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INHIBITIVE ACTION OF THIOLS ON THE CORROSION OF ZINC IN ACID SOLUTIONS

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Abstract- The inhibitive effect of a few thiols were examined as corrosion inhibitors for the corrosion of zinc in 1N HCl and 1N H_2SO_4 by conventional weight loss and gasometric methods. Results obtained show that all the thiols exhibited high inhibition efficiencies. The inhibition efficiency was found to increase with increase in the inhibitor concentration. The adsorption of the inhibitors obeyed Temkin adsorption isotherm.

Key words: Thiols, acidic solutions, zinc corrosion, hydrogen evolution.

Introduction

Zinc is a metal which finds application in various industries and used for different purposes under different environmental conditions. At the same time it is highly prone to corrosion by many acidic solutions. Prevention of corrosion is vital for extending the lifetime of metals. One of the methods employed to prevent the corrosion of metals is the use of corrosion inhibitors. It is well known that several organic compounds containing heteroatoms like nitrogen, sulphur and oxygen in their molecular structure exhibited good corrosion inhibiting property towards zinc metal in acidic solutions[1-10]. These compounds bring down the corrosion rate of the metals by getting adsorbed on the metal surface thereby blocking the active sites of the metal.

In the present work we have evaluated three organic sulphur compounds namely1- butanethiol,1-pentanethiol and 1- hexanethiol as inhibitors for the corrosion of zinc metal in hydrochloric acid and sulphuric acid solutions.

Experimental

(i) Material

The zinc metal specimens used in this work has the following composition: lead 1.03%, cadmium 0.04%, iron 0.001% and the remainder being zinc. Zinc metal specimens were pretreated before the experiments by polishing with a series of emery papers of various grades from 400- 1200, degreased with absolute ethanol and air dried. For weight loss and gasometric experiments zinc metal specimens of size 4cm*2cm* 0.08cm with a small hole of approximately 3mm near the end of the specimen were used. 1-Butanethiol,1- pentanethiol and 1-hexanethiol used as inhibitors were imported Alfa Aesar samples. The corrosion medium was 1N HCl and 1N H_2SO_4 prepared from A.R grade HCl and H_2SO_4 and deionised water. The zinc metal specimens were exposed to 1N HCl and 1N H_2SO_4 containing the inhibitors of various concentrations.

(ii) Weight loss experiments

In the weight loss experiments, the pre-weighed zinc metal specimens were suspended in a 200ml beaker containing 100ml of acidic solutions for two hours. Then the metal specimens are removed from the acid solution, washed with deionised water, cleaned, dried and reweighed . From this the metal weight loss was determined as the difference between the initial weight and weight after 2 hours immersion in acid solutions. The experiments were repeated with both acids in the absence and in the presence inhibitors of different concentrations. Each experiment was repeated thrice and the average of the three values was taken as the final value.

The % inhibition efficiency (I.E) and the degree of surface coverage (θ) were calculated by using the following equations.

$$I.E = \frac{Wo - Wi}{Wo} X\ 100$$

$$\theta = \frac{Wo - Wi}{WO}$$

Where W_o and W_i are the weight loss in the absence and presence of the inhibitors respectively.

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 exposure time (h) and D is the density of the metal (g/cm^3).

(iii) Gasometry experiments

The procedure for gasometry method for evaluation of inhibition efficiency of the inhibitors of various concentrations is described elsewhere[11]. The inhibition efficiency is calculated by using the following equation.

$$I.E = \frac{Vo - Vi}{Vo} X\ 100$$

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

Results and discussion

Weight loss and gasometry studies were carried out at four different concentrations and the inhibition efficiency values were calculated. Values of inhibition efficiency obtained from the weight loss and gasometry experiments for the inhibitors for the corrosion of zinc in 1N HCl and 1N H_2SO_4 in the presence of different concentrations of these compounds are presented in the tables 1and 2 respectively.

Table 1 Values of inhibition efficiency obtained from the weight loss experiments for the corrosion of zinc in 1N HCl and 1N H_2SO_4 in the presence of different concentrations of the inhibitors

	1N HCl medium	1N H_2SO_4 medium
	Values of I.E(%) for different	Values of I.E(%) for different

Inhibitors used	concentrations (mM) of the inhibitors				concentrations(mM) of the inhibitors			
	5	10	50	100	5	10	50	100
1-Butanethiol	51.5	59.7	77.9	85.4	52.0	60.2	78.4	85.9
1-Pentanethiol	59.4	67.8	84.7	92.5	59.9	68.5	85.3	93.2
1-Hexanethiol	66.1	74.3	91.4	98.4	66.9	74.8	92.4	98.9

Table 2 Values of inhibition efficiency obtained from the gasometry experiments for the corrosion of zinc in 1N HCl and 1N H_2SO_4 in the presence of different concentrations of the inhibitors

Inhibitors used	1N HCl medium				1N H_2SO_4 medium			
	Values of I.E(%) for different concentrations (mM) of the inhibitors				Values of I.E(%) for different concentrations(mM) of the inhibitors			
	5	10	50	100	5	10	50	100
1-Butanethiol	51.7	60.1	77.1	84.2	51.9	60.9	77.8	85.6
1-Pentanethiol	60.2	68.4	84.6	91.6	61.0	69.1	85.2	92.6
1-Hexanethiol	65.2	74.9	90.4	97.1	65.9	75.7	91.5	97.8

It can be observed from the tables 1and 2 that there is very good agreement between the values of inhibition efficiency obtained from both weight loss and gasometric methods. The results presented in the tables1 and 2 shows that the inhibition efficiencies increases with increase in the inhibitors concentration.

It can also be seen from these tables that all these compounds perform better in 1N H_2SO_4 than in 1N HCl. A similar observation has already been made by several authors[12-17]. Among the thiols used in this study 1-hexanethiol shows maximum inhibition efficiency in both the acids. It is found to perform better than 1-butanethiol and 1-pentanethiol. This can be attributed to the greater electron releasing tendency of the hexyl group in1- hexanethiol(+I effect) which leads to increased electron density on the sulphur atom which in turn leads to greater adsorption on the metal surface than the other two thiols, through bonding between zinc and electron rich sulphur atom in the molecule[18,19]. Infrared spectrum confirm that a metal sulphur bond may exist between the sulphur atom and the metal[20]. Next to 1- hexanethiol, 1-pentanethiol shows better performance. This can be attributed to the presence of pentyl group which is less electron releasing than the hexyl group. The same reason can be attributed to explain the performance of 1-butanethiol. The dependence of inhibition efficiency of the inhibitors on their concentration is shown in figure 1.

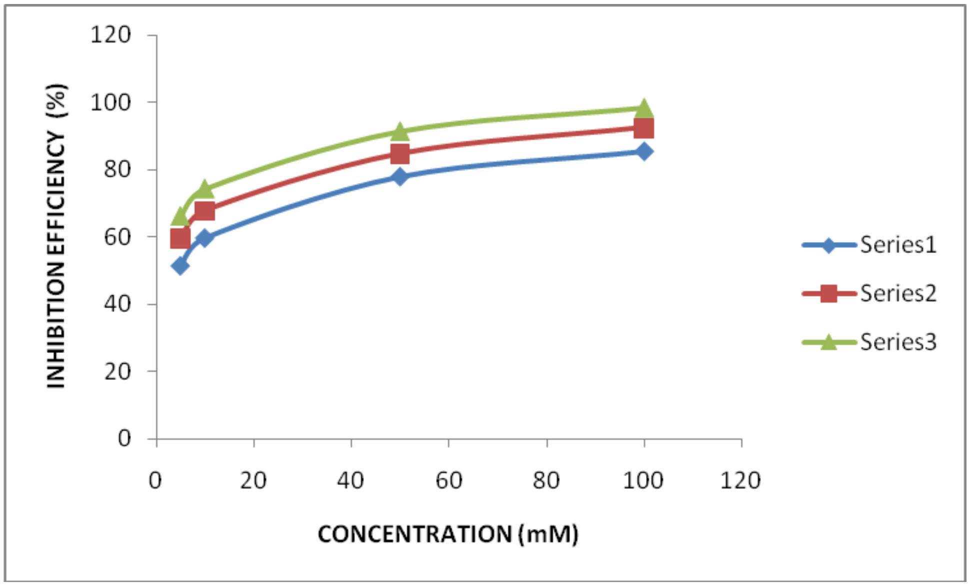

Figure 1 Variation of inhibition efficiency with concentration of the inhibitors for zinc in 1N HCl . Series 1: 1-Butanethiol, Series 2: 1-Pentanethiol, Series 3: 1-Hexanethiol

Values of corrosion rates(mm/year) obtained from the weight loss experiments for the inhibition for the corrosion of zinc in 1N HCl and 1N H_2SO_4 in the presence of different concentrations of these compounds are presented in the table3.

Table 3 Values of corrosion rates(mm/year) from the weight loss experiments for the inhibitors for the corrosion of zinc in 1N HCl and 1N H_2SO_4 in the presence of different concentrations of the inhibitors

Inhibitors used	1N HCl medium concentration (mM) of the inhibitors				1N H_2SO_4 medium concentration (mM) of the inhibitors			
	5	10	50	100	5	10	50	100
1-Butanethiol	67.90	56.42	30.94	20.44	49.44	41.00	22.24	14.52
1-Pentanethiol	56.84	45.08	21.42	10.50	41.30	32.44	15.14	07.00
1-Hexanethiol	47.46	35.98	12.04	02.24	34.09	25.95	07.82	01.13

From the table 3 it can be observed that the corrosion rates for the corrosion of zinc in in 1N HCl and 1N H_2SO_4 decreases with increasing concentration of the inhibitors. The effect of inhibitor concentration on the corrosion rates is shown in figure 2.

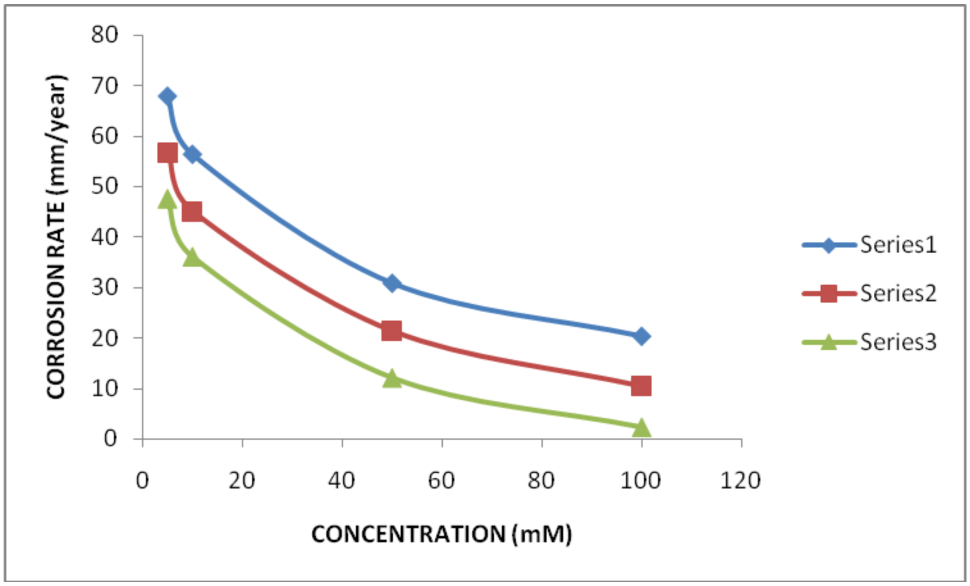

Figure 2 Variation of corrosion rates with concentration of the inhibitors for zinc in 1N HCl. Series 1: 1-Butanethiol, Series 2: 1-Pentanethiol, Series 3: 1- Hexanethiol

Adsorption isotherms

Adsorption isotherms are crucial to understand the mechanism of inhibition of corrosion of metals. From the weight loss values the degree of surface coverage (θ) for various concentration of the studied inhibitors were determined. These values were plotted against log C for different concentrations of the inhibitors and a straight line resulted. This indicates that the adsorption of the thiols on the zinc surface follows Temkin adsorption isotherm. Figure 3 shows the Temkin adsorption isotherm.

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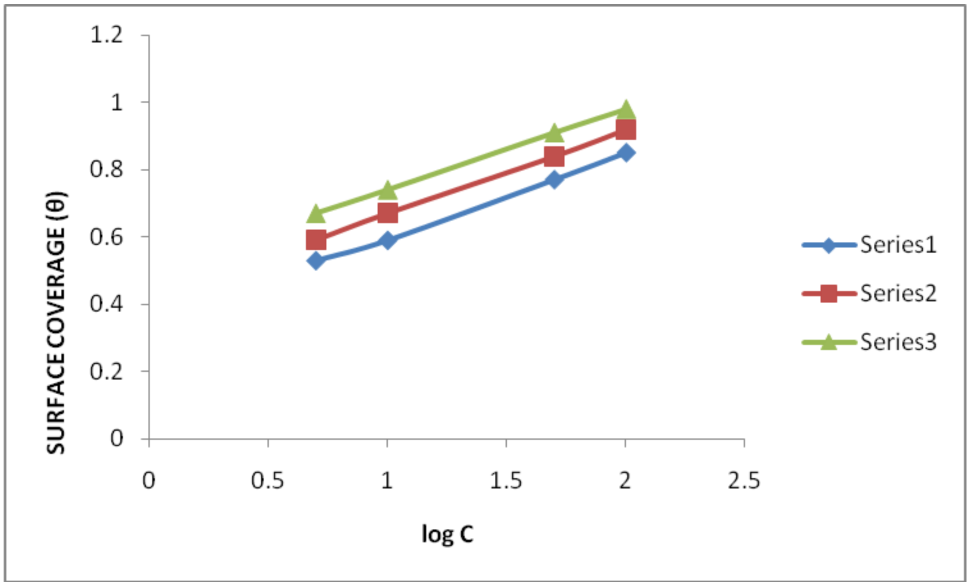

Figure-3 Temkin adsorption isotherm plot for corrosion of zinc in 1N HCl containing different concentrations of inhibitors.

Conclusions

All the examined thiols act a good corrosion inhibitor for zinc in 1N HCl and 1N H_2SO_4. The weight loss and gasometric measurements confirm the inhibitive nature of the examined inhibitors. Among the inhibitors studied 1-hexanethiol performed well and exhibited maximum inhibition efficiency of 98.4% and 98.9% in 1N HCl and 1N H_2SO_4 respectively. The adsorption of the inhibitor compounds on zinc surface obeyed Temkin adsorption isotherm.

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