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Effects of Different Amino-acid Derivatives on the Inhibition of NST-44 Mild Steel Corrosion in Lime Fluid

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Abstract: This study presents the report of an investigation on the effect of some amino acid based inhibitors on the corrosion characteristics of NST-44 mild steel in lime fluid (citrus aurantifolia). The corrosion rates of the exposed mild steel were obtained using the weight loss immersion method. The amino acid inhibitors investigated include leucine, alanine, methionine and glutamic acid. The corroded surfaces of the specimens were characterized using the optical microscopic techniques. It was observed that alanine showed the highest inhibitive potential on NST-44 mild steel in the lime fluid with at a lower concentration while glutamic acid showed the least potential with as low as 23% inhibition efficiency. Leucine and methionine, however showed considerable potentials with inhibition efficiencies of about 41 and 44.70%, respectively. The results of this research are expected to improve the corrosion resistance of this steel as a constructional material for lime processing industries in Nigeria.

Key words: Corrosion, amino acid inhibitors, mild steel, inhibition efficiency

INTRODUCTION

The use of inhibitors is one of the most practical means for protecting metals/alloys against corrosion, especially in acidic media. They are classified as anodic, cathodic, organic and inorganic etc. Several ideas have attempted to rationalize the actions of inorganic inhibitors, the oldest and still the widely accepted one assumes that inhibition is the result of the formation of a protective layer which acts as a physical barrier slowing down the dissolution process. Such barrier is often created in steel when the iron ions, Fe^{2+} which go into solution from defect sites in the passive film undergo oxidation by the inhibitor or by oxygen in the solution and deposit on the anode as an insoluble product layer able to produce an adherent barrier (Uhlig and Revie, 1985).

Various inorganic inhibitors that have been tested and used in corrosion prevention are well documented and established (Loto and Mohammed, 2000). In the Food Processing Industries, the interest is to use organic compounds as inhibitors due mainly to their inherent and non-toxic nature. The action of inhibition of the corrosion of mild steel in acidic compounds has been widely studied (Bentiss et al., 2000). In general, organic compounds such as amines, acetylenic alcohols, heterocyclic compounds etc have found use as inhibitors in industrial applications. It is well known that triazole

type of organic compounds and their derivatives are good corrosion inhibitors for many metals and alloys in various aggressive media (Memari et al., 1998; Agrawal and Namboodhiri, 1992; Bentiss et al., 1999; Bentiss et al. 2000).

Research has shown that amino acid derivatives can inhibit corrosion in either basic or acidic environments. In this study the effect of some amino acid derivatives, namely; alanine, leucine, glutamic acid and methionine will be evaluated for their inhibitive effects on mild steel corrosion in lime fluid.

MATERIALS AND METHODS

The NST-44 mild steel test specimen used had a percent nominal composition of 0.15 C, 0.22 Si, 0.04 S, 0.50 Mn, 0.04 P, 0.10 Cr, 0.10 Ni, 0.04 Sn, 0.25 Cu and 0.11 N, the rest being Fe. A cylindrical steel rod was cut into pieces of various dimensions and their surfaces were given similar surface finish in order to descale them. They were then ground with 240, 320, 400 and 600 grits silicon carbide abrasive paper, cleaned thoroughly, rinsed in ultrasonic cleaner, dried and then kept for further weight loss.

Lime juice was obtained from lime fruits by peeling off the outer cover and squeezing manually. The chemical formula of the inhibitors used are: Leucine

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((CH$_3$)$_2$CH.CH$_2$.CH(NH$_2$).COOH), alanine (CH$_3$.CH(NH$_2$).COOH), methionine (CH$_3$.S.(CH$_2$)$_2$. CH(NH$_2$).COOH) and glutamic acid (C$_5$H$_4$NO$_4$.). All the inhibitors were used at room temperature throughout the period of the tests.

Different concentrations (0.05, 0.1, 0.2, 0.3 and 0.4 M) of the different inhibitors were prepared and added to 100 ml of lime juice extract and another preparation of the juice extract of the lime was made without the addition of any of the inhibitors. This serves as a control.

Specimens were washed, degreased in benzene, dried and weighed prior to taking the initial weights, thereafter, they were immersed totally in 100 ml of stagnant solutions containing mixtures of different concentrations of inhibitors in lime fluid. The procedure was repeated for the environment without inhibitor. For each container, specimens were removed after every 2 days and weighed after cleaning off the corrosion products. This lasted for 10 days. The corrosion product formed on the surface of the specimen was removed by scrubbing under running water using fine rubber bung. After rinsing with methanol, the specimen were dried and then re-weighed. Curves of corrosion rates in mils per year (mpy) versus the exposure time were plotted for each inhibitor with various concentrations in the medium.

The efficiency of inhibition (%) for each of the inhibitors concentration in the lime fluid was then calculated from the relationship:

$$P = 100\frac{(W_1 - W_2)}{W_1} \qquad (i)$$

Where, W_1 and W_2 are respectively the corrosion rates in the absence and presence of the predetermined concentration of inhibitor

RESULTS

Figure 1 to 5 represent some of the micrographs of the corroded surfaces of the NST-44 mild steel after eight days of exposure in the uninhibited and inhibited lime fluid. All the micrographs showed evidence of localized attack with the appearance of small cavities (dark spots) on their surfaces. The micrograph of Fig. 1 representing the surface exposed to uninhibited lime fluid showed more distribution of the cavities. Figure 2 and 3 of surfaces exposed to 0.10 M alanine and 0.10 M methionine inhibited fluid respectively showed lesser distribution of the cavities. The size and distribution of cavities became

Table 1: Variation of the efficiencies of different concentrations of inhibitors with time of exposure

Duration of exposure (h)	Inhibitors efficiencies (%)				
	0.05 M	0.10 M	0.20 M	0.30 M	0.40 M
Leucine					
48	7.11	8.53	10.90	27.96	28.91
96	2.61	8.49	11.44	16.34	17.97
144	10.55	15.06	22.59	34.65	35.59
192	3.27	8.66	13.07	38.07	39.05
240	2.96	5.76	7.48	40.195	40.97
Alanine					
48	1.90	4.74	25.12	29.86	31.28
96	4.90	6.86	17.97	19.61	21.24
144	11.49	15.82	35.03	37.66	38.23
192	3.75	11.27	39.22	41.34	43.46
240	2.65	7.01	40.03	41.90	43.93
Methionine					
48	8.06	11.85	12.79	28.44	29.38
96	3.59	9.48	12.75	16.99	17.97
144	11.86	16.38	23.73	35.03	35.97
192	3.59	3.27	16.34	41.34	42.65
240	-1.71	7.79	13.08	43.61	44.70
Glutamic acid					
48	6.16	4.26	2.36	1.42	0.47
96	2.29	6.21	7.84	4.90	1.63
144	6.40	17.70	21.09	14.69	1.51
192	11.76	19.77	23.04	3.27	8.98
240	13.86	21.65	17.13	4.36	9.19

drastically reduced in respect of the mild steel surface exposed to 0.30 M alanine inhibited lime fluid (Fig. 4) The cavities as found on the surface in 0.30 M methionine inhibited fluid, however, are bigger in size and distribution compared to those of alanine environment of Fig. 4. In general, the surfaces exposed to inhibited lime fluid are brighter than those of the uninhibited fluid. In addition, Fig. 2 and 4 due to alanine inhibition are however brighter than Fig. 3 and 5 representing surfaces exposed to methionine inhibited lime fluid.

Figure 6-9 show the corrosion rates in (mpy) with duration of exposure for the NST-44 mild steel exposed to lime fluids inhibited with the amino acid derivatives; leucine, alanine, methionine and glutamic acid, respectively. From Fig. 6 it is clear that the inhibition level due to leucine increased with increase in its concentration. The effectiveness of inhibition became noticeable from 0.30 M concentration of leucine inhibition. Figure 7 in a similar manner to Fig. 6 shows the inhibition potential of alanine. The effectiveness of alanine inhibition became significant from 0.20 M concentration in the lime fluid.

The effect of methionine inhibition on the corrosion of NST-44 mild steel in lime fluid is contained in Fig. 8. Its inhibition characteristics in the lime showed semblance to what obtained for leucine because its inhibition in the lime environment also became sufficiently effective only at
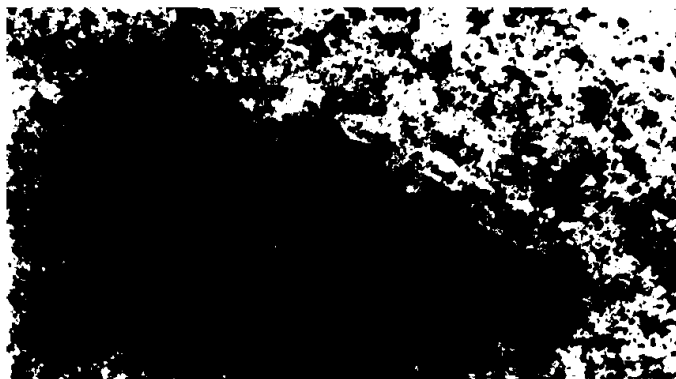
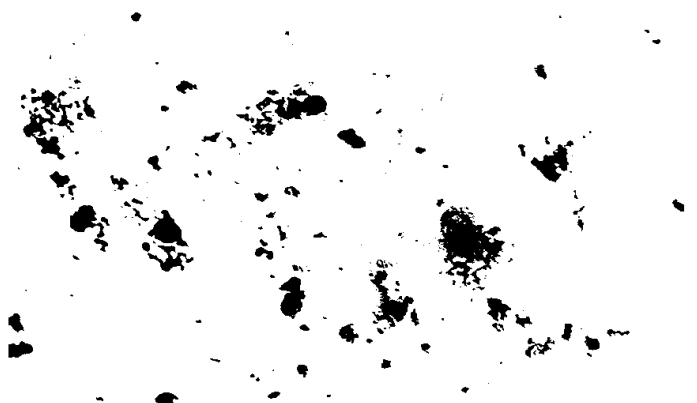Fig. 1: Micrograph of NST-44 mild steel surface after 8 days of exposure in lime fluid without inhibitor (×100)

Fig. 2: Micrograph of NST-44 mild steel surface after 8 days of exposure in lime fluid inhibited with 0.10 M alanine (×100)

Fig. 3: Micrograph of NST-44 mild steel surface after 8 days of exposure in lime fluid inhibited with 0.10 M methionine (×100)

Fig. 4: Micrograph of NST-44 mild steel surface after 8 days of exposure in lime fluid inhibited with 0.30 M (×100)

Fig. 5: Micrograph of NST-44 mild steel surface after 8 days of exposure in lime fluid inhibited with 0.30 M methionine
(×100)

0.30 M of the inhibitor. Figure 9 presents the effect of glutamic acid on the corrosion of mild steel in lime fluid. It exhibited quite different features compared to other inhibitors.. From the curves on this Fig. 9, it is understandable that glutamic acid could not effectively inhibit the corrosion of the NST-44 mild steel in lime.

Figure 10 shows the relative inhibitive powers of all the amino acid inhibitors in lime fluid as it declines from alanine through methionine, leucine to glutamic acid. The results have shown that the presence of alanine had the greatest tendency towards passivation of the steel

surface, since its protection potential was fixed at a concentration level (0.20 M) less than those for leucine and methionine (which only became active above 0.30 M).

Table 1 contains the results of the efficiencies of all the inhibitors at different concentrations as a function of time of exposure. Although all the efficiencies fall below 50%, only alanine at 0.20 M exhibited greater than 35% efficiency. Methionine has proved to be more efficient than either alanine or leucine at 0.30 M concentration. This not withstanding and with the support of the revelations contained in the micrographs of the inhibited
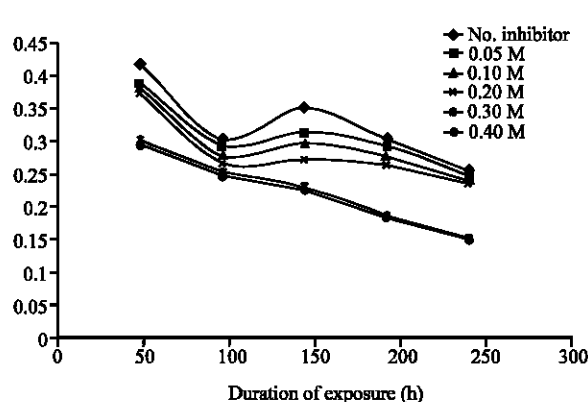
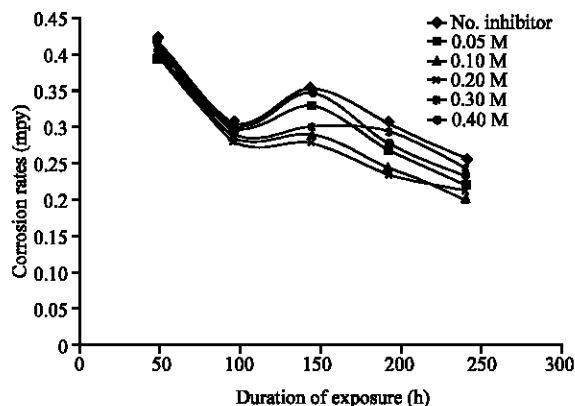Fig. 6: Effect of Leucine as a suitable inhibitor in lime fluid

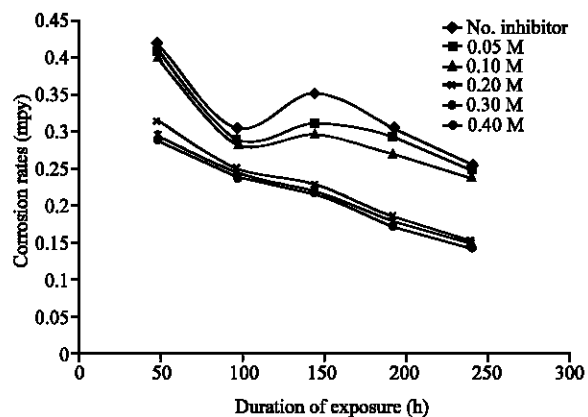Fig. 7: Effect of alanine as a suitable inhibitor of mild steel corrosion in lime fluid

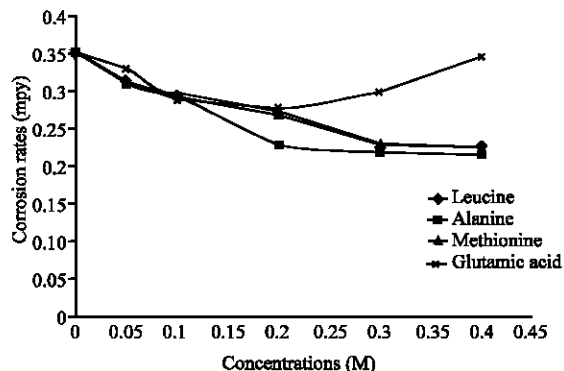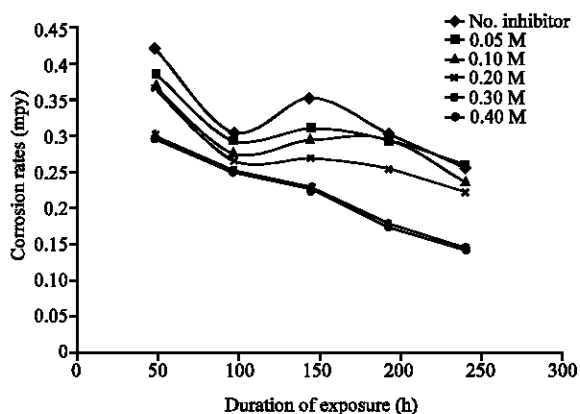Fig. 8: Effect of methionine as a suitable inhibitors of mild steel corrosion in lime fluid

surfaces it could be said that alanine is able to suppress more of the localized effects of the lime fluid than methionine. From Table 1, it is clear that a threshold

Fig. 9: Effect of glutamic acid as a suitable inhibitor of mild steel corrosion in lime fluid

Fig. 10: Relationship between corrosion rates and concentration of inhibitors after 144 h of exposure

concentration exist beyond which the efficiency of inhibition become significant as mentioned earlier for each inhibitor. At lower concentrations, the efficiency of inhibition increases with duration of exposure, reaching a maximum value after about 144 days of exposure and thereafter increasing gradually at a low rate.

DISCUSSION

Lime is known to contain citric acid naturally. This acid fall into the category of the organic acid that is known to be a weak acid. In solution, the citric acid dissociates as follows;

$$(CH_2)_2 \, COOH \rightarrow (CH_2)_2 \, COO^- + H^+ \qquad (ii)$$
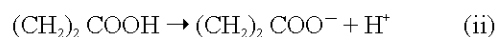
In the presence of this environment the iron in steel goes into solution at the anode as:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (iii)$$

At the cathode, the hydrogen ions produced by citric acid and dissociated water molecules take up the electrons produced at the anode and in the presence of oxygen form water molecules;

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O \qquad (iv)$$
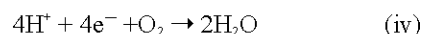
The overall reaction leading to corrosion products is due to the reaction between the followings;

$$(CH_2)_2 COO^- + Fe^{2+} \rightarrow (CH_2)_2 COOFe^+ \qquad (v)$$
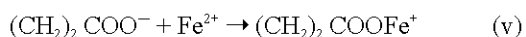
The $(CH_2)_2$ COO Fe$^+$ produced is a complex soluble products that is capable of leaving the anodic site as soon as it is formed thereby exposing another fresh surface. In the presence of inhibitors, particularly, the organic inhibitors and the amino acid derivatives investigated, the rate of iron dissolution and that of the formation of soluble complex $-(CH_2)_2$ COO Fe$^+$ decreased.

Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulphur, or oxygen, each of which is considered a chemisorption center. The protective properties of these compounds depend on the electron densities at the chemisorption center. The higher the electron density at the center the more effective is the inhibitor. Three of the inhibitors; leucine, alanine and glutamic acid studied contain nitrogen while methionine contain both nitrogen and sulphur.

The corrosion rates in the presence of the various inhibitors indicated that alanine has the greatest effect on the dissolution of Fe in the lime fluid. The mechanism of action of methionine as a corrosion inhibitor had already been established for different metals and alloys (Rajappa and Venkatesha, 2003). The reduction in the dissolution of Fe in the presence of these inhibitors may be attributed to the sulphur and nitrogen atoms present in the functional group. These groups suspected to be elecroactive may have interacted with the steel surface to an extent. According to Rajappa and Venkatesha, (2003) the –NH$_2$ of the inhibitors would have reacted with the available CHO in medium to give imine, a condensation product. Corrosion rate is lower in imine because it usually covers more of the metal surface. It may therefore be that the imine of the alanine is a most efficient corrosion inhibitor compared to other imines formed by other inhibitors. Naturally, it would seem as if methionine should confer the greatest inhibition of them all because of its additional chemisorptions center due to

sulphur. Table 1 results of efficiencies confirm this but only at higher concentration. According to earlier studies the compound due to sulphur of methionine exhibit lesser corrosion inhibition than imine compound (Muralidharan *et al.*, 1995; Rajappa and Venkatesha, 2003).

CONCLUSIONS

- Mild steel corrosion in lime fluid can be inhibited by the amino acid derivatives, viz., alanine, leucine and methionine characterized by equal amino group and carboxylic group
- the inhibitive efficiencies of the investigated inhibitors increase with concentrations but there are peaks beyond which the efficiencies drops.
- The efficiencies of inhibition of the amino acid derivatives in lime fluid decreases in the order; alanine, methionine and leucine

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