Corrosion resistance of zinc metal on acid solutions by using Dihexyl Sulphide as Inhibitor

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ABSTRACT: The effect of dihexyl sulphide as a corrosion inhibitor for Zinc in 0.5N HCl and 0.5N H_2SO_4 by conventional weight loss and gasometric methods. Results obtained from weight loss and gasometry methods indicate that dihexyl sulphide exhibited good composition inhibition efficiencies in both acids but performed better in 0.5N H_2SO_4 than in 0.5N HCl. The inhibition efficiency was found to increase with increase in the inhibitor molecules on the zinc metal surface, which obyed Temkin adsorption isotherm. The surface film formed over the zinc surface was characterized by Scanning Electron Microscope.

Key words- acidic solutions, dihexyl sulphide, gasometry, surface morphology, weight loss, zinc corrosion.

1. INTRODUCTION

Corrosion is gradual deterioration of metals and alloys by its chemical or electrochemical reaction with their environment. Acid pickling, acid cleaning and acid decaling are some of industrial process in which metals are exposed to different acids of various concentrations. In order to reduce the metal loss and acid consumption, the corrosion inhibitors are added to the solutions [1-8].Organic compounds containing nitrogen, oxygen and sulphur in their molecular structures have been reported to function as effective inhibitors for different metals in different corrosive media. The efficiency of these compound as corrosion inhibitors is attributed to the number of mobile electron pair present in the molecule. The efficiency of the corrosion inhibitors are also reported to be effect by their molecular structure, molecular size and the nature of the substituent groups [9, 10].These kind of inhibitors minimize the corrosion rate of the metal by getting adsorbed on the metal surface thereby blocking the active sites on the metals.

In the present work, dihexyl sulphide as an inhibitor for zinc metal immersed in 0.5N HCl and 0.5N H_2SO_4. The efficiency of the inhibitor was evaluated at different concentrations, by conventional weight loss and gasometry methods, The surface formed over the zinc metal surface between characterized by SEM.

2. MATERIALS AND METHODS

The zinc metal specimens of composition: lead 1.03%, cadmium 0.04%, iron 0.001% and the reminder being zinc and size of 4 × 2 × 0.08 cm with a small hole of approximately 3mm near the end of the specimen were polished with a series of emery papers of various grades from 400-1200, degreased with absolute ethanol and air dried. The inhibitor compound, dihexyl sulphide was imported from the Fluka AG of Switzerland. The corrosion medium was 0.5N HCl and 0.5N H_2SO_4 make ready from A.R grade HCl and H_2SO_4 and distilled water.

2.1. Weight loss measurements

Zinc coupons with dimensions of 3.0 cm x 3.0 cm were polished, cleaning 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 immersed in a beaker containing 100 ml of 0.5N HCl and 0.5N H_2SO_4 without and with 5, 10, 30, 50,100 mM concentrations of the inhibitors (organic inhibitor) using glass hooks and rods. The effect of the temperature was also studied an exposure period of 2 hours using a water-circulating thermostat (Equitron). All the test were open to the air standard system. After 2 hours, the specimens were taken out, washed with distilled water and re-weighed [11-16]. To obtain good reproducibility, experiments were carried out in triplicate, and the average values were obtained. The weight loss was recorded, and the inhibition efficiency as well as the surface coverage was calculated using the following equation. From the weight loss investigation the percentage of inhibition efficiency (I.E) and the degree of surface coverage (θ) were calculated by using the following equations.

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

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

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).

2.2. Gasometric measurements

The acidic corrosion of zinc is characterized 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, 3,.50 and 100 mM) and inhibitor concentrations respectively. It can be observed from table1 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 Dihexyl sulphide in 0.5N HCl and 0.5N H_2SO_4 solution. It is evident that higher the temperature provided then higher the volume of hydrogen gas per minutes resulting into a higher rate of reaction. Di hexyl sulphide 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, the inhibition efficiency increases and corrosion rate decreases. Homogeneous results were obtained from the weight loss experiments [18].

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

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

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

2.3. Surface characterization technique

The surface micrographs of the zinc specimens in various test solutions were acquire by SEM. SEM provides a pictorial representation of the zinc metal surface to understand the nature of the surface film in the absence and presence of different concentration of Dihexyl sulfide inhibitor. The scanning electron microscopy photographs were recorded at 10,000 x magnification using SEM ULTRA-60 nano fab, Hitachi scanning electron microscopes [19-20].

3. RESULTS AND DISCUSSION

3.1. Weight loss method

Values of inhibition efficiency given by from the weight loss and gasometry experiments for the inhibitor for the corrosion of zinc in 0.5N HCl and 0.5N H_2SO_4 in the presence of different concentrations of dihexyl sulphide are presented in the tables 1and 2 respectively.

Table 1 Values of inhibition efficiency obtained from the weight loss experiments.

Corrosive Medium	Values of I.E(%) for different Concentrations (mM) of Dihexyl Sulphide				
	5	10	30	50	100
0.5N HCl	35.8	45.9	54.0	72.8	85.6
0.5N H_2SO_4	42.5	53.6	62.7	79.7	98.4

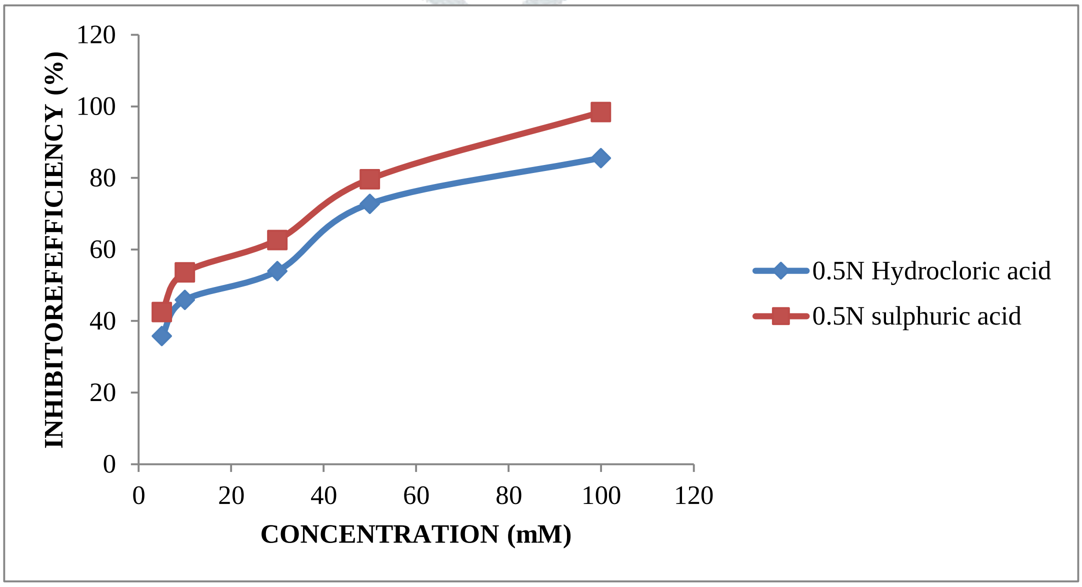


Figure- 1 Variation of inhibition efficiency with concentration of the dihexyl sulphide inhibitor for zinc in 0.5N HCl and 0.5N H_2SO_4.

3.2. Gasometry method

Table 2 Values of inhibition efficiency obtained from the gasometry experiments.

Corrosive Medium	Values of I.E(%) for different Concentrations (mM) of Dihexyl Sulphide				
	5	10	30	50	100
0.5N HCl	39.9	46.2	59.5	74.3	95.8
0.5N H_2SO_4	40.8	53.9	64.1	78.2	97.1

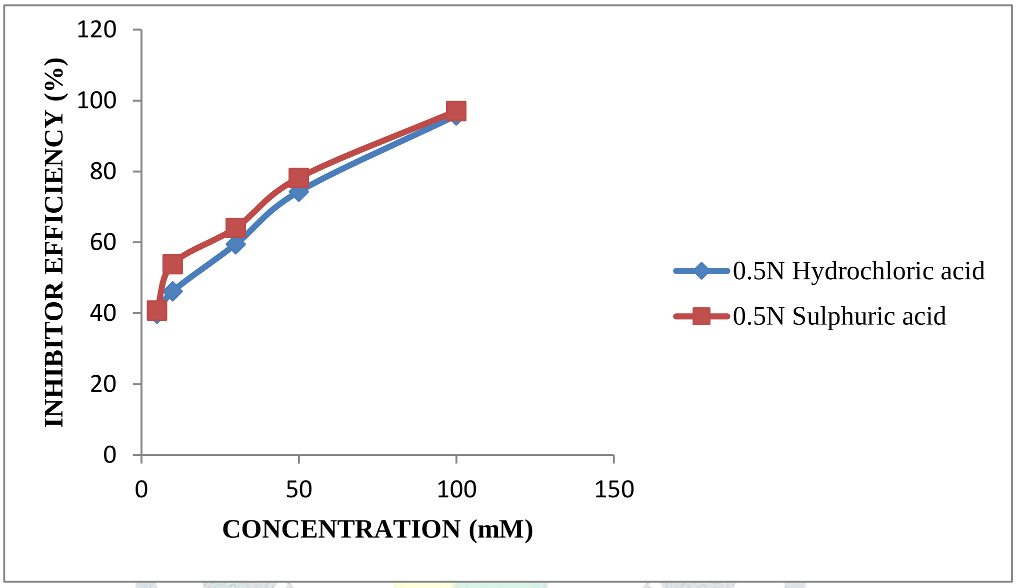


Figure- 2 Variation of inhibition efficiency with concentration of the dihexyl sulphide inhibitor for zinc in 0.5N HCl and 0.5N H_2SO_4

The results here in the tables 1&2 be seen that the inhibition efficiencies increase with increase in the inhibitor concentration. It can also be seen from these tables that dihexyl sulphide performed better in 0.5N H_2SO_4 than in 0.5N HCl.

The inhibitor used in this study contains two phenyl rings in its molecular structure which are rich sources of electrons apart from the sulphur atom which contains two lone pairs of electrons. The adsorption of this inhibitor molecule on the surface of zinc metal surface can be found in the following ways.

(i).The sulphur atom with its two lone pair of electrons can move as an efficient adsorption centre and get adsorbed on the positively charged metal surface leading to the formation of a protective layer on the zinc metal surface. This protective layer aet as a barrier between the zinc metal and the corrosive media thus count in down the corrosion rate of the metal. (ii.)The hexyl groups with their pi-electrons can also get adsorbed on the metal surface notable to the protection of the metal. (iii).The two hexyl groups being bulky in nature, on adsorption on the metal surface offers good surface coverage to the metal surface against attack by the corrosive media. (iv).The sulphur atom in the molecule in acid medium can be protonated to some area to form the cationic form of the inhibitor. The chloride and sulphate ions in the corrosive medium with less degree of hydration gets specifically adsorbed on the positively charged metal surface notable to the forming of excess negative charges on the metal surface. This situation highly esteems the adsorption of the inhibitor molecules on the metal surface resulting in reduced corrosion rate. The subordination of inhibition efficiency of the inhibitor on its concentration is shown in figure1&2.

Values of corrosion rates (mm/year) given by the weight loss and gasometry experiments for the inhibition of the corrosion of zinc in 0.5N HCl and 0.5N H_2SO_4 in the presence of different concentrations of dihexyl sulphide is presented in the table 3&4.

Table 3 Values of corrosion rates (mm/year) from the weight loss method.

Corrosive Medium	Values of corrosion rate (mm/year) different concentrations for (mM) of dihexyl sulphide				
	5	10	30	50	100
0.5N HCl	94.1	80.0	54.4	44.1	33.6
0.5N H_2SO_4	61.5	50.7	33.9	27.2	20.4

From the table 3&4 it can be observation that the corrosion rates (mm/year) of zinc in 0.5N HCl and 0.5N H_2SO_4 increases with increasing concentration of the inhibitor. The result of inhibitor concentration on the corrosion rates is shown in figure 3&4.

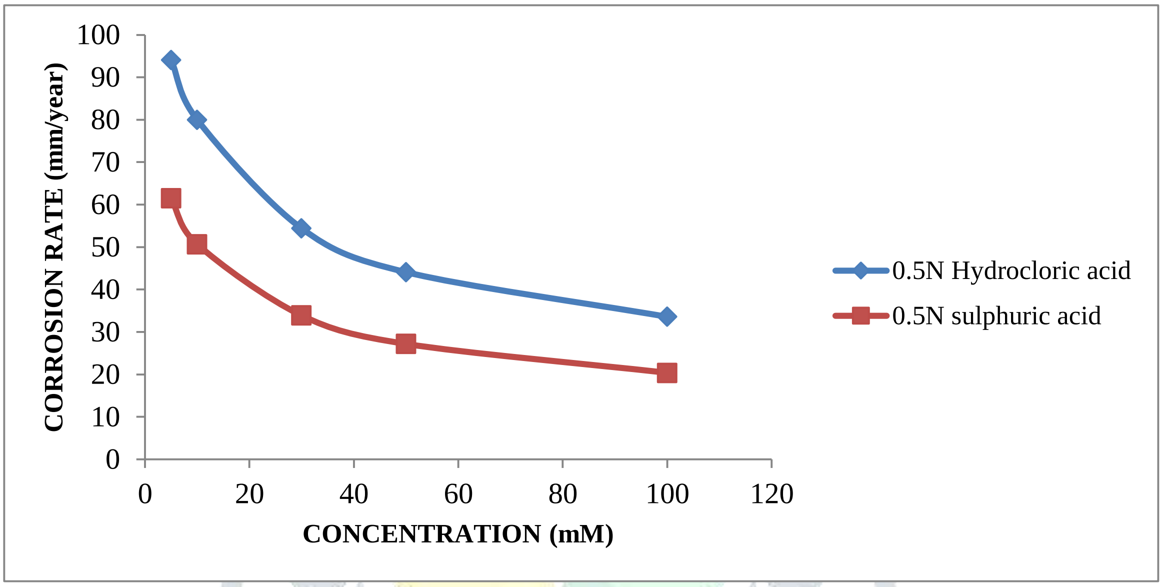


Figure- 3 Variation of corrosion rates with concentration of the dihexyl sulphide inhibitor for zinc in 0.5N HCl and 0.5N H_2SO_4.

Table 4 Values of corrosion rates (mm/year) from the gasometry evaluations.

Corrosive Medium	Values of corrosion rates (mm/year) different concentrations for (mM) dihexyl sulphide				
	5	10	30	50	100
0.5N HCl	96.2	82.1	56.2	46.1	35.7
0.5N H_2SO_4	63.0	53.5	34.8	29.5	22.6

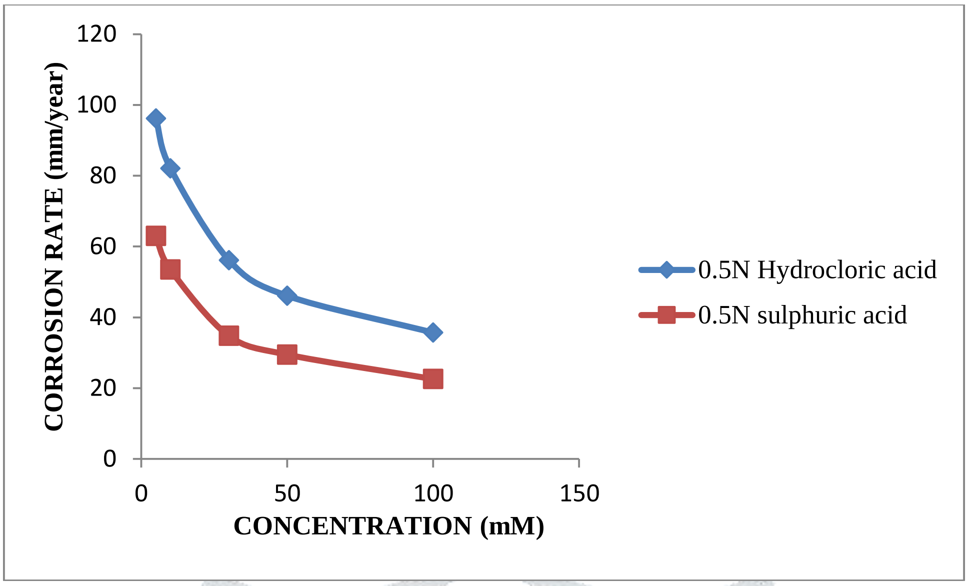


Figure-4 Variation of corrosion rates with concentration of the dihexyl sulphide inhibitor for zinc in 0.5N HCl and 0.5N H_2SO_4.

3.3. Adsorption isotherms

Adsorption isotherms play an important role in the absorption of the mechanism of inhibition of corrosion of metals. From the weight loss values the degree of surface coverage (θ) for various concentration of dihexyl sulphide inhibitor were full of determination and plotted against log C for different concentrations of the inhibitor. A straight line was observed indicating that the adsorption of the inhibitor on the zinc metal surface follows Temkin adsorption isotherm. Figure 5 shows the Temkin adsorption isotherm.

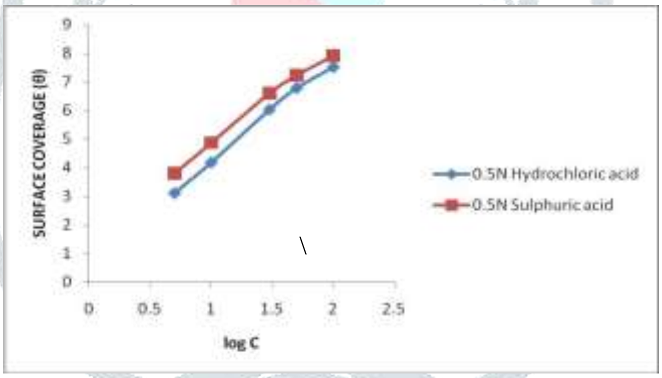
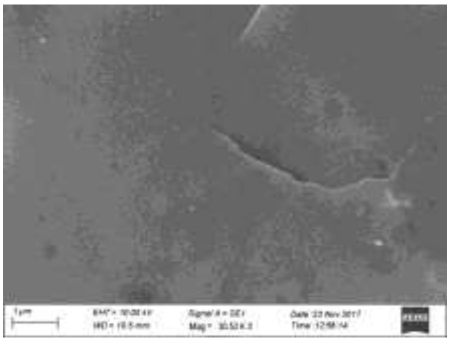
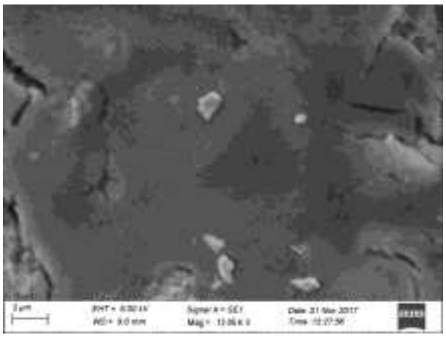


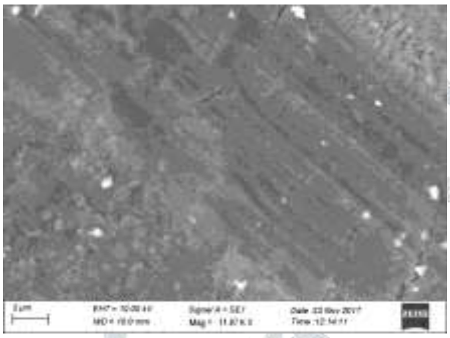
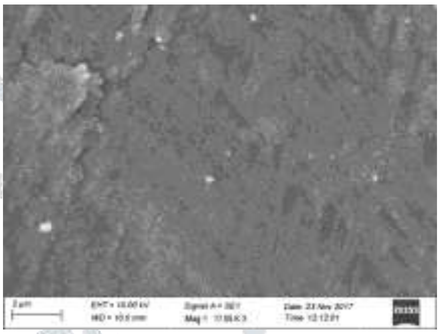
Figure-5 Temkin adsorption isotherm plot for corrosion of zinc in 0.5N HCl and 0.5N H_2SO_4 containing different concentrations of inhibitor.

3.4. SEM Analysis of Zinc Metal Surface

SEM provides a pictorial representation of the surface of zinc metal. The SEM images of zinc specimens immersed in 0.5N HCl and 0.5N H_2SO_4 for 30 min. in the absence and presence of the di hexylsulphide inhibitor systems are shown in Figures 6c and 6d, respectively. The SEM micrograph of the polished zinc surface in Figure 6a&7a show the smooth surface of the metal, with no corrosion products. The SEM micrographs of the zinc surface dunking in 0.5 N HCl (Figure 6b&7b) and 0.5N H_2SO_4 show the roughness of the metal surface, with highly corroded areas. However, Figure 6d&7d shows that in the presence of 10 mM Di hexyl Sulphide, the inhibition efficiency is enhanced, as seen from the decrease in the corroded areas compared to with the 5 mM Di hexyl sulphide inhibitor. In the presence of the 5 mM Di hexyl sulphide inhibitor and 10 mM Di hexyl sulphide inhibitor, the surface is covered by a thin layer of inhibitor that effectively controls the dissolution of the zinc [21,22] in both acids.

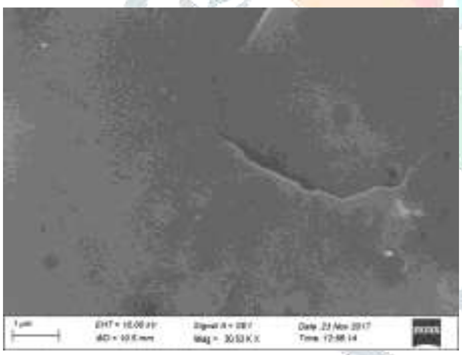
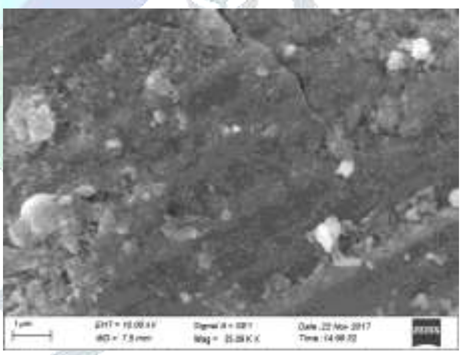
 

(6a) (6b)

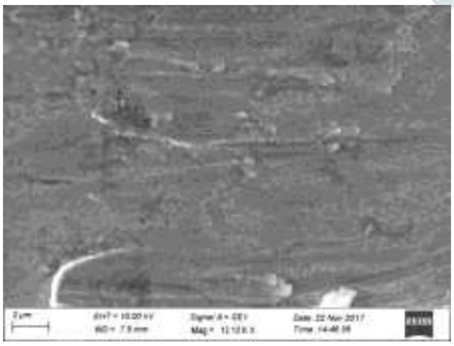
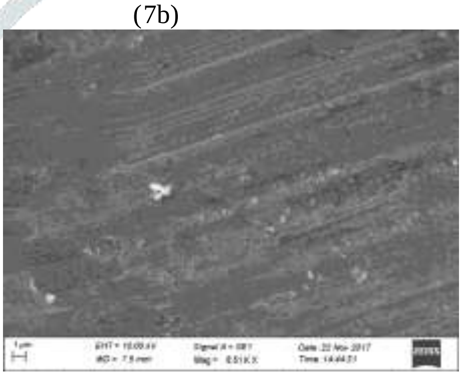
 

(6c) (6d)

Fig. 6: Scanning electron micrographs of zinc immersed for 30 minutes (6a) polished Zinc (6b) in 0.5 N HCl (6c) with 5 mM Di hexyl Sulphide inhibitor and (6d) with 10 mM Dihexyl sulphide inhibitor

(7a) (7b)

(7c) (7d)

Fig. 7: Scanning electron micrographs of zinc immersed for 30 minutes (7a) polished Zinc (7b) in 0.5 N H_2SO_4 (c) with 5 mM Di hexyl Sulphide inhibitor and (7d) with 10 mM Di hexyl sulphide inhibitor

5. CONCLUSIONS

The conclusion drawn from the above results.
i.The inhibitor Dihexyl sulphide which shows 97.1% of inhibitor efficiency 100 mM concentration in 0.5N H_2SO_4 medium has been evaluated by weight loss and gasometry method.
ii. Inhibition efficiency increases with increase in inhibitor concentration. The inhibitor performed better in 0.5N H_2SO_4 than in 0.5N HCl. The adsorption of the inhibitor molecules on the metal surface obeys Temkin's adsorption isotherm.
iii.The protective films formed on the surface of the zinc metal was analyzed by SEM.

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