INFLUENCE OF AMINO MERCAPTO METHYL TRIAZOLE ON THE CORROSION AND PERMEATION OF HYDROGEN THROUGH MILD STEEL IN ACIDIC SOLUTIONS

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SUMMARY

The influence of amino mercapto methyl triazole (AMMT) on the corrosion and hydrogen permeation of mild steel in 0.5 M H_2SO_4 and 1 M HCl has been studied using weight loss measurements and various electrochemical techniques. It is found to be more inhibitive in H_2SO_4. Potentiodynamic polarisation studies clearly prove that AMMT is a mixed type inhibitor, but predominantly a cathodic inhibitor. Hydrogen permeation studies and AC impedance measurements indicate an improved performance of the compound in H_2SO_4. The inhibitor of this type obeys Temkin adsorption isotherm.

1 INTRODUCTION

The study of organic corrosion inhibitors in acid medium is an attractive field of research due to its usefulness in several industries. In general, N-containing heterocyclics[1-3], show good inhibiting properties against the corrosion of steel in various acid media. The use of triazole, benzotriazole, naphthotriazole[4-6] as corrosion inhibitors has been mainly directed towards the protection of copper and its alloys. Molecular structure of inhibitors has clearly been established as a major influence on corrosion inhibition. Nitrogen and sulphur containing compounds particularly azoles, thiazoles, mercaptans have been shown to have a high degree of inhibition property. Ayer's et al [7] have reported that substances containing atoms of both nitrogen and sulphur in the molecule gave better inhibition efficiency. The focus of this research is to investigate the inhibitive properties of a suitable triazole derivative in acidic environments. In view of the diverse factors involved in the inhibition process, the present investigation was taken up to study the influence of 4-amino-5-mercapto-3-methyl-1,2,4 triazole (AMMT) on the corrosion of mild steel in acidic solutions by carrying out the estimation of inhibition efficiency, A.C.

Portugaliæ Electrochimica Acta, 11 (1993) 255-264

impedance spectroscopy and polarisation measurements. A systematic and detailed study using this compound for the corrosion of mild steel in acidic solutions has not been carried out so far and also not reported in literature. The effect of addition of the above mentioned compound on hydrogen diffusion through steel has also been studied, and the results are reported.

2 EXPERIMENTAL

2.1 Corrosion tests:

A.R.grade acids of appropriate concentrations were employed. Triplicate mild steel specimens (AISI 1079) of each size 50 mm x 20 mm x 0.25 mm having composition C = 0.07%, P = 0.084%, Mn = 0.34%, S = nil and remainder Fe were used for corrosion tests. Specimens were given fine mechanical polishing using pumice and then degreased with trichloroethylene before use. Potentiodynamic polarisation and A.C impedance measurements were carried out using a circular specimen of area 0.283 cm^2, the other portions being covered by araldite. Specimens were mechanically polished successively using 0/0, 1/0, 2/0, 3/0 and 4/0 emery and finally degreased with trichloroethylene.

2.2 Materials:

The inhibitor 4-amino-5-mercapto-3-methyl-1,2,4 triazole (AMMT) used was synthesised in the laboratory following the procedure reported in literature [8]. All solutions were prepared from conductivity water of resistance 10 M ohm.

2.3 Methods:

Weight loss experiments were carried out as described in earlier publications [9]. The inhibition efficiency was calculated from weight loss values obtained in the presence and absence of the inhibitor at 30 ± 2°C at the end of definite and known intervals of time.

Potentiodynamic polarisation studies were carried out using the corrosion measurement system BAS (Model 100 A). A platinum counter electrode and $Hg/Hg_2Cl_2/1M\ HCl$, Hg/Hg_2SO_4, 0.5 M H_2SO_4 reference electrodes were used throughout the study.

Charge transfer resistance(R_t) and double layer capacitance(C_{dl}) values were obtained from impedance measurements as described elsewhere[10].

Hydrogen permeation measurements were carried out using an adaptation of Devanathan and Stachurski's two compartment cell as described elsewhere [11]. Hydrogen permeation current was obtained in the presence and absence of the inhibitor.

3 RESULTS AND DISCUSSION

Table 1 gives values of inhibition efficiency in percentage of different concentrations of AMMT, for the corrosion of mild steel in both acids.

TABLE 1

Inhibition Efficiencies (I.E) for different concentrations of AMMT for the corrosion of mild steel in 0.5M H_2SO_4 and 1M HCl

Inhibitor mM	Inhibition efficiency(%) 0.5M H_2SO_4	Inhibition efficiency(%) 1M HCl
2	75.20	60.00
5	77.70	63.14
10	85.90	76.34
20	87.50	82.00
30	91.19	85.20

It was observed that the inhibitor AMMT inhibits the corrosion of mild steel in both acids. But it is found that, the inhibitor performs better in H_2SO_4 than in HCl solutions. This observation was confirmed earlier by Machu et al [12] and Schmitt [2] who pointed out that sulphur containing compounds are preferred for H_2SO_4 solutions. Hackerman and Makrides [13] explained that S-containing organic compounds have a special efficacy, as these chemisorbed compounds are better electron donors than compounds containing oxygen and nitrogen. Riggs [14] has suggested that the adsorption of the inhibitor molecule involves mixed molecules, called ambiodic inhibitors with more than one orienting group attached(- NH_2,-SH) and gave better efficiency.

The effectiveness of a given compound as a corrosion inhibitor depends on three major factors [15]:

(a) Structure of the inhibitor molecule

(b) Sign of the electric charge on the metal surface

(c) The anodic and cathodic processes determining the dissolution rate of the metal in an open circuit condition.

On the basis of the above factors, the structure of triazole ring has been modified by introducing a few substituents ($-CH_3$, $-NH_2$, $-SH$). The variation of inhibition efficiency mainly depends on the type and number of substituents present in the molecule[16]. In fact, however methyl group is an electron releasing group (+I effect) and it increases the charge densities at the centre of adsorptive power. Grigorev and Ekilik [17] have reported that amino groups are adsorbed either in RNH_2 or by RNH_3^+ forms, depending on the influence of the substituent on the electron density of the nitrogen atom. On the other hand chemisorption of RNH_2 molecules and the strength of their bonds with surface metal atoms increase with increasing electron donor properties. Hackermann and Hurd [18] concluded that the greater the percentage of orbitals of the free electrons on the nitrogen atom the more effective is the inhibiting action.

On the basis of above hypothesis, assumed above, it can be concluded that, the inhibition afforded depends upon the structure of the inhibitor and the reactivity of their functional groups such as $-SH$, $-NH_2$, $-CH_3$ and nitrogen atoms in the triazole ring. In AMMT, sulphur atom of mercapto group and nitrogen atom in position 4 are very active and involve in interaction with the metal surface [4]. The binding characteristics of the inhibitor AMMT on the metal surface can be interpreted by means of bonds coordinated with the electron pairs of the sulphur or of the nitrogen atom. It indicates that, the effective corrosion inhibition can be obtained through the formation of true chemical bonds between organic molecules and metal atoms.

Table 2 gives the values of Tafel parameters (b_c & b_a), I_{corr} and E_{corr} for the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl in the presence of different concentrations of the inhibitor.

TABLE 2

Electrochemical parameters for mild steel in 0.5 M H_2SO_4 and 1 M HCl containing different concentrations of AMMT

	0.5 M H_2SO_4				1 M HCl			
Inhibitor (mM)	E_{corr}/ (mV)	b_c (mV)	b_a (mV)	I_{corr}/ (mA cm^{-2})	E_{corr}/ (mV)	b_c (mV)	b_a (mV)	I_{corr}/ (mA cm^{-2})
Blank	-910	130	60	1.68	-515	120	60	2.02
2	-932	140	62	0.46	-527	129	66	0.86
5	-917	147	65	0.35	-515	131	68	0.75
10	-909	152	68	0.32	-530	139	69	0.50

It is found from the table that in both acids the values of cathodic Tafel slope (b_c) increases with increasing concentration of AMMT. But at the same time the values of anodic Tafel slope (b_a) also increase but to a lesser extent. These observations clearly bring out the fact that the corrosion of mild steel in both acids in the presence of AMMT is under mixed control, but predominantly under cathodic control.

Impedance diagrammes obtained for the frequency range of 6 Hz to 60 kHz at the OCP for mild steel in 0.5 M H_2SO_4 and 1 M HCl in the presence and absence of different concentrations of AMMT are shown in Fig.1 (a & b) and 2 (a & b). It is seen from these figures that the impedance diagrammes obtained are not perfect semicircles, and this difference has been attributed to frequency dispersion [19]. The charge transfer resistance R_t has been calculated from the difference in the impedance at low and high frequencies as suggested by Haruyama and Tsuru [20]. The value of R_t has been substituted in the Stern-Geary equation to get corrosion current. Double layer capacitance values are calculated from the frequency at which the imaginary component of the impedance ($-Z''$) is maximum i.e. $f(-Z''_{max})$ is found and the values of C_{dl} are obtained from the relationship

$$f(-Z''_{max}) = \frac{1}{2\pi C_{dl} RT}$$

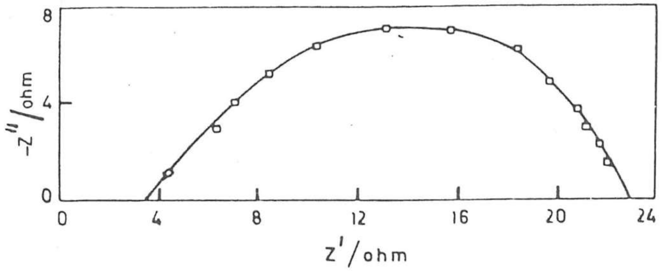

Fig.1a. Impedance diagramme of mild steel in 0.5M H_2SO_4

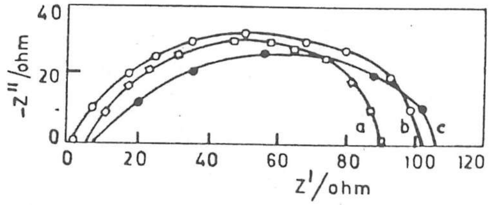

Fig.1b. Impedance diagrammes of mild steel in 0.5M H_2SO_4 containing AMMT
a. 2mM b. 5mM c. 10mM

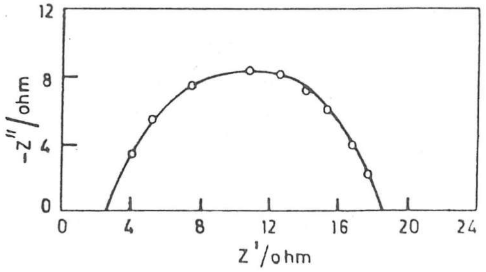

Fig.2a. Impedance diagramme of mild steel in 1M HCl

It is seen from the impedance diagrammes that an increase in the concentration of the organic compound increases the value of R_t and decreases the corrosion of steel. As the impedance diagrammes have a semicircle appearance, it indicates that the corrosion of steel is usually controlled by the charge transfer process and the presence of inhibitor does not alter the mechanism of the dissolution of steel. This observation was confirmed by an earlier worker [21].

Table 3 gives the values of R_t, C_{dl} and I_{corr} for mild steel in both the acids in the presence of different concentrations of AMMT.

TABLE 3

Impedance parameters for mild steel in 0.5 M H_2SO_4 and 1 M HCl containing different concentrations of AMMT

	0.5 M H_2SO_4			1 M HCl		
Inhibitor (mM)	R_t / (Ω cm^2)	I_{corr} / (mA cm^{-2})	C_{dl} / (μF cm^{-2})	R_t / (Ω cm^2)	I_{corr} / (mA cm^{-2})	C_{dl} / (μF cm^{-2})
Blank	5.5	3.39	183.2	4.13	4.21	244.0
2	23.65	0.79	107.0	23.60	1.58	169.5
5	27.43	0.65	91.7	24.80	0.98	138.0
10	29.41	0.64	85.8	29.00	0.79	101.7

It is found from the table that, the presence of organic compound in acidic solutions leads to enhancement of the R_t values and a decrease in the C_{dl} values. This influence may be due to the adsorption of the complex or the compound as such on the metal surface [22].

Hydrogen permeation versus time for both acids in the presence and absence of the inhibitor are shown in Fig.3. The hydrogen permeation current for plain acids are found to be more for HCl, because of the more corrosive nature of chloride ions. But the presence of AMMT in H_2SO_4 reduces the permeation current to a greater extent than in HCl. These observations are in keeping with the facts observed for weight loss experiments.

Surface coverage (θ) values have been obtained from values of inhibition efficiency in the presence and absence of the inhibitor. It is observed that a plot of θ vs. log c for the inhibitor gives a straight line indicating that the adsorption of inhibitor on the mild steel surface from both acids, obeys Temkin adsorption isotherm.

4 CONCLUSION

The main conclusions reported in this paper are the following:

1 The inhibitor AMMT is a very promising inhibitor for bringing down the self corrosion of mild steel in both H_2SO_4 and HCl. An inhibition efficiency of 90% has been obtained even with a small amount of AMMT.

2 The inhibition of corrosion is due to the adsorption of metal-triazole complex, coordinated with the electron pairs of the sulphur or of the nitrogen atom.

3 The inhibitor AMMT was found to affect both the anodic and cathodic processes i.e. the inhibitor is of the mixed type, although the inhibition of cathodic reaction is predominant.

4 The inhibitor AMMT brings down the hydrogen permeation current considerably in both the acids, but more in H_2SO_4.

5 The adsorption of AMMT on the mild steel surface obeys Temkin adsorption isotherm.

ACKNOWLEDGEMENT

Authors thank Director, CECRI for his kind permission to publish this paper. One of the authors (S.M.) wishes to thank Council of Scientific and Industrial Research (CSIR), New Delhi, for the award of Senior Research Fellowship to him.

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(Recivedi 3 Juni 1993
Revised form 10 August 1993)

A NOVEL APPROACH OF THE SILVER ELECTRODEPOSITION MECHANISM

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Abstract

In regard to the understanding of the silver electrodeposition process at carbom microelectrodes three different mechanisms have been proposed and its theoretical simulations are presented. A comparison between experimental and simulated voltammograms shows that several kinetic complexities occurs during the electrodeposition process.

Introduction

The electrodeposition and electrocrystallisation of silver was investigated repeatedly during the 1960s using a variety of electrochemical techniques such as A.C. impedance,