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Highly effective organic corrosion inhibitor for zinc metal in 0.5 N Hydrochloric acid solution

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ABSTRACT

Highly effective 2-phenyl imidazole has been used as an organic corrosion inhibitor in controlling the corrosion of zinc metal immersed in 0.5 N HCl. Inhibition efficiency and corrosion rates were calculated from Weight loss, gasometric and thermometric methods. The inhibition efficiency was found to increase with increase in the concentration of inhibitor molecules on the zinc metal surface which obyed Temkin adsorption isotherm. The surface film formed over the zinc metal was characterized by Scanning Electron Microscopy.

KEYWORDS: Acidic solution, Atomic force microscopy, Gasometry, 2-phenyl imidazole, Surface morphology, Thermometric, Weight loss, Zinc corrosion.

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1. INTRODUCTION

Corrosion inhibitors are substances which when added in small concentrations to corrosive media decreases or prevent the reaction of the metal with the media[1]. The use of inhibitors is one of the most practical methods for protecting metals or alloys from corrosion. Compared with organic and inorganic salt corrosion inhibitors, using organic corrosion inhibitors is an effective, inexpensive and less pollution means of reducing the degradation of metals or alloys in many fields of applications and which has been extensively investigated during the last decade [2-8]. The proposed action to be earning to control the corrosion process is to isolate the metals and alloys from the corrosive environments. Use of corrosion inhibitors is one of the available methods for metals against corrosion. Organic compounds with heteroatom, multiple bonds and aromatic rings proved to be effective corrosion inhibitors. Diversity of organic compounds were used as corrosion inhibitors for zinc metal in different environments. These inhibitors restraint the corrosion action by adsorption on to the metal surface. In this work, The 2-phenyl imidazole used as a corrosion inhibitor for zinc metal in 0.5 N HCl acid solution by weight loss, gasometry and thermometric methods. The inhibition efficiency and corrosion rates were calculated from weight loss, gasometric and thermometric methods. The surface film formed over the zinc metal has been characterized by SEM and AFM. An organic compound to interact with a metal surface is closely connected with chemical adsorption. The efficiency of this inhibitor is correlated to the presence of polar functional groups with S, O or N atoms, ð-electrons in the molecule.

2. EXPERIMENTAL SECTION

2.1 Materials and Methods

Specimen preparation

Composition of zinc specimen: lead 0.03%, cadmium 0.04%, iron 0.001% and the quantity left over being zinc and size of 4 × 2 × 0.08 cm were used for weight loss, gasometry and thermometry studies. Zinc metal specimens were polished with a sequence of emery papers of different grades from 400-1200, degreased with absolute ethanol and dried. The inhibitor compound, 2-phenyl imidazole was customary Alfa Aesar Chemicals United Kingdom. The working surface was at a subsequent time ground with acetone followed by double-distilled water, dried in warm air and then stored in moisture-free desiccators before ducking in a corrosive medium.[10].

2.2 Preparation of Organic inhibitor

2-phenyl imidazole was prepared by different concentration with 100 ml of ethanol. Test solutions with different concentrations from 0.19 g/L to 1.32 g/L were prepared by diluting the stock solution in 0.5 N HCl[11,12]

2.3 Weight loss measurements

Zinc specimens with dimensions of 3.0 cm × 3.0 cm were polished, degreased with acetone and dried. A Mettler balance – M5 type was used to weigh the zinc specimens to an accuracy of 0.0001 gm. The specimens were deep in a beaker containing 100 ml of 0.5 N HCl without and with 5,10,30,50,100 mM concentrations of the inhibitor (organic inhibitor) using glass hooks and rods[13]. The effect of the temperature was also studied an contact period of 2 hours using a water-circulating thermostat (Equitron). All the test standard systems were open to the air. After 2 hours, the specimens were taken out, washed with distilled water and re-weighed[14]. To obtain good reproducibility, experiments were carried out in triplicate, and the average values were be given. The weight loss was recorded, and the inhibition efficiency as well as the surface area coverage was calculated using the following equation[15,16].

$$I.E\,(\%) = [W_0 - W_i / W_0]100$$

$$\theta = W_0 - W_i / W_0$$

Where W_o and W_i are the weight loss of the metal in the absence and presence of the inhibitor separately. The corrosion rate (C.R) of the metal was calculated by using the following equation.

$$C.R\,(mmy) = \frac{87.6 / W}{A\,t\,D}$$

Where W is the weight loss of the zinc metal (mg), A is the surface area of the metal specimen (cm^2), t is the frostbite time (h) and D is the density of the metal (g/cm^3).

2.4 Gasometric measurements

The acidic corrosion of zinc is characterised by evolution of hydrogen and the rate of corrosion is proportional to the amount of hydrogen gas evolved [17]. Gasometric experiments were carried out respectively by varying the corrodent (5, 10, 30.50 and 100 mM) and inhibitor concentrations respectively. It can be observed that the higher the corrodent concentration the higher the volume of gas evolved per minute at room temperature. The results of the effect of temperature variation in the absence of 2-phenyl imidazole in 0.5 N HCl solution[18]. It is evident that higher temperature of provided higher volume of hydrogen gas per minutes resulting into a higher rate of reaction. 2-phenyl imidazole systems were tested. To establish, regardless of temperature or corrodent concentration, the higher the volume of gas evolved per minutes the higher the rate of reaction. Concentration increases also inhibitor efficiency increases and corrosion rate decreases.

From the gasometry experiments, the inhibition efficiency is calculated by using the following equation.

$$I.E\ (\%) = [V_0\text{-}V_i / V_0]\ 100$$

Where V_o and V_i are the volume of hydrogen gas evolved in the absence and presence of the inhibitor respectively.

2.5 Thermometric measurement

The reaction vessel is a three-necked round bottom flask and the flask was well lagged to prevent heat losses. In this technique the corrodent (HCl) concentration was also at 0.5N and different concentration 5, 10, 30, 50 100 mM of inhibitors respectively. The volume of the test solution used was 100 cm^3. The initial temperature in all the experiments was kept at room temperature. The progress of the corrosion reaction was monitored by determining the changes in temperature with time (each minute for the first five minutes, each five minutes for the next 25 minutes and each ten minutes for the last thirty minutes) using a calibrated thermometer (0 - 100°C) to the nearest ± 0.05°C. The data was generated for a period of one hour. This method enabled the computation of the reaction number (RN). From the rise in temperature of the system per minute, the reaction number (RN) was calculated using equation[19].

$$R_N = T_m - T_i / t$$

Where T_m is the maximum temperature, T_i is the initial temperature and t is the time taken to attain the maximum temperature. The inhibition efficiency is calculated by using the following equation

$$I.E\ (\%) = RN_0 - RN_i / RN_0$$

Where RN_o is the reaction number in the absence of the inhibitor and RN_i is the reaction number in the presence of various concentrations of the inhibitor.

2.6 Surface morphology

The surface micrographs of the zinc specimens in different test solutions were obtained by SEM. SEM provides a pictorial representation of the surface of the zinc metal to understand the nature of the surface film in the absence and presence 2-phenyl imidazole inhibitor. The scanning electron microscopy photographs were recorded at 10,000 x magnification using SEM ULTRA-60 nanofab, and Hitachi scanning electron microscopes. AFM measurement was performed using a Bruker Icon Dimension with the Scan Asyst module including tapping mode. The scan rate and area of the images were 0.6 Hz and 5 ìm × 5 ìm, respectively [20].

3. RESULTS AND DISCUSSION

3.1 Weight loss studies

Weight loss studies were conducted and the inhibition efficiency (IE) values were calculated. Values of inhibition efficiency obtained from these experiments are presented in the table-1

Table 1 Values of inhibition efficiency (I.E (%)) obtained from various weights loss experiments.

Weight loss method	Values of I.E(%) different Concentrations (mM) of 2-phenyl imidazole inhibitor for zinc immersed in0.5 N HCl				
Concentration	5	10	30	50	100
Inhibition efficiency (%)	38.0	60.1	77.5	86.2	96.5

It can be observed from the table 1 that there is very good agreement between the values of inhibition efficiency obtained from these three methods. The results show that the inhibition efficiency increases with increase in the inhibitor concentration. The dependence of inhibition efficiency of the inhibitor concentration is shown in figure-1

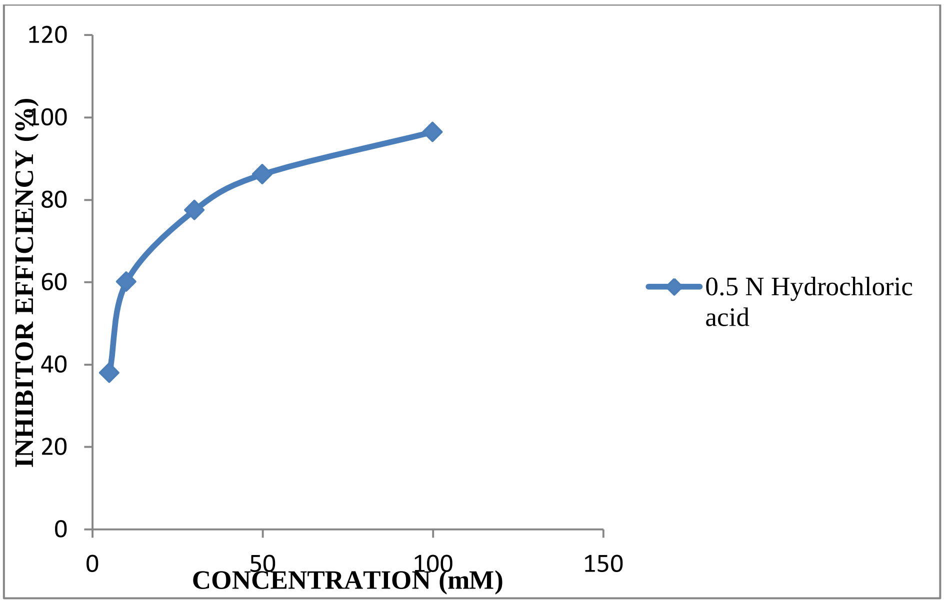


Figure 1 Variation of inhibition efficiency with concentration of the 2-phenyl imidazol inhibitor for zinc in 0.5 N HCl

Values of corrosion rates obtained from the weight loss experiments for the inhibitor for the corrosion of zinc in 0.5 N HCl in the presence of different concentrations of the inhibitor are presented in the table-2

Table 2 Values of corrosion rates obtained from the weight loss experiments.

Corrosive medium 0.5 N HCl	Values of corrosion rates and different concentrations (mM) of 2-phenyl imidazole inhibitor				
Concentration	5	10	30	50	100
Corrosion rates	86.2	75.1	52.4	35.3	20.6

From the table-2 it can be seen that the corrosion rates for the corrosion of zinc in 0.5 N HCl decreases with increasing concentration of the inhibitor. The effect of inhibitor concentration on the corrosion rates is shown in figure-2.

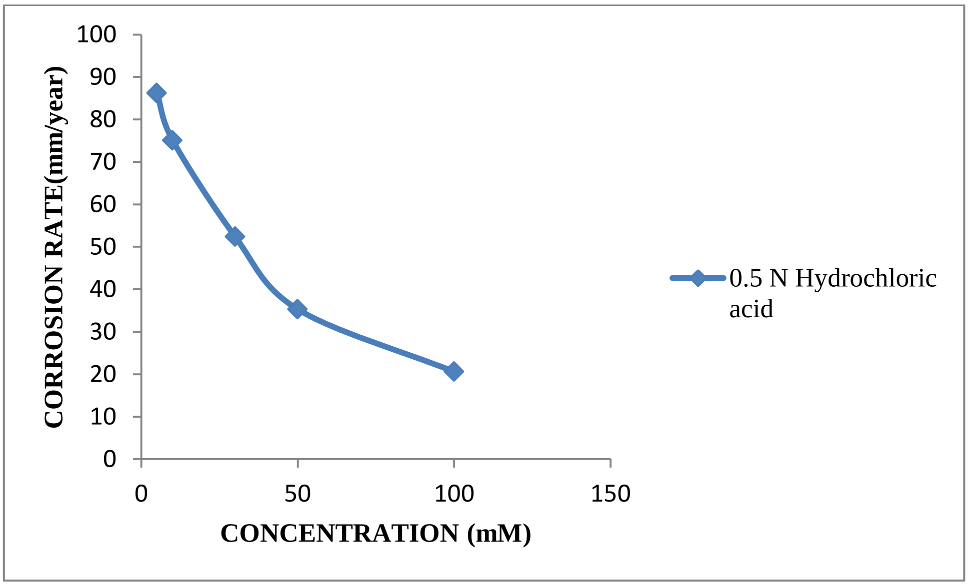


Figure 2 Variation of corrosion rates with concentration of the 2-phenyl imidazole inhibitor for zinc in 0.5 N HCl

3.2 Gasometric studies

Table 3 Values of inhibition efficiency (I.E (%)) obtained from various gasometric experiments.

Method Employed Gasometric	Values of I.E(%) different Concentrations (mM) of 2-phenyl imidazole inhibitor for zinc immersed in 0.5 N HCl				
Concentration (mM)	5	10	30	50	100
Inhibitor efficiency (%)	35.2	60.4	74.4	83.0	93.8

It can be observed from the table 3 that there is very good agreement between the values of inhibition efficiency obtained from these gasometric method. The results show that the inhibition efficiency increases with increase in the inhibitor concentration. The dependence of inhibition efficiency of the inhibitor concentration is shown in figure-3

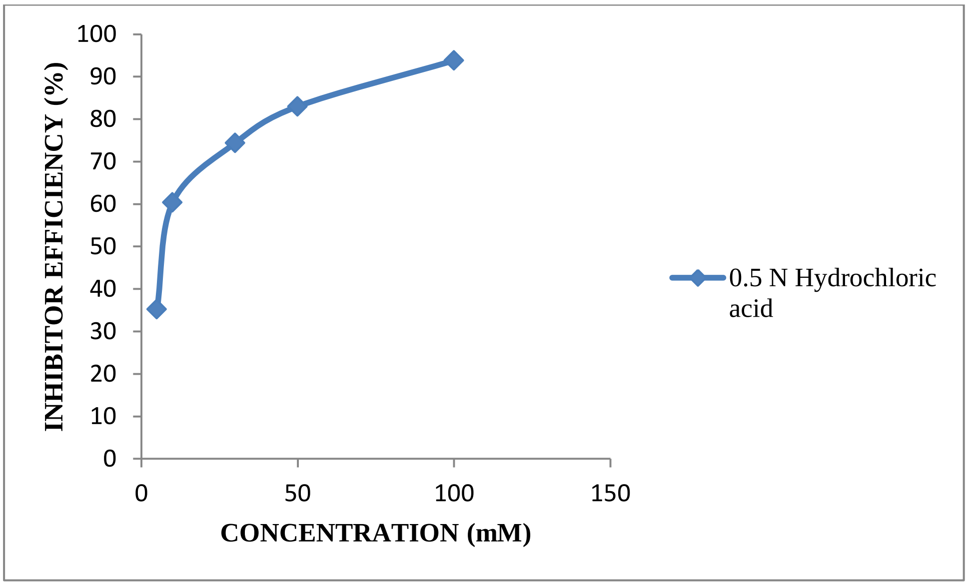


Figure 3 Variation of inhibition efficiency with concentration of the 2-phenyl imidazole inhibitor for zinc in 0.5 N HCl

Table 4 Values of corrosion rates obtained from the Gasometric experiments.

Method Employed Gasometric	Values of Corrosion rate different Concentrations (mM) of 2-phenyl imidazole inhibitor for zinc immersed in 0.5 N HCl				
Concentration (mM)	5	10	30	50	100
Corrosion rate (mm/year)	96.1	78.3	55.5	33.4	26.2

From the table-4 it can be seen that the corrosion rates for the corrosion of zinc in 0.5 N HCl decreases with increasing concentration of the inhibitor. The effect of inhibitor concentration on the corrosion rates is shown in figure-4.

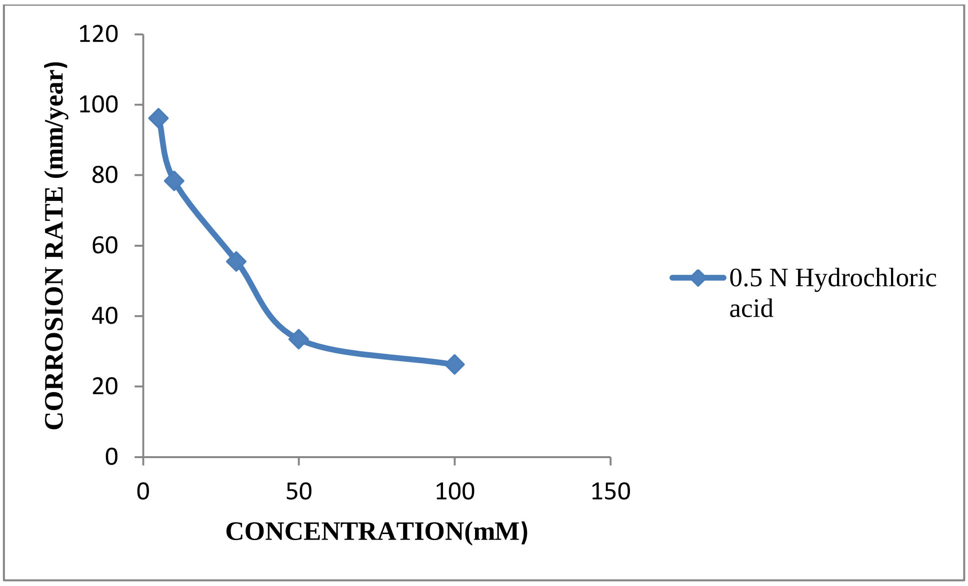


Figure 4 Variation of corrosion rates with concentration of the the 2-phenyl imidazole inhibitor for zinc in 0.5 N HCl

3. 3 Thermometric studies

Table 5 Values of inhibition efficiency (I.E (%)) obtained from various thermometric experiments.

Method Employed Thermometric	Values of I.E(%) different Concentrations (mM) of 2-phenyl imidazole inhibitor for zinc immersed in0.5 N HCl				
Concentration (mM)	5	10	30	50	100
Inhibitor efficiency (%)	38.4	61.3	78.2	85.6	95.4

It can be observed from the table 5 that there is very good agreement between the values of inhibition efficiency obtained from these Thermometric method. The results show that the inhibition efficiency increases with increase in the inhibitor concentration. The dependence of inhibition efficiency of the inhibitor concentration is shown in figure-5

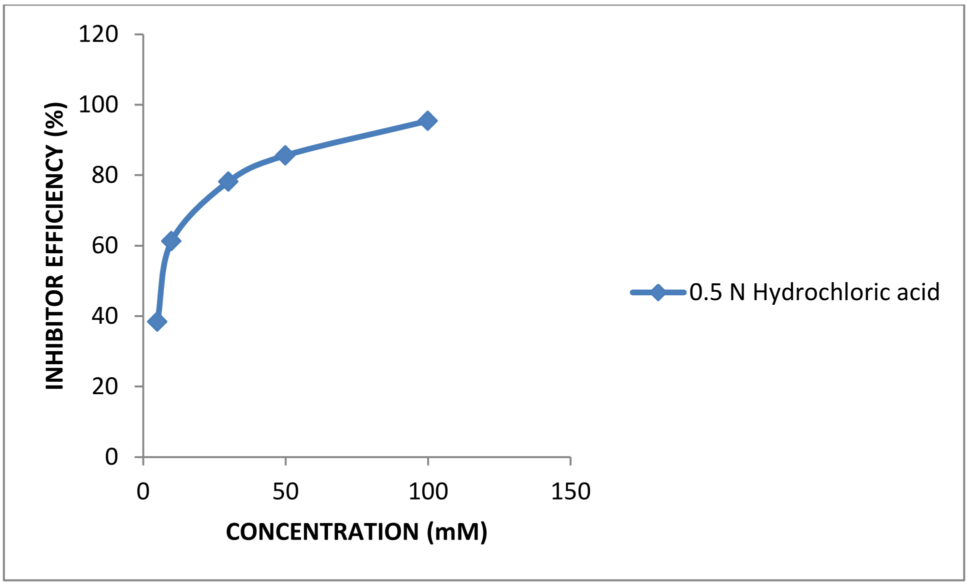


Figure 5 Variation of inhibition efficiency with concentration of the 2-phenyl imidazole inhibitor for zinc in 0.5 N HCl

Table 6 Values of corrosion rates obtained from the Thermometric experiments.

Method Employed Gasometric	Values of corrosion rate different concentration(mM) of 2-phenyl imidazole inhibitor for zinc immersed in 0.5 N HCl				
Concentration (mM)	5	10	30	50	100
Corrosion rate (mm/year)	95.7	76.4	55.5	30.1	24.6

From the table-6 it can be seen that the corrosion rates for the corrosion of zinc in 0.5 N HCl decreases with increasing concentration of the inhibitor. The effect of inhibitor concentration on the corrosion rates is shown in figure-6.

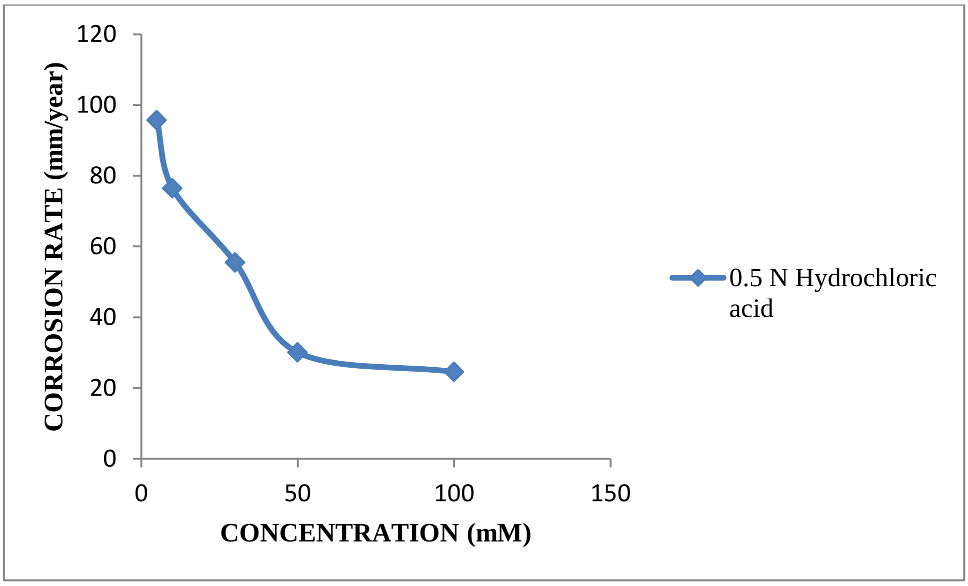


Figure 6 Variation of corrosion rates with concentration of the the 2-phenyl imidazole inhibitor for zinc in 0.5 N HCl

The inhibitor molecule contains two nitrogen atoms and one sulfur in its molecular structure. These nitrogen atoms possess lone pairs of electrons required for the adsorption process. On adsorption strongly adherent layer is formed on the metal surface. This layer acts as a barrier between the metal and the environment giving protection to the metal. In addition to these, the amino groups present in the molecule can be easily protonated in acid medium to form the cationic form of the inhibitor. The chloride ions present in the acid medium gets adsorbed specifically on the positively charged metal surface due to its lesser degree of hydration leading to the creation of excess negative charges on the metal surface which enhances more adsorption hence protection of the metal. Another factor responsible for the higher inhibition efficiency of the inhibitor is the large surface area of the inhibitor molecules which provides higher surface coverage to the metal after getting adsorbed on to the metal surface. The structure of the inhibitor is shown in figure 7

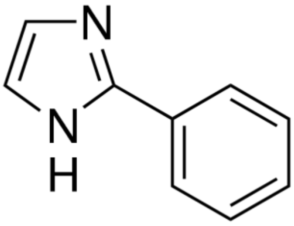
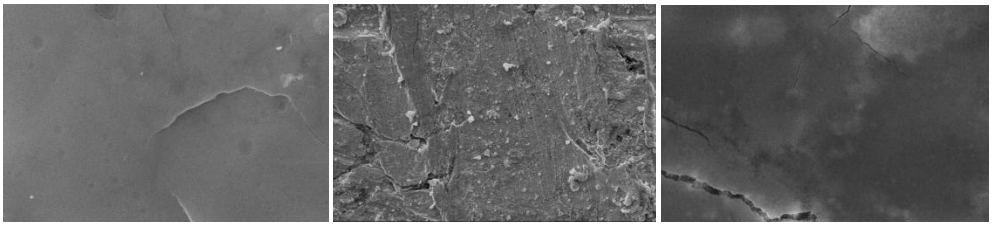


Figure 7 The structure of the 2-phenyl imidazole

3. 4 Analysis of SEM

SEM provides a pictorial representation of the zinc metal surface. The SEM images of zinc specimens immersed in 0.5 N HCl for 30 min. in the absence and presence of 2-phenyl imidazole inhibitor systems is shown in Figures 8c, respectively. The SEM micrograph of the polished zinc surface in Figure.8a show the smooth surface of the metal, without any corrosion inhibitor, smooth surface of zinc metal and decrease the corroded area of zinc metal [21]. The SEM micrographs of the zinc surface immersed in 0.5 N HCl (Figure 8b) show the roughness of the metal surface, with highly corroded areas. However, Figure 4c shows that in the presence of 5 mM 2-phenyl imidazole, the inhibition efficiency is enhanced, as seen from the decrease in the corroded areas.



8a 8b 8c

Fig. 8: Scanning electron micrographs of zinc immersed for 30 minutes (a) polished Zinc (b) zinc metal immersed in 0.5 N HCl (c) zinc metal immersed in 0.5 N HCl with 2-phenyl imidazole

In the presence of the 5 mM 2-phenyl imidazole, the surface is covered by a thin layer of inhibitor that effectively controls the dissolution of the zinc[22].

3.5 Atomic force microscopy analysis

AFM is a powerful technique to investigative the surface morphology at the nano-to micro-scale and has become a new choice to study the influence of the inhibitor on the generation and the progress of the corrosion at the metal solution interface. Three dimensional (3D) AFM morphologies for a polished zinc surface (reference sample), a zinc surface immersed in0.5 N HCl (blank) and zinc surfaces immersed in 0.5 N HCl containing 5 mM 2-phenyl imidazole inhibitor is shown in Figure 9a, b, and c, respectively[23]. The roughness of the zinc coupons for the polished plate, in the presence of H_2SO_4, and with added 5 mM 2-phenyl imidazole inhibitor is 15.9 nm, 181 nm, 33.4 nm and 28 nm, respectively[24]. This finding indicates that the addition of the different concentration inhibitor reduces the surface roughness, with the 2-phenyl imidazole inhibitor providing better protection[25].

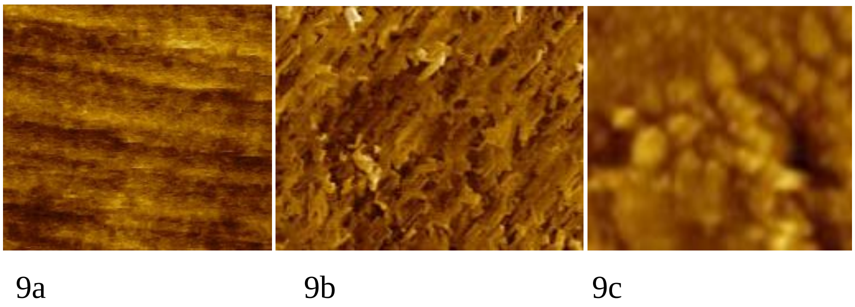


Fig. 9: AFM 3D images of zinc immersed for 30 minutes (9a) polished coupon, (9b) zinc metal immersed in 0.5 N HCl, (9c) zinc metal immersed in 0.5 N HCl with the addition of 5 mM 2-phenyl imidazole inhibitor.

4. ADSORPTION ISOTHERMS

From the weight loss measurements, the degree of surface coverage (θ) for various concentrations of the inhibitor were determined. Temkin's adsorption isotherm was tested by plotting logC vs θ which gave a straight line thereby indicating that the adsorption of the inhibitor on the surface of zinc from 0.5 N HCl obeys Temkin's adsorption isotherm. Figure -10 shows the Temkin adsorption isotherm plot for zinc in 0.5 N HCl containing different concentrations of the inhibitor.

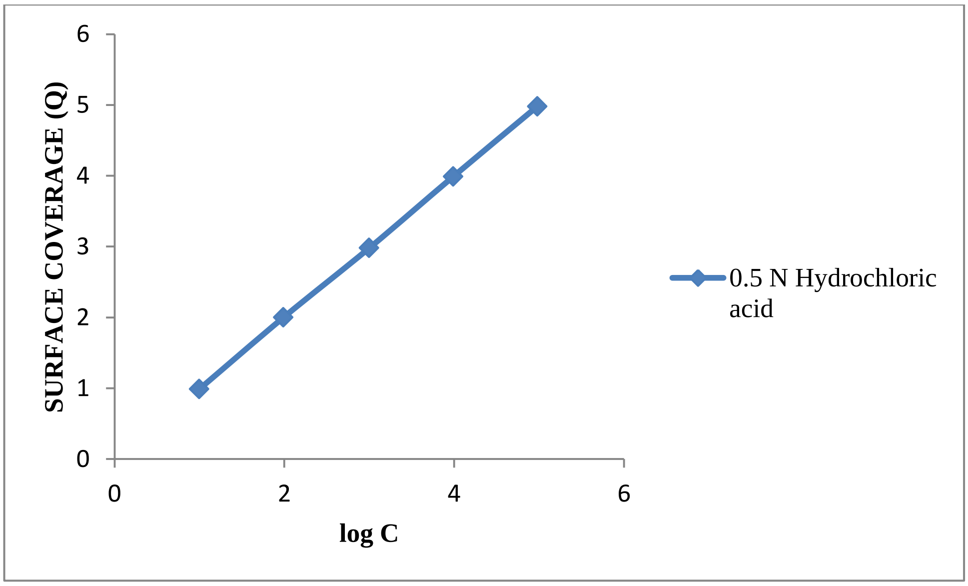


Figure 10. Temkin adsorption isotherm plot for zinc in 0.5 N HCl containing different concentrations of the inhibitor.

5. CONCLUSION

2-phenyl imidazole used as a corrosion inhibitor in controlling the control of zinc metal in 0.5 N HCl The inhibition efficiency and corrosion rates determined by weight loss, gasometric, and thermometric methods. All these techniques indicates that 0.5 N HCl concentration of inhibitor exhibit 96.5 % inhibitor efficiency and 20.6 % corrosion rates. The concentration of the inhibitor increases, the inhibitor efficiency increases and corrosion rate decreases. Performed well and gave high percentage of inhibition efficiency. The indicates that protective film formed over the zinc metal surface. The protective film was characterized by SEM and AFM. The adsorption of the inhibitor on to zinc surface obeyed Temkin adsorption isotherm.

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