

# INHIBITION OF METALLIC CORROSION BY SOME ORGANIC COMPOUNDS CONTAINING HETEROATOMS



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**Doctor of Philosophy**

By

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## CHAPTER-4 SUMMARY

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### 4.1 Summary

Hydrochloric acid solutions are used in industries for acid cleaning and pickling process to remove the unwanted scale and salt deposits on MS surface. MS is susceptible to corrosion in acidic medium. To avoid the aggressive attack of acid, inhibitors are incorporated along with the acid solution. Among various types of organic corrosion inhibitors, heterocyclic compounds (S, N, and O) exemplify as an attractive class of corrosion inhibitors because they are readily adsorbed on the metal surface through the lone pair of electrons and  $\pi$  electrons present in these molecules.

The present thesis is constructed to investigate the corrosion inhibition performance of four classes of heterocyclic compounds namely Nicotinonitriles, Naphthyridines, Quinolines and Thiopyrimidines for MS in 1 M HCl. The thesis contains four chapters. The first chapter presents a general introduction about corrosion and its economic impact, basic concept and theories of corrosion to understand the mechanism of corrosion. The main emphasis is given to corrosion inhibitors and their mode of action towards corrosion control. A literature survey on corrosion inhibitors for MS in acid solutions has been given in this chapter. The aims and objectives of the study have also been mentioned.

The synthetic procedure of corrosion inhibitors and various experimental techniques for the corrosion inhibition testing such as weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) are discussed in chapter second. The surface analysis techniques and computational simulations have also been discussed in this chapter.

The discussions of obtained results from these studies have been given in third chapter. The fourth and last chapter is summary and conclusions.

The nicotinonitriles based inhibitors namely, 2-amino-6-phenyl-4-(p-tolyl) nicotinonitriles (ATN) and 2-amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile (AMN) show good corrosion inhibition performance for MS in 1 M HCl. The corrosion inhibition efficiency ( $\eta\%$ ) increases from 80-97% on increasing the concentration of ATN and AMN from 0.08-0.33 mM. The maximum inhibition efficiency 97.14% was obtained for AMN and 95.23% for ATN at 0.33 mM, after 3 h immersion period and 308 K temperature. Both the inhibitors efficiently inhibit corrosion via adsorption on the MS surface and are found to obey the Langmuir adsorption isotherm. On increasing the temperature the corrosion inhibition efficiency decreases. The obtained free energy of adsorption,  $\Delta G_{\text{ads}}$  ranges between -38.45 to -39.54 kJ mol<sup>-1</sup> for AMN and ATN, which suggests both physical as well as chemical adsorption but predominantly chemisorption.

EIS analysis reveals an increase in the charge transfer resistance ( $R_{\text{ct}}$ ) along with the decrease in double layer capacitance ( $C_{\text{dl}}$ ), due to the adsorption of inhibitors molecules on the metal surface. The potentiodynamic polarization data reveals that the addition of ATN and AMN decreases the corrosion current density,  $i_{\text{corr}}$  and causes shift in the corrosion potential towards more negative direction with respect to blank acid solution. Both ATN and AMN act as cathodic type of inhibitors.

The surface micrographs obtained by SEM/AFM analysis showed that the inhibitor treated MS surfaces are smooth and protected from acid attack. Both the surface analysis methods support the corrosion inhibition for MS in presence of ATN and AMN.

The experimental trend obtained was well supported by the theoretical computational simulation methods. The obtained  $E_{\text{HOMO}}$  values by the quantum chemical study for both the ATN and AMN in neutral and protonated forms, in the gas phase are in the order: AMN > ATN and the obtained global electronegativity,  $\chi$  values are in the following order: ATN > AMN, which is in good agreement with the order of the experimental corrosion inhibition efficiencies. The observed trend is due to electron-donating tendency of the attached groups  $-\text{OCH}_3$  (in AMN) >  $-\text{CH}_3$  (in ATN) in the studied compounds. The higher negative adsorption energy suggests the stronger interaction between a metal and an inhibitor molecule. The adsorption energy obtained by Monte Carlo simulation shows the following order AMN > ATN which very well supports to the experimental trend.

The three tested naphthyridine derivatives namely, 5-amino-9-hydroxy-2-phenylchromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (N-1), 5-amino-9-hydroxy-2-(p-tolyl)chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (N-2), and 5-amino-9-hydroxy-2-(4-methoxyphenyl)chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (N-3) give excellent corrosion inhibition performance for MS in 1 M HCl. All the three naphthyridines show high inhibition performance; N-1(94.28%), N-2 (96.66%), N-3 (98.09%) at  $6.54 \times 10^{-5}$  M after 3 h at 308 K. The difference in inhibition efficiency is attributed to substituent groups  $-\text{OCH}_3$ ,  $-\text{CH}_3$  and  $-\text{H}$ , attached to the para position of the phenyl ring of N-1, N-2, and N-3. The N-3, N-2 show higher inhibition efficiency than N-1 due to presence of addition electron releasing groups  $-\text{OCH}_3$  and  $-\text{CH}_3$  attached to the benzene ring whereas N-1 is devoid of any substituent. The corrosion inhibition efficiency for N-1, N-2, and N-3 decreased with an increase in temperature from 308-338 K. This can be attributed to desorption of the adsorbed inhibitor molecules from the surface of MS. To study the interaction between the inhibitor molecules and MS surface

various adsorption isotherms were used to fit to the observed experimental results and among them Langmuir adsorption isotherm was the best fitted isotherm. The obtained  $\Delta G_{\text{ads}}$  for N-1, N-2, and N-3, ranges from -42 to -43 kJ mol<sup>-1</sup> at 308-338 K suggests mixed mode of adsorption but predominant chemisorption.

The EIS analysis reveals an increase in  $R_{\text{ct}}$  and  $\eta\%$  whereas a decrease in  $C_{\text{dl}}$  on addition of N-1, N-2, and N-3 in 1 M HCl solution as compared to blank acid solution. The Potentiodynamic polarization study showed that all the three naphthyridines performed as mixed-type inhibitors but predominantly mode is of cathodic type.

Surface morphology examined by SEM/ AFM analysis showed a smoother MS surface in presence of naphthyridines as compared to blank acidic solution confirming corrosion inhibition.

The obtained trend of  $E_{\text{HOMO}}$ ,  $\chi$  and  $\Delta N$ , for the naphthyridines by quantum chemical study are in good agreement with the order of observed corrosion inhibition efficiency. The  $E_{\text{HOMO}}$  and  $\Delta N$  obtained for the studied compounds are in the order: N-3 > N-2 > N-1 and  $\chi$  are in this order N-3 < N-2 < N-1. The higher inhibition efficiency of N-3, N-2 is due to electron-donating effect of -OCH<sub>3</sub> and -CH<sub>3</sub> substituents respectively, than N-1 which is devoid of any substituent. The adsorption energies obtained from Monte Carlo simulations also agree with the trend of the experimental inhibition efficiency.

The four quinoline derivatives such as 2-amino-7-hydroxy-4-phenyl-1,4-dihydroquinoline-3-carbonitrile (Q-1), 2-amino-7-hydroxy-4-(p-tolyl)-1,4-dihydroquinoline-3-carbonitrile (Q-2), 2-amino-7-hydroxy-4-(4-methoxyphenyl)-1,4-dihydroquinoline-3 carbonitrile (Q-3), 2-amino-4-(4-(dimethylamino)phenyl)-7-hydroxy-1,4-dihydroquinoline-3-carbonitrile (Q-4) showed good corrosion inhibition

action for MS in 1 M HCl. It is observed that in presence of quinolines, the corrosion inhibition efficiency increases (80.95 to 98.09 %) with increasing concentration (50-150 mg/l) after 3 h of immersion at 308 K. The difference in inhibition efficiency is attributed to the presence of substituent group attached to the para position of the phenyl ring of Q-1, Q-2, Q-3 and Q-4 (-H, -CH<sub>3</sub>, -OCH<sub>3</sub>, -N(CH<sub>3</sub>)<sub>2</sub>). The rise in temperature showed decrease in inhibition efficiency due to desorption of inhibitor molecules from MS surface. The quinolines adsorption on the MS surface was found to follow the Langmuir adsorption isotherm. The obtained  $\Delta G_{\text{ads}}$  values range from 39.7 to -35.8 kJ mol<sup>-1</sup> suggesting both physical and chemical modes of adsorption but predominantly chemisorption. The activation energy ( $E_a$ ) is higher for inhibited solution than uninhibited one which suggests creation of energy barrier thereby giving strong inhibition action of additives.

The EIS measurements revealed increase in  $R_{\text{ct}}$  and  $\eta\%$ , and decrease in  $C_{\text{dl}}$ , this is attributed to the adsorption of inhibitor molecules on the MS surface. Potentiodynamic polarization showed a decrease in,  $i_{\text{corr}}$  values in presence of quinolines as compared to blank which suggests corrosion inhibition. Among the four quinolines Q-1, Q-2, Q-3 act as a mixed-type inhibitors while Q-4 acts as a cathodic type inhibitor.

The SEM and AFM micrographs for MS surface in presence of quinolines shows protected surface as compared to blank acid solution, this is attributed to the adsorption of inhibitor molecules on MS surface. The results obtained by XPS analysis further supports the adsorption of quinolines on MS surface.

The four thiopyrimidines derivatives viz 5-cyano-6-phenyl-2-thioxo-2,3-dihydropyrimidin-4-one (TP-1), 5-cyano-2-thioxo-6-(p-tolyl)-2,3 dihydropyrimidin-4-one (TP-2), 5-cyano-6-(4-methoxyphenyl)-2-thioxo-2,3-dihydropyrimidin-4-one (TP-

3), 6-(4-(dimethylamino)phenyl)-5-cyano-2-thioxo-2,3-dihydropyrimidin-4-one (TP-4) performed well as corrosion inhibitors for MS in 1 M HCl. These thiopyrimidine derivatives offered maximum inhibition efficiency of 90 % (TP-1), 94.28 % (TP-2) 95.47 % (TP-3) and 97.61 % for (TP-4) at  $200 \text{ mgL}^{-1}$ , after 3h of immersion time and 308 K temperature. The difference among the four inhibitors in inhibition efficiency is attributed to substituent groups attached to the para position of the phenyl ring of TP-1, TP-2, TP-3 and TP-4 (-H, -CH<sub>3</sub>, -OCH<sub>3</sub>, -N(CH<sub>3</sub>)<sub>2</sub>). The inhibition efficiency increases with increasing concentration and decreases upon increasing temperature due to desorption of inhibitor molecules from MS surface. All the studied four TPs inhibit the MS corrosion via adsorption and Langmuir adsorption isotherm is found to be the best fitted isotherm. The values of  $\Delta G_{\text{ads}}$  obtained ranges from -34 to -37 kJ mol<sup>-1</sup>, suggest both physisorption and chemisorption but chemical mode is dominant. The higher values of  $E_a$  in presence of TPs as compared in their absence reveal that a higher barrier is created for corrosion process

The results obtained by EIS study reveal that all four TPs adsorbed on the metal surface by adsorption mechanism cause increase in  $R_{\text{ct}}$  and  $\eta\%$ , and decrease in  $C_{\text{dl}}$ . The potentiodynamic polarization observation shows decrease in  $i_{\text{corr}}$  in presence of thiopyrimidines indicates corrosion inhibition and the entire four thiopyrimidine derivative behave as mixed type inhibitors with predominant control on cathodic reaction.

The SEM and AFM images show smooth surfaces of MS in presence of thiopyrimidines as compared to blank confirmed corrosion inhibition. The XPS analyses result confirms the adsorption of the inhibitor on the MS. The obtained corrosion inhibition trend from experimental results follows the order TP-4>TP-3>TP-2>TP-1 and was very well supported by Quantum chemical study.

## 4.2 Conclusions

The following conclusions have been drawn from the work embodied in the present thesis:

(i) All the thirteen synthesized heterocyclic compounds exhibited excellent inhibition efficiency ( $> 90\%$ ). The Best inhibitor, Naphthyridines (N-3) exhibited a maximum efficiency of 98% at a concentration as low as  $25 \text{ mg l}^{-1}$  concentration.

(ii) The inhibition efficiency of all the studied heterocycles was found to depend upon the molecular structure of the inhibitors containing electron donating substituents ( $-\text{CH}_3, -\text{OCH}_3, -\text{N}(\text{CH}_3)_2$ ) and showed better inhibition performance than those which are devoid of any substituent.

(iii) The free energy of adsorption  $\Delta G$  for all inhibitors ranges from 34- to  $-43 \text{ kJ mol}^{-1}$  indicating the of their mixed mode of adsorption, physical as well as chemical but predominant as chemisorption.

(iv) Electrochemical impedance spectroscopic study revealed that all the tested heterocyclic compounds inhibit metallic corrosion by adsorbing at metal/ electrolyte interfaces and thereby enhancing the surface resistance.

(v) Potentiodynamic polarization study showed that all the tested heterocyclic compounds acted as mixed type inhibitors but predominantly behaved as cathodic inhibitors.

(vi) All the thirteen tested heterocyclic compounds inhibit the corrosion by getting adsorbed on the mild steel surface. The adsorption of these inhibitors obeyed the Langmuir isotherm.

(vii) The Adsorption of inhibitor molecules on the mild steel surface was corroborated using atomic force microscopy (AFM) scanning electron microscopy (SEM) analyses.

(viii) Experimental results were supported by DFT based quantum chemical calculations and molecular dynamics simulations. Both experimental and theoretical results showed good agreement.

## 4.3 Scope for future work

The organic compounds used in the present thesis work showed good inhibition performance for MS in hydrochloric acid solution, so these compounds can also be tried for other metals like copper, aluminum in different acidic environments.