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Investigation of the effect of piperidin-1-yl-phosphonic acid on corrosion of iron in sulfuric acid

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Abstract The inhibitive effect of the piperidin-1-yl-phosphonic acid (PPA) on the corrosion of iron in 1 M H_2SO_4 solution has been investigated by weight loss measurement, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The presence of (PPA) reduces remarkably the corrosion rate of iron in acidic solution. The effect of temperature on the corrosion behavior of iron was studied in the range of 298–328 K. Results clearly reveal that the (PPA) behaves as a mixed type corrosion inhibitor with the highest inhibition at 5×10^{-3} M. The adsorption of PPA on the iron surface obeys the Langmuir's adsorption isotherm.

1. Introduction

Corrosion inhibition as a protective method is of great importance. Inhibitors often work by adsorbing themselves on the metallic surface, protecting it by forming a film. The strength of the adsorption bond is the dominant factor for organic inhibitors. Their effectiveness depends on the chemical composition, their chemical structure and their affinity for the metal surface. A wide variety of compounds are used as corrosion inhibitors for metals in acidic media (Schmitt, 1984; Mernari et al., 1998; Onuchukwu, 1988; Ashassi-Sorkhabi and Nabavi-Amri, 2000; Ebenso, 2002; Gomma, 1998; Ayers and Hackerman, 1963; Szauer and Brandt, 1981; Morad, 2008).

Phosphonates, which were originally introduced as scale inhibitors in water treatment, were later proved to be good corrosion inhibitors also (Awad and Turgoose, 2004). Their impact on the environment was reported to be negligible at the concentration levels used for corrosion inhibition (Awad, 2005; Jaworska et al., 2002). There are excellent sequestering agents for electroplating, chemical plating, degreasing and cleaning (Fang et al., 1993). The use of phosphonic acids for the protection of iron and its alloys from corrosion in different

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media has been the subject of several research works (Choi et al., 2002; Gonzalez et al., 1996; Ebenso, 2002; Telegdi et al., 2001; Amar et al., 2003, 2008; Laamari et al., 2001, 2004, 2010, 2011a,b).

In this work we continue our investigations on piperidin-1-yl-phosphonic acid as inhibitors of Armco iron corrosion mainly in 1 M H_2SO_4. The assessment of the corrosion behavior was studied using weight loss, potentiodynamic polarization measurement and electrochemical impedance spectroscopy (EIS). Thermodynamic data were also obtained from adsorption isotherms and Arrhenius plots.

2. Experimental

2.1. Electrochemical cell

Electrochemical experiments were performed using a conventional three electrode cell assembly. The working electrode is a carbon steel rotating disk with a surface area of 1 cm^2 and had the following composition (O: 0.03%, Mn: 0.03%, N: 0.018%, S: 0.018%, C: 0.012%, P: 0.004%, Fe: 99.8%). It is abraded with different emery papers up to 1200 grade, washed thoroughly with double-distilled water, degreased with AR grade ethanol, acetone, and subjected to drying at room temperature.

A saturated calomel electrode (SCE) was used as the reference electrode. All the measured potentials presented in this paper are referred to this electrode. The counter electrode was a platinum plate with a surface area of 2 cm^2.

The aggressive solution of 1.0 M H_2SO_4 was prepared by the dilution of AR grade 98% H_2SO_4 with distilled water. The inhibitor is added to freshly prepared 1 M H_2SO_4 in the concentration range of 10^{-4} to 5×10^{-3} M.

The corrosion inhibitor used in this work is piperidin-1-yl-phosphonic acid (PPA). The organic compound is synthesized by the micro-wave technique. The obtained product is purified and characterized by ^1H NMR, ^{13}C NMR, ^{31}P NMR spectroscopy and IR techniques. The molecular structure is shown in Fig. 1.

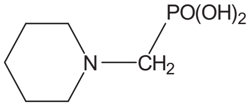

Figure 1 Structure of piperidin-1-yl-phosphonic acid (PPA).

2.2. Methods

2.2.1. Gravimetric measurements

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 mL of 1 M H_2SO_4 with and without the addition of different concentrations of inhibitor. The iron specimens used have a rectangular form ($2 \times 2 \times 0.05$ cm). The immersion time for the weight loss was 24 h at 298 K and 6 h at other temperatures. After the corrosion test, the specimens of Armco iron were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Triplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in mg cm^{-2} h^{-1}. The inhibition efficiency (IE %) was determined by using the following equation:

$$IE\% = \frac{CR_0 - CR}{CR_0} \times 100 \tag{1}$$

where, CR and CR_0 are the corrosion rates of carbon steel with and without the inhibitor, respectively.

2.2.2. Electrochemical measurements

Two electrochemical techniques, namely DC-Tafel slope and AC-electrochemical impedance spectroscopy (EIS), were used to study the corrosion behavior. All experiments were performed in one-compartment cell with three electrodes connected to a Voltalab 10 (Radiometer PGZ 100) system controlled by the Volta master 4 corrosion analysis software model.

Polarization curves were obtained by changing the electrode potential automatically from −800 to −200 mV versus open circuit potential (E_{ocp}) at a scan rate of 1 mVs^{-1}. The inhibition efficiency is calculated by the following equation:

$$IE\% = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \tag{2}$$

Where i^0_{corr} and i_{corr} are the corrosion current density values without and with the inhibitor, respectively. EIS measurements were carried out under potentiostatic conditions in the frequency range of 100–0.1 Hz, with an amplitude of 10 mV peak-to-peak, using AC signal at E_{ocp}. All experiments were performed after immersion for 60 min in 1 M H_2SO_4 with and without the addition of inhibitor.

3. Results and discussion

3.1. Weight loss measurements

3.1.1. Effect of inhibitor concentration

Corrosion inhibition performance of organic compounds as corrosion inhibitors can be evaluated using electrochemical and chemical techniques. For the chemical methods, a weight loss measurement is ideally suited for long term immersion tests. Corroborative results between weight loss and other techniques have been reported (El-Naggar, 2007; Umoren and Ebenso, 2007; El-Etre, 2003; Lebrini et al., 2006).

The anodic dissolution of iron in acidic media and the corresponding cathodic reaction have been reported to proceed as follows (Solomon et al., 2010):

$$Fe \rightarrow Fe^{2+} + 2e- \tag{3}$$

$$2H^+ + 2e- \rightarrow 2H_{ads} \rightarrow H_2 \tag{4}$$

As a result of these reactions, including the high solubility of the corrosion products, the metal loses weight in the solution. The values of corrosion rate and inhibition efficiency from gravimetric measurements at different concentrations of PPT are summarized in Table 1, and the inhibition efficiency as a function of concentration is shown in Fig. 2. The results show that as the inhibitor concentration increases, the corrosion rate decreases and therefore the inhibition efficiency increases. It can be concluded that this inhibitor acts through adsorption on the iron surface and formation of a barrier layer between the metal and the corrosive media. A detailed study on the corrosion behavior of iron was carried out at a temperature range of 298–328 K using the weight loss technique.

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