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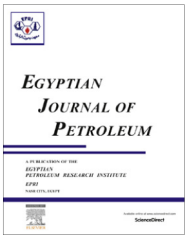

FULL LENGTH ARTICLE

Corrosion protection of mild steel by a new binary inhibitor system in hydrochloric acid solution

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Abstract In the present study, synergistic effect between polysaccharide (*Azadirachta indica* gum) and four variously substituted piperidin-4-one derivatives on the corrosion inhibition of mild steel in 1 mol L^{-1} HCl has been analyzed using weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy. Results of the weight loss measurements clearly reveal that depending on the conformations of the piperidin-4-one derivatives, the concentration of *A. indica* gum varies to achieve its maximum protection level. Detailed FTIR studies of the surface adsorbed layers of inhibitors have been done to elucidate the origin of the synergistic effect on the co-adsorption and subsequent corrosion inhibition of the mild steel.

1. Introduction

The corrosion protection of mild steel is a significant concern among the corrosion scientist and material technologist. Although, mild steel has remarkable economic and substantial applications, its deprived corrosion resistance in acids limits the usage. Acid solutions are essentially used in metal finishing industries, acidizing of oil wells, cleaning of boilers and heat exchangers [1–4]. The application of inhibitors is used to reduce the metal dissolution and iron build up in the pickling baths. The most effective and efficient inhibitors are organic compounds containing heteroatom (O, N, S and P) and having π bonds in their structures. The efficiency of an inhibitor is largely dependent on its adsorption on the metal surface. The adsorption of these molecules depend mainly on certain physicochemical properties of the inhibitor molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms and π orbital character of donating electrons [5,6] and the electronic structure of the molecules [7]. Piperidin-4-one derivatives with two potential anchoring sites act as very good corrosion inhibitors in acidic medium [8]. The substitution effect of piperidin-4-one derivatives for the corrosion inhibition of mild steel in acidic medium has been already reported [8]. The increasing ecological awareness and strict environmental regulations, as well as the inevitable drive toward sustainable and environmentally friendly processes, drew attention towards the development of nontoxic alternatives to inorganic and organic inhibitors. Currently, research in corrosion is focused on the development of green corrosion inhibitors with a good inhibition efficiency and a low risk of

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environmental pollution [9,10]. Even though these green corrosion inhibitors possess excellent inhibition properties in acidic media at room temperature, they are not stable at a higher temperature and longer immersion period [11,12]. Already we have reported the corrosion inhibition performance of *Azadirachta indica* gum in combination with Zn^{2+}/Ni^{2+} on mild steel in acidic medium [13]. In our continuous quest for exploring stable corrosion inhibitors at a higher temperature and longer immersion time, the present work reports on the effect of *A. indica* gum (AIG) in combination with variously substituted piperidin-4-one derivatives for inhibition of mild steel corrosion in 1 mol L^{-1} HCl.

2. Materials and methods

2.1. Materials

2.1.1. Collection and purification of gum

The gum exudates of *Azadirachta indica A. Juss. Meliaceae* was collected locally and identified taxonomically and authenticated by the Botanical Survey of India (BSI), Coimbatore, Tamil Nadu, India. The collected gum exudates were washed with double distilled water and dried in a desiccator to obtain a glassy mass of gum exudates.

2.1.2. Synthesis of variously substituted piperidin-4-one derivatives

Four variously substituted piperidin-4-one derivatives, *r*-2,*c*-6-diphenylpiperidin-4-one (01), *r*-2,*c*-6-diphenyl-*t*-3-methylpiperidin-4-one (02) *r*-2,*c*-6-diphenyl-*t*-3,*t*-5-dimethylpiperidin-4-one (03) and *r*-2,*c*-6-diphenyl-N-methylpiperidin-4-one (04) have been synthesized via the procedure given by Noller and Baliah [14].

2.2. Methods

The mild steel of the composition 0.07 wt.% C, 0.008 wt.% P, 0.34 wt.% Mn, remaining iron (Fe) was used in the study. The metal specimens used for weight loss measurements were cut to obtain rectangular surfaces with dimensions of 25 × 10 × 1 mm with a hole drilled at the upper edge in order to hook them to a glass rod and immerse in the aggressive medium. Substantial layer of the specimen was removed by using various grades of abrasive papers and degreased by scrubbing with bleach-free scouring powder, followed by thorough rinsing in water and acetone.

The gravimetric experiments were carried out according to the ASTM practice standard G-31 [15]. Before carrying out the experiments, the pre-cleaned specimens were weighed on a balance using 0.1 mg precision. The weighed specimens were immersed in the corrosive medium with and without inhibitors for 1 h. At the end of experiment, the specimens were removed from the corrosive medium and immersed in the Clark solution (1000 ml of hydrochloric acid, 20 g of antimony trioxide (Sb_2O_3) and 50 g of stannous chloride ($SnCl_2$)) for 40 s, rinsed with water, cleaned with acetone, dried in hot air and finally weighed. The mean of weight loss values of three identical specimens was used to calculate the corrosion rate and inhibition efficiency of the inhibitor. Corrosion rate and inhibition efficiency were calculated using the formulae given in Eqs. (1) and (2)

$$\text{Corrosion rate (mmpy)} = 87.6 \times \frac{W}{\rho A t} \quad (1)$$

where, W is the weight loss (g), 'ρ' the density of the mild steel specimen (g cm^{-3}), 'A' the area of specimen (cm^2) and t the time of exposure (h).

$$\text{Inhibition efficiency (\%)} = \frac{W_o - W_i}{W_o} \times 100 \quad (2)$$

where, W_i and W_o are the weight losses of mild steel in inhibited and uninhibited solutions respectively.

The electrochemical experiments were performed using three-electrode cell assembly. The cell consisted of a platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was immersed in the acid solution and the constant steady-state (open circuit) potential was recorded as a function of time, when it became virtually constant. The polarization studies were carried out over a potential of +200 to −200 mV with respect to the open circuit potential at a scan rate of 1 mV s^{-1}. The linear Tafel segments of the cathodic curves and the calculated anodic Tafel lines were extrapolated to the point of intersection to obtain the corrosion potential (E_{corr}) and corrosion current density (i_{corr}). The inhibition efficiency was evaluated from the measured I_{corr} values using Eq. (3)

$$\text{Inhibtion efficiency (\%)} = \frac{i^o_{corr} - i_{corr}}{i_{corr}} \times 100 \quad (3)$$

where, i^o_{corr} is the corrosion current density without inhibitor and i_{corr} is the corrosion current density with inhibitor.

The electrochemical impedance spectroscopic (EIS) measurements were carried out using AC signals of 10 mV amplitude over the frequency range of 10 kHz–0.01 Hz. The electrode was immersed in the solution for half an hour before starting the impedance measurements. All the impedance data were automatically controlled by Z_{view} software and the diagrams were given as Nyquist plots. The charge transfer resistance (R_{ct}) values were obtained from the diameter of the semicircles of the Nyquist plots. The inhibition efficiency of the inhibitor has been obtained from the charge transfer resistance values using the following Eq. (4)

$$\text{Inhibition efficiency(\%)} = \frac{R_{ct} - R^o_{ct}}{R_{ct}} \times 100 \quad (4)$$

where, R_{ct} and R^o_{ct} are the charge transfer resistance with and without inhibitors respectively.

To determine the effect of inhibitors with the mild steel specimen, a Shimadzu FT- IR 8000 spectrophotometer is employed in the 4000–400 cm^{-1} region with KBr disk technique.

3. Results and discussion

3.1. Weight loss measurements

3.1.1. Corrosion inhibition performance of AIG

The corrosion of mild steel in 1 mol L^{-1} HCl in the absence and presence of various concentrations (2–80 × 10^{-3} g L^{-1}) of AIG was investigated at room temperature using weight loss measurements for 1 h immersion period. Corrosion rate (mmpy), inhibition efficiency (%) and surface coverage (θ) were calculated using the Eqs. (1)–(3) and the results are given in Table 1.