Research Journal of Pharmaceutical, Biological and Chemical Sciences

Corrosion inhibition study of New Mercaptotriazoles and complementary effect of halide ions on mild steel in 0.5M sulphuric acid medium

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ABSTRACT

The inhibition efficiency of mercapto triazoles N-{3-[(4-chloro phenoxy)methyl]-5-mercapto-4H-1,2,4-triazole-4-yl}benzamide (MTZ1), N-{3-mercapto-5-[(4-nitro phenoxy)methyl]-4H-1,2,4- triazole-4-yl}benzamide(MTZ2), N-{3-[(3-bromophenoxy)methyl]-5-mercapto)-4H-1,2,4-triazole-4-yl}benzamide(MTZ3) and complementary effect of halide ions on mild steel has been studied using weight loss method. The inhibition efficiency increases with the increases in the concentration of triazoles with a fixed concentration of halide ions (Cl⁻ .Br⁻ and I⁻ ions). Experiments are carried at a temperature of 303K. The thermodynamic parameters Ea and ΔG were evaluated. The results showed that these compounds are physically adsorbed over the surface of the steel, blocking the corroding sites.

Keywords: Triazoles,Corrosion,complementary,Weight loss

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INTRODUCTION

Literature survey reveals that the triazole derivatives are used as corrosion inhibitors in acid solutions [6, 7]. Due to the presence of three nitrogen atoms triazoles have shown corrosion inhibition efficiency on brass and bronze [9, 10] but to a very little on mild steel in acid medium. Synergistic effect of halide ions and methyl red indicators are also tried as corrosion inhibitors. In view of this an attempt is made to study the complementary effect of halide ions with new mercapto triazoles are used as corrosion inhibitors.

EXPERIMENTAL

All the corrosion inhibition studies were carried out using weight loss method. The reports of Cham pion[24], Spellar[7], Ailer [9], Evans [1] and ASTM [12] have been suitably adopted. Wherever correlation were required identical conditions for specimen, temperature, stirred condition, materials used and time of exposure of the mild steel to corroding atmosphere are maintained to the best of the ability.

All the solutions were prepared in Deionized water. All the chemicals used were of analytical grade. Analytical grade sulphuric acid was used as the corrosion medium in this work. The acid was first treated with activated charcoal to remove organic impurities present in traces. Then subjected to electrolytic distillation using 1:1 ratio of sulphuric acid and distilled water in pre electrolysis cell using platinum electrodes for 10 hours at a current density greater than used in anodic dissolution experiments.

Finally the acid was filtered through sintered glass crucible. For each dissolution study, 0.1 N sulphuric acid was freshly prepared.

Preparation of the electrode surface

Mild steel having surface area 0.986cm^2 fixed in Tygon tubing but exposing only the desired surface. The surface of the metal was first polished with 8/0 emery papers followed by Chamois leather, and finally by 4/0 emery paper. Ethyl alcohol was used as lubricant to get a mirror finish. Further the cell was electro polished in 1:1 orthophosporic acid for 25 minutes at a cell potential of 12 V. Electro polished cell was washed with 10% phosphoric acid followed by distilled water and immediately transferred to the corrosion cell containing the 0.1N sulphuric acid. The cell was tested for corrosion and corrosion control under selected inhibitors.

Weight loss method

For weight loss measurements dissolution cell was used .The cell was a three necked 100 ml round bottomed flask. 50 ml of the corrosive medium (acid) was taken in the cell with and with out inhibitor. A constant temperature with accuracy of ± 0.1 was maintained using a thermostat. For stirring, a magnetic stirrer was used. The metal under study was polished mechanically with emery

paper number 3 and 4 and it was immersed in the acid medium through the central neck of the cell. The dissolution studies were carried out under specified conditions.

For the dissolution, corrosion potential was measured by coupling working electrode with standard calomel electrode using a digital multimeter (MASTECH MAS 830). The solution from the dissolution cell was used to determine the amount of Fe (Iron) present in it using a spectrophotometer LS 17 of Elico make. After determining the amount of iron, the rate of dissolution was calculated. Experiments were repeated till concordant readings were obtained. The dissolution study was made under different conditions viz., varying concentration and time of dissolution (1hr to 6hr) at a constant temperature of 300K.
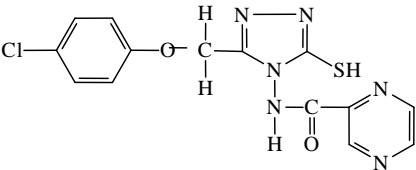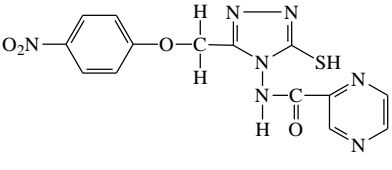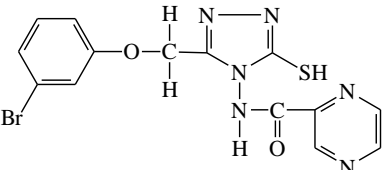
Composition of mild steel

The metal analysis of mild steel was carried by preparing 1 ppm solution in 1:1 hydrochloric acid. Themo Jarrel AAS Corporation make Smith- Heieftjee – 1000 was used for the analysis. The values are shown in Table-1

Table 1

Metal	% Of elements present in the metal (ppm)					
	Fe	Mn	Ni	Cu	Zn	Pb
Mild steel	98.228	0.0326	1.158	0.0917	0.243	0.1697

New Mercaptotriazoles (MTZ)

Following triazoles were prepared by the methods available in the literature [13]

Mercapto triazoles (MTZ1)	. Mercapto triazoles(MTZ1)	. Mercapto triazoles(MTZ3)

All the inhibitors prepared have been charcterised by elemental and spectral analysis.

Analysis of Fe

Iron, which has been dissolved in the dissolution cell, was determined by spectrophotometric method using spectrophotometer (LS 17 Elico make). First a standard spectr0scopic graph was drawn for known concentration of Fe from a standard solution of Iron by known procedure. Similarly the solution from dissolution cell was treated with 1,10 phenontralene to get the iron complex and its absorption was measured at 420nm in the spectrophotometer. With the help of standard graph, amount of Fe in dissolution cell was calculated.

RESULTS

This chapter presents the corrosion inhibition study of mild steel by the addition of chosen inhibitors mercapto triazoles (MTZ1 - MTZ3) and the complementary effect of halide ions(Cl^-,Br^-,I^-). It is reported that triazoles act as good inhibitors on copper, aluminum and on some types of steel[6] Effect of halide ions with some inhibitors is also reported[1]. It is quite interesting to note the dual role of halide ions [2]. They are corrosion promoters as well as considered as corrosion inhibitors along with (MTZ1 to MTZ3).

The corrosion study here is based on weight loss method. Weight loss method is considered under different conditions like effect of concentration of inhibitors, effect of temperature, effect of concentration of the acid medium and effect of immersion time in the acid medium. In this paper it is considered with immersion time and concentration of inhibitor. The efficiency of the inhibitor depends on the capability of its adsorption on the surface of the mild steel and of blocking the anodic sites. This has been probed by considering the surface coverage of the inhibitors. Thermodynamic parameters like enthalpy change, entropy change and free energy change are perused towards the feasibility of the process of corrosion inhibition.

Corrosion rates

Corrosion rate of mild steel in presence of inhibitors of different concentration ranging from 10^{-6}M to 10^{-1}M was measured under stirred conditions at 303 K for one hour of immersion. Following inhibitors are used for the corrosion study.

Corrosion rate was evaluated by estimating the amount of iron present in the medium by spectrophotometric method [3]. The weight loss measurements show that MTZ1, MTZ2 and MTZ3 are good inhibitors. Table 2 represent the effect of concentration of inhibitors on dissolution of mild steel.

Table-2 Change in corrosion rate with varying concentration of inhibitors

Medium: 0.1N H_2SO_4 Temp. : 303 K
MTZ: $10^{-6} - 10^{-1}$ M

Concentration of inhibitors (M)	Corrosion rate (g/l/hr)		
	MTZ1	MTZ2	MTZ3
10^{-6}	2.920	3.220	2.431
10^{-5}	2.224	2.780	2.113
10^{-4}	1.162	1.290	1.034
10^{-3}	0.429	0.514	0.386
10^{-2}	0.312	0.356	0.298
10^{-1}	0.189	0.202	0.175

From the Tables 2 it is evident that MTZ1, MTZ2 and MTZ3 act as good inhibitors. The inhibitor efficiency reaches up to 85% at 10^{-1}M concentrations. The percentage of protection was calculated by using the equation.

$$\%I = \frac{W_1 - W_2}{W_1} \times 100$$

W_1 and W_2 are the weight loss of iron in 0.1 N sulphuric acid in absence and in presence of inhibitors.

It has been observed that all inhibitors show significant inhibitor efficiency in general and MTZ3 in particular. Tables 2 Reflect the inhibition effect of Inhibitors.

Effect of concentration of inhibitors with halide ions

Table 3 Change in the corrosion rate with varying concentration of inhibitors and chloride ions

Medium: 0.1N H_2SO_4 Temp:303K
KCl:0.1N   Inhibitors: 10^{-6} to 10^{-1} M

Concentration of Inhibitors (M)	Corrosion rate (g/l/hr)		
	MTZ1	MTZ2	MTZ3
10^{-6}	2.396	2.589	2.165
10^{-5}	1.587	1.476	1.328
10^{-4}	0.501	0.398	0.362
10^{-3}	0.279	0.265	0.249
10^{-2}	0.206	0.209	0.192
10^{-1}	0.196	0.189	0.175

Table-4 Change in the corrosion rate with varying concentration of inhibitors and bromide ions

Medium: 0.1N H_2SO_4 Temp:303K
KBr:0.1N   Inhibitors: 10^{-6} to 10^{-1} M

Concentration of Inhibitors (M)	Corrosion rate (g/l/hr)		
	MTZ1	MTZ2	MTZ3
10^{-6}	2.376	2.523	2.198
10^{-5}	1.576	1.471	1.432
10^{-4}	0.509	0.398	0.365
10^{-3}	0.284	0.269	0.265
10^{-2}	0.209	0.207	0.192
10^{-1}	0.184	0.179	0.165

Table-5 Change in the corrosion rate with varying concentration of inhibitors and iodide ions

Medium: 0.1N H_2SO_4 Temp:303K
KI:0.1N   Inhibitors: 10^{-6} to 10^{-1} M

Concentration of Inhibitors (M)	Corrosion rate (g/l/hr)		
	MTZ1	MTZ2	MTZ3
10^{-6}	2.373	2.670	2.188
10^{-5}	1.564	1.459	1.376
10^{-4}	0.474	0.374	0.345
10^{-3}	0.274	0.259	0.232
10^{-2}	0.204	0.199	0.184
10^{-1}	0.175	0.176	0.154

Inhibitor efficiency of (MTZ1 to MTZ3) was studied with a fixed concentration of halide ions. Halide ions seem to complement the inhibitors with respect to the inhibitor efficiency. The dissolution of mild steel in 0.1 N sulphuric acid was carried at different concentration (10^{-6}M to 10^{-1}M) of inhibitors along with 0.1 N chloride, bromide and iodide ions, at 303 K. The increase in the concentration of inhibitors along with halide ions shows a remarkable decrease in corrosion rate. Tables 3, 4 and 5, represent the experimental data of the variation in corrosion rate at 303K.

Table-6 Thermodynamic parameters

Thermodynamic parameters	MTZ3+KCl	MTZ3+KBr	MTZ3+KI
E_a KJ mol^{-1}	23.6	24.7	26.2
ΔG KJ mol^{-1}	-18.0	-19.4	-24.0

Table-7 Synergetic values at 303K

Inhibitors	Synergetic value
KCl +MTZ3	1.03
KBr + MTZ3	1.29
KI + MTZ3	1.32

DISCUSSION

The profound influence of inhibitors (new mercapto triazoles) on decreasing the dissolution of mild steel in sulphuric acid medium is discussed based on the results.

The corrosion rate of mild steel at 0.1N sulphuric acid in absence and presence of inhibitor have been determined by immersion test at 303 K for 1 to 6 hours exposure period. It has been observed that corrosion rate increased with increase in immersion time and there is a linear relationship. The results calculated from weight loss data are given in Tables-4.1 to 4.2. The tables show that the rate of corrosion increases with decrease in concentration of inhibitor. The inhibitor efficiency increases with the increase in inhibitor concentration which agrees with reported results for similar systems [5]. The inhibitor efficiency is around 85% at 10^{-1}M concentration.

The nature of the interaction of the inhibitor on the metal surface during corrosion process can be understood from adsorption characteristics. The metal surface is known to be covered by aqueous solution with adsorbed water dipoles. Therefore the adsorption of inhibitor molecules from aqueous solution can be regarded as a quasi substitution process.

Inhibitor	+	nH_2O	$\rightarrow$	Inhibitor	+	nH_2O
(solution)		(adsorbed)		(adsorbed)		(solution)
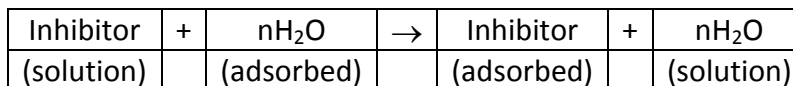
The thermodynamics of such a process depends on the number of water molecules replaced by the adsorbing inhibitor molecule and 'n', the configuration function or the size factor and is related to the mode of adsorption of the molecule by the equation.

$$n = \frac{\text{Molar volume of inhibitor}}{\text{Molar volume of water}}$$

Adsorption of the inhibitor has been studied by considering Langmuir's adsorption isotherms by plotting log of surface coverage against log of concentration. Surface coverage 'θ' is determined by equation $1-(W_1/W_2)$. Figure 1 represents Langmuir's[3] adsorption isotherms, From Langmuir's adsorption isotherms ΔG values are calculated. Further, energy of activation has been calculated from Arrhenius plots by plotting log corrosion rate Vs 1/T (Fig. 2). Table-6 represents the values of activation energy and free energy change. Increase in activation energy and negative values of free energy may be indicative of adsorption of the inhibitors on the surface of the metal.

ΔG is calculated using equation

$$\log C = \{[\log \theta / (1 - \theta)] - \log \beta\}$$
$$\log \beta = -1.74 - (\Delta G / 2.303\ RT)$$

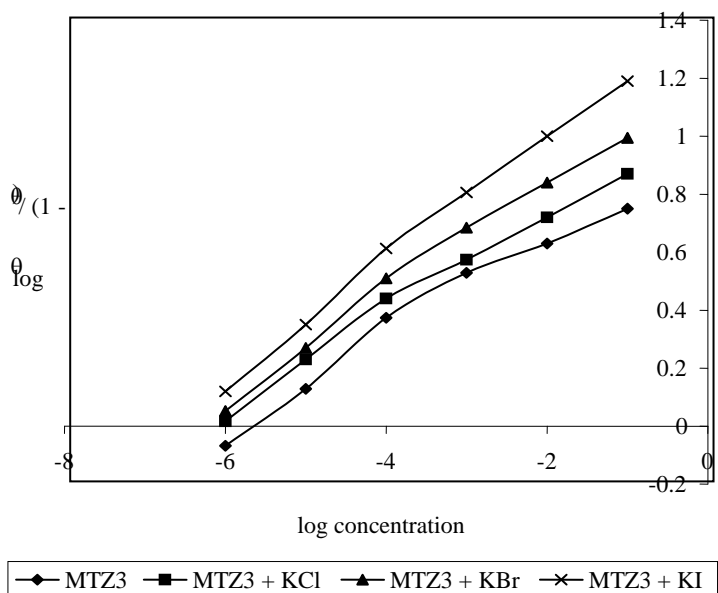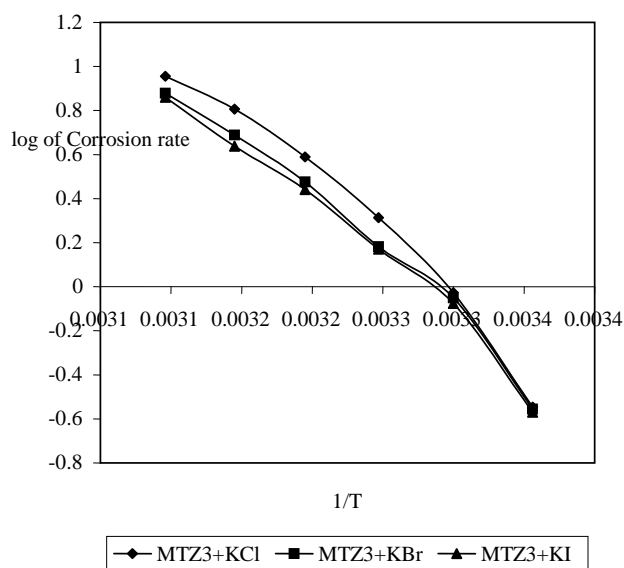**Fig. 1. Langmuir's adsorption isotherm**

Fig. 2. Arrhenius plots

With the increase in the concentration of inhibitor, there is increase in the inhibition efficiency, which may indicate that more reaction sites are blocked at higher concentration (10⁻

[1]M) of inhibitors along with iodide ions. At this concentration, the observed inhibition efficiency of 94% shows that dissolution of Fe at this stage is more difficult, due to the total blockage of reaction sites. Further synergetic calculations are made to substantiate this using the equation

$$S = 1 - I_2 / 1 - I_1$$

Where I_2 and I_1 are inhibition efficiency in presence of inhibitors alone and along with halide ions. All the synergetic values which are more than unity (Table-7) indicate that the halide ions and

Based on the experimental observations, calculated parameters and the resulting figures, the following inferences may be drawn regarding the efficiency of the inhibitors, used along with halide ions towards corrosion inhibition of mild steel in H_2SO_4 medium. The variations in the conditions for the dissolution of mild steel are analysed.

The weight loss of the mild steel in H_2SO_4 increased with increase in acid concentration at all temperatures. This trend may be due to the fact that the rate of a chemical reaction increases with acid concentration.

The weight loss was minimum at the highest concentration of the inhibitors (MTZ1 to MTZ3) compared to both zero concentration and other lower concentrations of the inhibitors. The design of the inhibitors seems to be made to order for adsorption on the mild steel surface. Among the three inhibitors MTZ3 seems to be ahead in corrosion minimization. The substituents may have played their usual role though to a small extent.

The inhibitors contain a large number of active donor hetero atoms O, N and S. The possibility of co-ordination with the metal can not be completely ruled out. It could well be a loose bond with high orientation towards physical adoption. This later phenomenon is supported by the parameters calculated and the nature of the plots.

The weight loss with immersion time decreases in presence of inhibitors as compared to only H_2SO_4 medium. This is again attributed to the fact that the rate of many reactions increases with temperature (Dissolution). This could occur in presence of inhibitors also in view of the possibility of desorption with increase in temperature.

Even in the presence of halide ions similar trend has been noted at all the conditions of the experiment. The salient observation is that, the efficiency of the inhibitors used increases to a reasonable extent in presence of halide ions. The order of influence of the halide ions in augmenting the efficiency of the corrosion inhibitors is $I^- > Br^- > Cl^-$.

This complementary effect of halide ions on the corrosion inhibition efficiency of mercapto triazoles (MTZ1 to MTZ3) may be attributed to the ligands nature of the halide ions and the order of complementing effect to the size as well as the electro negativity of the halide ions. Similar observations are available in the earlier report [8, 10]. It is also reported that

addition of halide salts to sulphuric acid solution in presence of organic inhibitors enhances the inhibition of iron corrosion due to co-operative effect [1]. It is stated that the influence of halide ions depend on the ionic size and charge [1, 8, 10]. These anions have profound effect through electrostatic field [11,13]. The atomic radii also have a role to play [14-15]. Further, these adsorbed halide ions interact with the inhibitors so that greater surface is covered and hence increase in the inhibitor efficiency. The increase in the inhibitor efficiency with its increasing concentration and decreasing efficiency with temperature predominantly supports physical adsorption [15]. The Langmuir adsorption isotherms plotted also favour adsorption.

The values of energy of activations are less than 40 KJ mol^{-1}. This also validates our observation [5]. The negative ΔG values also favour spontaneous adsorption of both inhibitor and halide ions on the mild steel surface. Such observations are available in the literature [16-19]. It is very difficult to categorise the mechanism as an electrochemical process or chemical adsorption or even physical adsorption. It could be both or either [20-22]. Banking upon the observations of Aramaki and Hackerman [22] it may be inferred that the aim of the work carried out the thesis is achieved because the synergistic parameters calculated are greater than unity and the halide ions have exhibited synergism towards the mercapto triazoles used as inhibitors in the corrosion study of mild steel in H_2SO_4 medium.

The halide ions used as complementary have facilitated the chosen organic inhibitor to adsorb on the mild steel surface as anticipated.

The over potentials measured also substantiate the above arguments. This is in agreement with the reports of formation of a protective layer of adsorbed inhibition species at the electrode surface [24].

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