
CHAPTER 4

SUMMARY AND CONCLUSION

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4.1. Summary

Metals and alloys undergo chemical and/or electrochemical reactions with the environment to form relatively more stable compounds and consequently there is loss of metals takes place due to the corrosion which adversely affects both the cost and productivity of the industries. Among different available methods, the use of synthetic corrosion inhibitors is one of the most appropriate, effective and economic ways of mitigating corrosion.

The purpose of present study mainly aimed at the investigation of corrosion inhibition behaviour of organic compounds mainly Pyrano-pyrazole derivatives, Schiff base derived from 2, 6 diaminopyridine derivatives, Imidazole derivatives, and Pyrazolo-pyridine derivatives respectively, which containing heteroatoms (nitrogen and oxygen). The corrosion inhibition property of these heterocyclic compounds was evaluated using gravimetric measurements, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), scanning electron microscopy (SEM), atomic force microscopy (AFM), quantum chemical calculations and molecular dynamics techniques. The twelve heterocyclic inhibitors used in the present investigation have been discussed in four sections. The inhibitors in each section are given bellows:

Pyrano-pyrazole derivatives (EPPs);

- (i) Ethyl 6-amino-3-methyl-4-(*p*-tolyl) 2,4-dihydropyrano [2,3,C] pyrazole-5-carboxylate (EPP-1)
- (ii) Ethyl 6-amino-3-methyl-4(phenyl)-2,4dihydropyrano [2,3,C] pyrazole-5- carboxylate (EPP-2)

(iii) Ethyl 6-amino-3-methyl-4-(3-nitrophenyl) 2,4-dihydropyrano [2,3,C] pyrazole-5-carboxylate (EPP-3)

Showed good inhibition efficiency for mild steel corrosion in 1M HCl solution. The inhibition efficiency orders for EPPs series are (EPP-1, 98.57%), (EPP-2, 96.19%) and (EPP-3, 91.90%) respectively at 100mgL^{-1} 3h exposure period and 308 K. The inhibition efficiency of EPPs decreased with increasing the temperature and increased with increasing concentration of inhibitors. The action of EPPs inhibition towards corrosion was by adsorption over the metal surface and they follow Langmuir adsorption isotherm. The free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$) values were found to be -39.16, -37.19 and -34.57 kJ mol^{-1} for EPP-1, EPP-2 and EPP-3 respectively at 308 K. These values of $\Delta G^{\circ}_{\text{ads}}$ indicate that the adsorptions of EPPs are both physisorptions and chemisorptions (mixed adsorption). The values of apparent activation energy (E_a) in presence of EPPs are higher than in their absence, which indicates that dissolution of mild steel was decreased due to formation of a barrier by the adsorption of the EPPs on metal surface.

In EIS measurement studies the polarization resistance values were increased and the values of double layer capacitance decreased in presence of EPPs, which indicates the adsorption of EPPs at the surface of mild steel. Potentiodynamic polarization reveals that corrosion current density was decreased in presence of EPPs and the values of E_{corr} shifts towards more negative direction with respect to blank. These EPPs are mixed type inhibitors but dominantly cathodic. SEM and AFM studies showed the adsorption of EPPs molecules on the mild steel surface. The quantum chemical results of EPPs are well correlated with the experimental results obtained by gravimetric measurement and electrochemical methods. The values of energy gap (ΔE) are lowest in case of EPP-1 both in neutral and protonated forms

and thus it is the best inhibitor among the series. From the Monte Carlo simulation study, The values of the binding energies (E_{binding}) in both vacuum and aqueous phase are as follows: EPP-1 > EPP-2 > EPP-3, which are in accordance with the order of their inhibition efficiencies obtained by experiment methods.

Schiff bases derived from 2, 6 diamino-pyridine (DAPs)

- (i) N2, N6- bis(4-methylbenzylidene)pyridine-2,6-diamine (DAP-1),
- (ii) N2, N6-dibenzylidenepyridine- 2,6-diamine (DAP-2),
- (iii) N2, N6- bis(4-nitrobenzylidene)pyridine-2,6-diamine (DAP-3)

are good corrosion inhibitors for mild steel in 1M HCl and showed maximum inhibition efficiency of 98.5% , 95.7% and 91.9 for DAP-1, DAP-2 and DAP-3 respectively, at 40 mgL⁻¹ when exposed for 3h at 308 K. The inhibition efficiency of the inhibitors decreased as the temperature increased due to desorption of adsorbed inhibitors at higher temperature and increased with the increase in concentration. The inhibitors obeyed the Langmuir adsorption isotherm. The obtained values of $\Delta G^{\circ}_{\text{ads}}$ for DAP-1, DAP-2 and DAP-3 were 40.16, 39.19 and 38.67 kJ mol⁻¹ respectively at 308K, suggesting mixed adsorption (physiosorptions as well as chemisorptions) of inhibitor molecules at the surface of mild steel. The apparent activation energy (E_a) for the inhibited solutions were higher than that for the uninhibited solution, indicating the retardation in corrosion rate due to adsorption of the inhibitors at the surface of mild steel. The result of EIS indicated that the values of C_{dl} decreased whereas values of R_p and $\eta\%$ increased as the inhibitors were added, due to increase in the thickness of the electrical double layer and adsorption of inhibitor molecules on the surface of mild steel. The potentiodynamic study suggested that the displacement in E_{corr} is towards cathodic direction, which indicates that DAPs are mixed type inhibitors favoring the cathodic

side. Bode and phase plots contain only single maxima at intermediate frequency. SEM and AFM images revealed the formation of inhibitor film on the mild steel surface.

Quantum chemical study well supports the results obtained experimentally in the studied inhibitors. The value of ΔE is lower in case DAP-1, both in neutral and protonated forms. The protonated species are more likely to adsorb over the mild steel surface than neutral species. The result obtains from the Monte Carlo Simulation methods showed the order DAP-1 > DAP-2 > DAP-3 which is according to the experimental results.

(c) Imidazole derivatives (IMs);

(i) 2-(3-methoxyphenyl)-4,5-diphenyl-1H-imidazole (IM-1)

(ii) 2,4,5-triphenyl-1H-imidazole (IM-2)

(iii) 2-(3-nitrophenyl)-4,5-diphenyl-1H-imidazole (IM-3)

offered substantial inhibition efficiencies for mild steel corrosion in 1M HCl solution. The inhibitors IM-1, IM-2 and IM-3 impart maximum inhibition efficiency of 98.5 % and 96.6% and 94.7% respectively, at 100 mgL⁻¹ concentration, 3 h exposure period and at 308 K. The Inhibition efficiency offered by IMs was increased on increasing their concentration indicated that adsorption of inhibitors increased as concentration increased resulting in reduction of corrosion rate. The inhibition efficiency of the inhibitors (IMs) decreased with increasing temperature due shift of the equilibrium constant towards desorption of the inhibitors molecules. The adsorption of IMs followed Langmuir adsorption isotherm. The values of free energy of adsorption were found to be -41.84, -39.74 and -38.51 kJ mol⁻¹ for IM-1, IM-2 and IM-3 respectively, suggested physical as well as chemical adsorption of IMs molecules at the surface of mild steel. The values of E_a were found to be higher in presence of IMs than in their absence, indicating that the dissolution of mild steel was decreased due

to formation of a barrier by the adsorption of the IMs on mild steel surface. The result of EIS showed that the values of R_p increased and the values of C_{dl} decreased when IMs were added, suggesting the adsorption of these inhibitors on the surface of mild steel. In polarization studies both tested inhibitors are mixed type inhibitor but predominantly cathodic type because they shift the values of corrosion potential (E_{corr}) towards more negative direction with respect to blank. Both SEM and AFM analysis affirmed the adsorption of IMs molecules over the surface of mild steel. Quantum chemical calculations showed that the ΔE value for IM-1 is lower than IM-2 and IM-3, indicating that IM-1 adsorbed on the mild steel surface more strongly than IM-2 and IM-3 and thus resulting its greater inhibition tendency. The MD simulation follows the order; IM-1 > IM-2 > IM-3, which is according to the experimental results.

Pyrazolopyridine derivatives (PPs);

- (i) (4-(4-methoxyphenyl)-3,5-dimethyl-1,4,7,8-tetrahydrodipyrzoloypyridine) (PP-1)
- (ii) 3,5-dimethyl-4-phenyl-1,4,7,8-tetrahydrodipyrzoloypyridine (PP-2)
- (iii) (3,5-dimethyl-4-(3-nitrophenyl)-1,4,7,8-tetrahydrodipyrzoloypyridine) (PP-3)

offered good inhibition efficiencies for mild steel corrosion in 1M HCl solution. These Pyrazolopyridine derivatives offered maximum inhibition efficiency of 98.5 % (PP-1), 97.26 % (PP-2) and 93.80% (PP-3) respectively at 100 mgL⁻¹ concentration, 3h exposure period and at 308 K. The inhibition efficiency of Pyrazolopyridine (PPs) increased with increasing concentration of inhibitors. All the three Pyrazolopyridine derivatives inhibit corrosion by adsorption on the mild steel surface and follow Langmuir adsorption isotherm. The calculated ΔG°_{ads} were -36.26 kJ mol⁻¹ (P1), -35.38 kJ mol⁻¹ (P2), and -34.57 (P3) kJ mol⁻¹, which probably means that both physical adsorption and chemical adsorption

(comprehensive adsorption) would take place. In EIS studies R_p values increased while C_{dl} values decreased in presence of inhibitors, due to the adsorption of inhibitors molecules on the metal surface. The potentiodynamic polarization data reveals that the addition of PPs decreases the corrosion current density, i_{corr} and causes shift in the corrosion potential towards more negative direction with respect to blank acid solution. The shifts in corrosion potential (E_{corr}) values in presence of inhibitors is towards positive or anodic potential direction as compared to the E_{corr} value in absence of inhibitors indicating that PP-1, PP-2 and PP-3 act as mixed type inhibitor but dominantly acting as anodic type. 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 PPs. Quantum chemical calculations showed that the ΔE value for PP-1 is lower than PP-2 and PP-3, indicating that PP-1 adsorbed on the MS surface more strongly than PP-2 and PP-3 and thus resulting its greater inhibition tendency. Molecular dynamic simulations revealed the greater adsorption of PP-1 as compared to PP-2 and PP-3.

4.2. Conclusion

The studied four series of heterocyclic compounds viz: Pyrano-pyrazoles, Schiff base derived from 2, 6 diaminopyridine, Imidazoles and Pyrazolo-pyridine derivatives performed as excellent corrosion inhibitors for MS in 1M HCl at relatively lower concentration. All the three techniques such as: weight loss, electrochemical impedance spectroscopy and potentiodynamic polarization were studied to investigate the corrosion inhibition behaviour of selected heterocyclic compounds. The inhibition efficiency increases in presence of inhibitors due to extent of adsorption of inhibitor molecules on metal surface and follows the

Langmuir adsorption isotherm. All the investigated inhibitors follow both the type of adsorption process i.e. physisorptions and chemisorptions but chemical is more dominant. The increase in the polarization resistance and decrease in the C_{dl} values on increasing the inhibitor concentration suggests that these inhibitor molecules acted by the adsorption mechanism and follows order: DAPs> EPPs> PPs> IMs. Potentiodynamic polarization study suggests that all the studied inhibitor molecules behave as mixed type inhibitors, predominantly cathodic in nature. The results for the all the studied series is DAPs> EPPs> PPs> IMs. The surface analysis (SEM/AFM) showed that MS surface was protected in presence of inhibitors as compared to blank acid solution. The quantum chemical calculations, using the DFT method on the studied inhibitors was carried out to elucidate their reactivity and selectivity. The Fukui functions suggest the electrophilic and nucleophilic centres in the inhibitor molecules. From the DFT calculation results the lowest energy difference was obtained for the above series is as follows; IMs> DAPs> EPPs> PPs. The values of adsorption energy ($E_{adsorption}$) energies were calculated from molecular dynamics simulations method. A higher value of ($E_{adsorption}$) energies suggests strong interaction between metal and inhibitors. the order for among all the series is as follows; DAPs> IMs> EPPs> PPs.

4.3. Scope for future work

1. The organic compounds used in the present thesis work showed good inhibition performance for MS in hydrochloric acid solution so these compounds may be tried for other metal in acid solution and for coating purpose.
2. The corrosion measurements may be tried with various inhibitors above 65°C.

3. The combination of inhibitors may be tried for the studied metals as well as other metal or alloys in other acid medium.
4. The surface study may be done by using XPS, SECM, and SVET etc. for confirming type of corrosion product.

REFERENCES
