/j.ejpe.2017.01.008>

2. Material and experimental procedure

2.1. Preparation of specimen

The mild steel (MS) specimen of dimension $3.5 \times 1.5 \times 0.2$ cm in size with 1 hole in the upper edge was used for the weight loss measurement and $1.0 \times 1.0 \times 0.2$ cm in size was used for the surface study. For an electrochemical investigation, 1.0 cm^2 area of the MS specimen was exposed to the 100 ml of 1 M acidic chloride (HCl) solution and the balance being covered by commercially available resin. The surfaces of the mild steel specimens were polished with various grades (1/0–7/0) of emery papers and then degreased with acetone. Finally, it is dried in air drier before all the investigation. The composition (wt.%) of the mild steel is: C 0.104, Mn 0.580, P 0.035, S 0.026 and balance is Fe.

2.2. Preparation of acidic chloride solution

The acidic chloride solution (1 M HCl) was prepared by dilution of analytical grade 37% hydrochloric acid with bidistilled water.

2.3. Preparation of inhibitor solution

The investigated inhibitor molecule 5-Nitro-8-Hydroxy Quinoline was purchased from Sigma-Aldrich and used as a green corrosion inhibitor in an acidic chloride medium. It is commercially known as Nitroxoline. The optimized structure of NHQ is given in Fig. 1. The investigated compound contains many active centre's like 3 oxygen and 2 nitrogen atoms. The preparation of different concentrations (50–300 ppm) of inhibitor solution was done according to the standard method as described earlier [20].

2.4. Weight loss studies

In this study, the pre-cleaned and pre-weighed mild steel specimens were suspended in 100 ml of 1 M acidic chloride (HCl) solution with and without various concentrations of inhibitor for a period of 3 h. After that, the mild steel specimens were taken out, washed with distilled water, dried with air drier and weighed accurately. The weight loss studies were made in triplicate and the loss of weight was calculated by taking an average (mean) of these values. The standard deviation in the observed weight loss values was calculated and reported. The corrosion rate (CR) is calculated by the following equation.

$$CR = \frac{W}{St} \quad (1)$$

where W is the average (mean value) weight loss of three mild steel specimens, S is the total area of mild steel specimen and t is the immersion time.

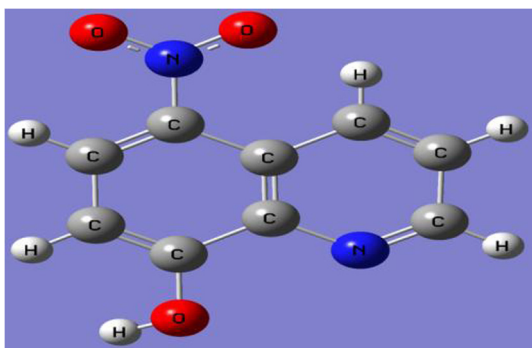


Fig. 1. The optimized structure of NHQ.

From the calculated CR value, the inhibition efficiency (IE%) was calculated according to the following equation:

$$IE(\%) = \left[\frac{W_o - W_i}{W_o} \right] \times 100 \quad (2)$$

where W_o and W_i are the corrosion rate in the absence and presence of various concentrations of NHQ, respectively.

2.5. Electrochemical studies

Electrochemical studies (AC impedance measurements, Tafel polarization measurements and Linear polarization measurements) were carried out by using CH-Electrochemical analyzer model 760 D with CHI 760 D software. The used electrochemical analyzer contains three electrodes that are working electrode, auxiliary electrode and reference electrode. In this setup, the mild steel act as a working electrode, a saturated calomel electrode as a reference electrode and the platinum foil as an auxiliary electrode. Before starting the measurements, the working electrode (MS) was allowed to reach steady-state value of OCP. All the three electrodes were kept immersed in blank and various concentrations of inhibitor solution. The measurements were carried out after 30 min of immersion time at room temperature.

Impedance measurements were carried out in the frequency range from 10 kHz to 0.1 Hz with ac impedance signal of 0.01 V amplitude. From this measurement, the impedance diagrams like Nyquist and Bode were plotted. R_{ct} and C_{dl} values were obtained from the Nyquist plots and the inhibition efficiency (IE) was calculated from the following equation:

$$IE(\%) = \left[\frac{R_{ct}^i - R_{ct}^o}{R_{ct}^i} \right] \times 100 \quad (3)$$

where R_{ct}^i and R_{ct}^o is the charge transfer resistance values of with and without NHQ, respectively.

The Tafel polarization measurements were carried out by changing the electrode potential automatically from -300 mV to $+300$ mV with respect to OCP at a scan rate of 0.1 mV/s. From this study, the inhibition efficiency was calculated from corrosion current density (I_{corr}) values by using the formula:

$$IE(\%) = \left[\frac{I_{corr}^o - I_{corr}^i}{I_{corr}^o} \right] \times 100 \quad (4)$$

where I_{corr}^o and I_{corr}^i are the corrosion current density values in the absence and presence of various concentrations of NHQ, respectively.

For the linear polarization measurements, the potential of the electrode was scanned from -0.02 to $+0.02$ V versus E_{corr} at a scan rate of 0.125 mV/s. The surface coverage (θ) and inhibition efficiency (IE%) were calculated using the following relationship [21].

$$\theta = \left[\frac{R_p^i - R_p^o}{R_p^i} \right] \quad (5)$$

$$IE(\%) = \left[\frac{R_p^i - R_p^o}{R_p^i} \right] \times 100 \quad (6)$$

where R_p^i and R_p^o are the linear polarization resistance values in the presence and absence of NHQ, respectively.

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