A Comparative Study on the Corrosion Inhibition of Mild Steel and Aluminium by Synthesized Inhibitors in Organic Acidic Medium

Lalita Saini and R. K. Upadhyay

Synthesis and Surface Science Laboratory, Department of Chemistry, Government College Ajmer, Rajasthan, India.

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

ABSTRACT

Mass loss and Scanning Electron Microscope method (SEM) have been used to study the corrosion inhibition efficiency on mild steel and aluminium using synthesized inhibitors i.e. N-Benzylidene aniline (CI1) and N-Benzylidene 4-methylaniline (CI2) in Trichloroacetic acid (TCAA). Study reveals that both mild steel and aluminium are prone to corrosion in organic acid like TCAA. Out of these two metals, aluminium is more vigorously corroded by the TCAA in comparison to mild steel in same conditions and synthesized inhibitors CI1 and CI2 are almost same effective for mild steel and aluminium.

Keywords: Corrosion inhibition; mass loss; inhibition efficiency; surface coverage; corrosion rate SEM.

1. INTRODUCTION

Corrosion is noxious attack on the metal due to its reaction with environment. Corrosion word stems from the latin word “Corrodere” meaning “to eat away”. Generally this phenomena is found when a metal or alloy gives a chemical or electrical reactions [1-3]. In simple technology,
corrosion processes involve reaction of metals with environmental species. Metals corrode because we use them in environment where they are chemically unstable [4-6]. Corrosion is the destructive result of chemical reaction between a metal and environment. All metals tend to corrode, Corrosion destroys metals by converting them into oxides or other corrosion products. Mild steel and aluminium both metals are well known constructional metals these metals are widely used because of their low cost and excellent mechanical properties. Because of this both metals have been a subject of numerous studies. They both are however highly reactive metals and are prone to corrosion, therefore the inhibition of aluminium and mild steel by organic compounds in acids have been studied by many workers [7-11]. For corrosion inhibition, different methods are there, among all these methods, addition of corrosion inhibitor is best, most economic and highly effective method. This method is more useful because of low cost [12-17]. Several scientific studies have been recently reported to the subject of corrosion inhibitors. A corrosion inhibitor is a species, natural or synthesized in laboratory when added in very small quantity in corrosive medium decreases or minimize the rate of corrosion [18].

2. MATERIALS AND METHODS

To synthesize CI1 equimolar quantity of aniline and benzaldehyde were taken in round bottom flask (250 mL) in ethanol and were refluxed for 8-9 hours and then the reaction mixture was poured in ice cold water yellowish colored crystal were obtained which were recrystallized by alcohol and dry it and collected. The purity of CI1 was checked by IR, NMR and elemental analysis [19-21].

Similar procedure was adopted to synthesize CI2 taking equimolar quantity of aniline and 4-Methyl benzaldehyde.

Solutions of TCAA were prepared using double distilled water. All chemicals used were of analytical reagent grade.

![Chemical structure](image)

To study corrosion rate in mass loss method square shaped sheet having thickness 1 mm and 2.5 × 2.5 cm dimensions were taken. A small hole of about 2 mm diameter near the upper edge of each specimen was made. Specimen of both metals (mild steel and aluminium) was cut from a sheet of respective metal. Specimen was cleaned by buffing to remove polished surface and produce immaculate finish and finally they were kept in an oven to remove any moisture on the surface of specimen.

Specimen was suspended by V-shaped glass hook made by fine glass capillary tubes at room temperature in a beaker containing 50 mL of the test solution at 298K. After the test, specimens were cleaned by running water and then dried with hot air dryer. Duplicate experiments were performed in each case and then weighed again mean values of the mass loss were calculated.
The percentage inhibition efficiency was calculated as [22].

\[
\eta\% = \frac{100(\Delta M_u - \Delta M_i)}{\Delta M_u} \quad (i)
\]

Where \(\Delta M_u\) and \(\Delta M_i\) are the mass loss of the specimen in uninhibited acid and in inhibited solution respectively.

The corrosion rate (CR) in milli meter per year (mmpy) can be obtained by the following equation [23].

\[
\text{Corrosion rate (mmpy)} = \frac{87.6\Delta M}{\text{ATD}} \quad (ii)
\]

Where \(\Delta M\) is the mass loss of specimen in mg, \(A\) is the area of exposure of specimen in square cm, \(T\) is the time of exposure in hours and \(D\) is the density of specimen in g/cm\(^3\).

The degree of surface coverage \(\theta\) can be calculated as [24].

\[
\theta = \frac{(\Delta M_u - \Delta M_i)}{\Delta M_u} \quad (iii)
\]

Where \(\Delta M_u\) and \(\Delta M_i\) are the mass loss of the specimen in uninhibited acid and in inhibited solution respectively.

Electron Microscope method (SEM) has also been used to study the surface examination of mild steel and aluminium that includes magnifications up to 15000 times with corresponding resolution enhancement and 5KV and 15KV operations.

SEM for the sample in different concentration of TCAA with the inhibitors and changes are observed shown in the figure.

3. RESULTS AND DISCUSSION

The calculated Mass loss (\(\Delta M\)), percentage inhibition efficiency (\(\eta\%\)) and the corrosion rate (CR) in different concentrations i.e. 0.1N, 0.5N, 1.0N and 2N of trichloroacetic acid for mild steel and aluminium are are shown in Tables 1 to 4 at 298K. It is clear from the Table 1 that the maximum efficiency 99.13\% was shown by CI\(_1\) whereas CI\(_2\) shows maximum efficacy 82.13\%. It means CI\(_1\) is a better corrosion inhibitor than CI\(_2\).

Same trends are observed in Table 3 for aluminium as were seen for mild steel in TCAA. The maximum efficiency in the case of aluminium is 99.88\% and 84.14\% for CI\(_1\) and CI\(_2\) respectively. Tables 2 and 4 show the variation of surface coverage (\(\theta\)) and log\(\theta/ (1-\theta)\) with \(\eta\%\) in different concentrations of TCAA for both metals. Tables 2 and 4 show that surface coverage (\(\theta\)) of both metals i.e. mild steel and aluminium surface increases with increasing concentration of inhibitors as well as that of TCAA for both the inhibitors i.e. CI\(_1\) and CI\(_2\).

Fig. 3.1(a) to 3.4(a) show the variation of inhibition efficiency with concentration of inhibitor for mild steel and in TCAA whereas Fig. 3.1(b) to 3.4(b) show the variation of inhibition efficiency (\(\eta\%\)) with concentration for aluminium in TCAA.

Corrosion inhibition behaviour of metals i.e. mild steel and aluminium using synthesized inhibitors in TCAA solutions were determined by Electron Microscope method (SEM) also. Observation of mild steel and aluminium specimen were made using ZEISS-50-Scanning electron microscope (SEM) for the specimen in pure state, dipped in acid solution and also in acid solution with inhibitor. The SEM analysis study represents the surface structural changes in given specimen. Fig. 1(a) shows the structural view of pure mild steel sample, Fig. 1(b) is in 1N TCAA after the exposure of specimen for about 3.33 hours whereas Fig. 1(c) is in 1N TCAA with inhibitor CI\(_1\) (40 ppm) for the same time. Fig. 2(a) shows the structural view of pure aluminium sample, Fig. 2(b) is in 1N TCAA after the exposure of specimen for about 3 hours whereas Fig. 2(c) is in 1N TCAA with inhibitor CI\(_1\) (40 ppm) for the same time.

Figs. 1(a) and 2 (a) show SEM for mild steel and aluminium in pure state i.e. in absence of TCAA. Figs. 1(b) and 2 (b) show SEM for mild steel and aluminium in uninhibited (blank) TCAA. It is clear from the figure that both specimen show drastic changes in the surface it means both aluminium and mild steel surfaces have been adversely effected in 1N TCAA. Figs. 1(c) and 2(c) show SEM for mild steel and aluminium in TCAA in presence of inhibitor. It is clear from the SEM that Figs. 1(a), 2(a) and Figs. 1(c), 2(c) are almost same for both specimen it means the surfaces of both metal are not affected in TCAA in presence of inhibitor.

SEM analysis is useful in determining the change in metal surface due to presence of inhibitors and acid solutions. SEM studies show the aluminium and mild steel in pure acids and in presence of inhibitors. Pictures obtained from SEM analysis show that the surface structure of aluminium and mild steel do not change very much in presence of inhibitors which indicates that inhibitors protect the surface efficiency.
Table 1. Mass loss ($\Delta M$) and inhibition efficiency (%) for Mild steel in TCAA solution with given inhibitor addition at 298K Surface Area: 6.25 cm$^2$

| Inhibitor addition | 0.1 N TCAA (93 hrs.) | 0.5 N TCAA (51 hrs.) | 1N TCAA (3.33 hrs.) | 2N TCAA A(2.25 hrs.) |
|--------------------|----------------------|----------------------|----------------------|----------------------|
|                    | DM, mg               | h%                   | C.R.                 | DM, mg               | h%                   | C.R.                 | DM, mg               | h%                   | C.R.                 |
| Uninhibited Cl$_2$| 282.2                | --                   | 5.41                 | 282.2                | 9.87                 | 193.6                | 103.80               | 2000.0               | 1587.09              |
| 10 PPM             | 144.0                | 48.97                | 2.76                 | 201.2                | 28.34                | 7.91                 | 103.2                | 46.70                | 55.33                |
|                    |                      |                      |                      |                      |                      |                      |                      |                      |                      |
| 20 PPM             | 122.5                | 56.59                | 2.35                 | 74.2                 | 73.70                | 2.59                 | 39.3                 | 79.70                | 21.07                |
| 30 PPM             | 109.2                | 61.30                | 2.09                 | 67.3                 | 76.15                | 2.35                 | 36.4                 | 81.19                | 19.51                |
| 40 PPM             | 75.1                 | 73.38                | 1.44                 | 64.3                 | 77.21                | 2.25                 | 33.2                 | 82.85                | 17.80                |
|                    |                      |                      |                      |                      |                      |                      |                      |                      |                      |
| 10 PPM             | 221.2                | 21.61                | 4.24                 | 215.4                | 23.56                | 7.54                 | 861.6                | 33.23                | 461.99               |
|                    |                      |                      |                      |                      |                      |                      |                      |                      |                      |
| 20 PPM             | 216.8                | 23.17                | 4.16                 | 213.9                | 24.20                | 7.48                 | 810.1                | 37.66                | 434.38               |
| 30 PPM             | 215.4                | 23.67                | 4.13                 | 75.9                 | 73.10                | 2.65                 | 655.0                | 49.98                | 351.21               |
| 40 PPM             | 213.9                | 24.20                | 4.10                 | 69.7                 | 75.30                | 2.44                 | 293.5                | 77.41                | 157.37               |

Table 2. Inhibition efficiency (h%) and surface coverage (q) for mild steel in TCAA solution with given inhibitor addition at 298K Surface Area: 6.25 cm$^2$

| Inhibitor addition | 0.1 N TCA A(93 hrs.) | 0.5 N TCAA (51 hrs.) | 1N TCAA (3.33 hrs.) | 2N TCAA A(2.25 hrs.) |
|--------------------|----------------------|----------------------|----------------------|----------------------|
|                    | h%                   | q                    | log q                | h%                   | q                    | log q                | h%                   | q                    | log q                |
| Uninhibited Cl$_2$|                      |                      |                      |                      |                      |                      |                      |                      |                      |
| 10 PPM             | 48.97                | 0.4897               | -0.0177              | 28.34                | 0.2834               | -0.4026              | 46.70                | 0.4670               | -0.0573              | 78.88                | 0.7888               | 0.5722               |
| 20 PPM             | 56.59                | 0.5659               | 0.1151               | 73.70                | 0.7370               | 0.1196               | 79.70                | 0.7970               | 0.5939               | 79.85                | 0.7985               | 0.5958               |
| 30 PPM             | 61.30                | 0.6130               | 0.1998               | 76.15                | 0.7615               | 0.5127               | 81.19                | 0.8119               | 0.6352               | 98.98                | 0.9898               | 1.9891               |
| 40 PPM             | 73.38                | 0.7338               | 0.4003               | 77.21                | 0.7721               | 0.5289               | 82.85                | 0.8285               | 0.6840               | 99.13                | 0.9913               | 2.0566               |
| Cl$_2$             |                      |                      |                      |                      |                      |                      |                      |                      |                      |
| 10 PPM             | 21.61                | 0.2161               | -0.4923              | 23.56                | 0.2356               | -0.5084              | 33.23                | 0.3323               | -0.3029              | 69.44                | 0.6944               | 0.3565               |
| 20 PPM             | 23.17                | 0.2317               | -0.4607              | 24.20                | 0.2420               | -0.4958              | 37.66                | 0.3766               | -0.2188              | 73.11                | 0.7311               | 0.4345               |
| 30 PPM             | 23.67                | 0.2367               | -0.4509              | 73.10                | 0.7310               | 0.4342               | 49.98                | 0.4998               | -0.0003              | 79.11                | 0.7911               | 0.5781               |
| 40 PPM             | 24.20                | 0.2420               | -0.4408              | 75.30                | 0.7530               | 0.4041               | 77.41                | 0.7741               | 0.5348               | 82.13                | 0.8213               | 0.6625               |
### Table 3. Mass loss (ΔM) and inhibition efficiency (%) for aluminium in TCAA solution with given inhibitor addition at 298K Surface Area: 6.25 cm²

| Inhibitor addition | 0.1 N TCAA (94 hrs.) | 0.5 N TCAA (51 hrs.) | 1N TCAA (3.33 hrs.) | 2N TCAA (2.25 hrs.) |
|--------------------|----------------------|----------------------|---------------------|---------------------|
|                    | DM, mg | h% | C.R. | DM, mg | h% | C.R. | DM, mg | h% | C.R. | DM, mg | h% | C.R. |
| Uninhibited        | 188.7  | -- | 10.42 | 189.0  | -- | 20.44 | 439.2  | -- | 759.97 | 259.2  | -- | 1035.02 |
| Cl<sub>2</sub>      | 10 PPM | 156.1 | 17.27 | 8.62 | 141.2 | 25.29 | 15.27 | 273.5 | 37.72 | 473.25 | 33.3 | 87.15 | 132.97 |
|                    | 20 PPM | 140.2 | 25.70 | 7.74 | 139.7 | 26.08 | 15.10 | 148.0 | 66.30 | 256.09 | 25.1 | 90.31 | 100.22 |
|                    | 30 PPM | 128.1 | 32.11 | 7.07 | 98.9  | 47.67 | 10.69 | 110.6 | 74.81 | 191.37 | 07.1 | 97.26 | 28.35 |
|                    | 40 PPM | 119.0 | 36.93 | 6.57 | 65.0  | 65.60 | 07.02 | 005.0 | 98.86 | 86.5 | 00.5 | 99.88 | 01.99 |

### Table 4. Inhibition efficiency (%) and surface coverage (q) for aluminium in TCAA solution with given inhibitor addition at 298K Surface Area: 6.25 cm²

| Inhibitor addition | 0.1 N TCAA (93 hrs.) | 0.5 N TCAA (51 hrs.) | 1N TCAA (3.33 hrs.) | 2N TCAA (2.25 hrs.) |
|--------------------|----------------------|----------------------|---------------------|---------------------|
|                    | h% | q | log q | 1-q | h% | q | log q | 1-q | h% | q | log q | 1-q | h% | q | log q | 1-q |
| Uninhibited        | Cl<sub>2</sub>      | 10 PPM | 17.27 | 0.1727 | -0.6803 | 25.27 | 0.2527 | -0.4708 | 37.72 | 0.3772 | -0.2177 | 87.15 | 0.8715 | 0.8313 |
|                    | 20 PPM | 25.70 | 0.2570 | -0.4610 | 26.08 | 0.2608 | -0.4524 | 66.30 | 0.6630 | 0.2938 | 90.31 | 0.9031 | 0.9694 |
|                    | 30 PPM | 32.93 | 0.3293 | -0.3251 | 47.67 | 0.4767 | -0.0405 | 74.81 | 0.7481 | 0.4727 | 97.26 | 0.9726 | 1.5501 |
|                    | 40 PPM | 36.93 | 0.3693 | -0.2324 | 65.60 | 0.6560 | 0.2803 | 98.07 | 0.9807 | 1.7059 | 99.88 | 0.9988 | 2.9202 |
| Cl<sub>2</sub>      | 10 PPM | 23.79 | 0.2379 | -0.5056 | 35.55 | 0.3555 | -0.2583 | 44.28 | 0.4428 | -0.0998 | 66.04 | 0.6604 | 0.2888 |
|                    | 20 PPM | 29.67 | 0.2967 | -0.3748 | 40.31 | 0.4031 | -0.1704 | 46.33 | 0.4633 | -0.6386 | 69.40 | 0.6940 | 0.3556 |
|                    | 30 PPM | 32.48 | 0.3248 | -0.3178 | 47.13 | 0.4713 | -0.0499 | 66.68 | 0.6668 | 0.3012 | 77.89 | 0.7789 | 0.5468 |
|                    | 40 PPM | 38.27 | 0.3827 | -0.2075 | 58.78 | 0.5878 | 0.1541 | 91.64 | 0.9164 | 1.0398 | 84.14 | 0.8414 | 0.7246 |
Fig. 1(a). SEM Analysis of pure mild steel surface

Fig. 1(b). SEM analysis of pure mild steel surface in 1N TCAA

Fig. 1(c). SEM analysis of pure mild steel surface in 1N TCAA with given inhibitor

The mechanism of corrosion inhibition by synthesized compounds CI$_1$ and CI$_2$ which are basic in nature depends upon the fact that these basic compounds dissociates in acidic media and form a monolayer on the surface of metal by the phenomena of chemisorption the adsorption is due to hetero atom N present in these inhibitors which has high electron density due to lone pair of electrons which form chemical bond with the metal surface.
thus these inhibitors block the active sites on the metallic surface consequently the rate of electrochemical reaction of corrosion reduces on the surfaces and the corrosion decreases. More the concentration of inhibitor, more will be its adsorption on the surface similarly in more acidic condition more dissociation of inhibitor take place which ultimately block more site on metallic surface and decreases the corrosion.

Fig. 2(a). SEM analysis of pure aluminium surface

Fig. 2(b). SEM analysis of pure aluminium surface in 1N TCAA

Fig. 2(c). SEM analysis of pure aluminium surface in 1N TCAA with given inhibitor
Fig. 3.1(a). Variation of inhibition efficiency with concentration of inhibitor for mild steel in 0.1 N TCAA

Fig. 3.2(a). Variation of inhibition efficiency with concentration of inhibitor for mild steel in 0.5 N TCAA

Fig. 3.3(a). Variation of inhibition efficiency with concentration of inhibitor for mild steel in 1 N TCAA

Fig. 3.4(a). Variation of inhibition efficiency with concentration of inhibitor for mild steel in 2 N TCAA
Fig. 3.1(b). Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 0.1 N TCAA

Fig. 3.2(b). Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 0.5 N TCAA

Fig. 3.3(b). Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 1 N TCAA

Fig. 3.4(b). Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 2 N TCAA
4. CONCLUSION

The present study shows that
1. Aluminium and mild steel both metal corrode in organic acid like TCAA.
2. Aluminium is more prone to corrosion than mild steel in TCAA in same condition.
3. Synthesized ligand is effective corrosion inhibitor for both metals in TCAA.
4. Both synthesized ligand have almost same corrosion inhibition efficiency for both the metal.
5. However Cl$_i$ is better corrosion inhibitor than Cl$_2$.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Upadhyay RK, Mathur SP. Effect of Schiff’s bases as corrosion inhibitors on mild steel in sulphuric acid. E-Journal of Chemistry. 2007;4:408-414.
2. Upadhyay RK, Anthony S, Mathur SP. Efficiency of some newly synthesized Mannich bases as corrosion inhibitor for mild steel in HNO$_3$ solution. Russian Journal of Electrochemistry. 2007;2:252-256.
3. Landolt D. Corrosion and surface chemistry of metals. E P E L Press, Lausane; 2007.
4. Introduction on to corrosion and corrosion inhibitors, Chapter 1.
5. Upadhyay RK, Mathur SP. Inhibitive effect of Schiff’s bases as corrosion inhibitor for mild steel in acid media. J. Electrochem. Soc. Ind. 2006:2:55.
6. Sharma P, Upadhyay RK, Chaturvedi A. A comparative study of corrosion inhibitive efficiency of some newly synthesize Mannich bases with their parent amine for Al in HCl solution. Res. J. Chem. Sci. 2011;1(5).
7. Keera ST, Farid NA, Mohamed KZ. Imidazoline derivatives as corrosion inhibitors of carbon steel in crude oils and associated water. Energy Sources, Part A. 2012;34:137.
8. Ashassi-Sorkhabi H, Shabani B, Alighalipour B, Seifzadeh D. The effect of some schiff bases on the corrosion of aluminium in HCl solution. Applied Surface Science. 2006;252(12):4039-4047.
9. Zhang DQ, Gao LX, Zhou GD. Polyamine compound as a volatile corrosion inhibitor for atmospheric corrosion of mild steel. Material and Corrosion. 2007;58:594-598.
10. Yildirim A, Oztürk S, Cetin M. Long chain Alkylthiabenimidazoles as corrosion inhibitors for carbon steel in H$_2$SO$_4$ solutions. Phosphorus, Sulfur and Silicon Relat. Elem. 2013;188:855.
11. Fontana MG. Corrosion Engineering, 3rd Ed. McGraw-Hill Book Com. New York; 1987.
12. Mahor DK, Upadhyay RK, Chaturvedi A. A study of corrosion inhibition efficiency of some Schiff’s bases on aluminium in trichloroacetic acid solution. Rev. Room. Chim. 2010;55:227.
13. Kumar Mahor Devender, Kumar Upadhyay Rajesh, Chaturvedi Alok. Study of corrosion inhibition efficiency of some schiff’s bases on aluminium in trichloroacetic acid solution. Revue Roumaine de Chimie. 2012:1-7.
14. Al-Otaibi MS, Al-Mayouf AM, Khan M, Mousa AA, Al-Mazroae SA, Alkhathlan HZ. Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media. Arabian Journal of Chemistry. 2012:1-7.
15. Anderson FE, Duca CJ, Scudi JV. Some heterocyclic thiosemicarbazones. J. Am. Chem. Soc. 1951;73:4967.
16. Eddy NO, Odiongenyi AO. Corrosion inhibition and adsorption properties of ethanol extract of Heinsia crinata on mild steel in H$_2$SO$_4$. Pigment & Resin Technology. 2010;39(5):288–295.
17. Sethi T, Chaturvedi A, Upadhyay RK, Mathur SP. Corrosion inhibitory effects of some Schiff's bases on mild steel in acidic media. J. Chil. Chem. Soc. 2007:3:52.
18. Ailor WH. Handbook on corrosion testing and evaluation. N. Y. London: John and Sons, Inc. 1971;174.
19. Obot IB, Obi-Egbedi NO, Umoren SA. Antifungal drugs as corrosion inhibitor for aluminium in 0.1 M HCl. Corrosion Science. 2009;51:1868-1875.
20. Yıldırım A, Çetin M. Synthesis and evaluation of new long alkyl side chain acer-amide, isoaxazolidine and isoaxazoline derivatives as corrosion inhibitors. Corrosion Science. 2008;50:155-165.
21. Gentle V. Corrosão, 4a Ed. Rio de Janeiro: LTC; 2003.
22. Ailor WH. Handbook on corrosion testing and evaluation. N.Y.; London: John Wiley and Sons, Inc. 1971;174.
23. Talati JD, Gandhi DK. Derivatives to control corrosion of Al alloys in O<sub>3</sub> phosphoric acid. J. Electrochem. Soc. 1993;42(4):239.

24. Upadhyay D, Panchal MA, Dubey RS, Srivastava VK. Corrosion of alloys used in industry: A review. Materials Science Engineering. 2006;432:1-11.

© 2020 Saini and Upadhyay; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sdiarticle4.com/review-history/58926