Electrochemical and Quantum Chemical Investigations of Carbon Steel Corrosion Inhibition by Organic Compounds

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by

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CHAPTER-4

SUMMARY AND CONCLUSION

4.1. Summary

The purpose of present study mainly aimed at the investigation of corrosion inhibition behavior of organic compounds which are containing heteroatoms (nitrogen, sulphur and oxygen) on mild, N80 and J55 steel in different acid environment like 20% H_2SO_4, 15% HCl and 3.5% NaCl saturated with CO_2 respectively. The organic compounds used are Napthyridine, Pyridine, Isatin, Porphyrin derivatives respectively.

The synthesized Napthyridine derivatives namely 2-amino-4-(4-methoxyphenyl)-1,8-naphthyridine-3-carbonitrile (ANC-1), 2-amino-4-(4-methylphenyl)-1,8-naphthyridine-3-carbonitrile (ANC-2) and 2-amino-4-(3-nitrophenyl)-1,8-naphthyridine-3-carbonitrile (ANC-3) are good corrosion inhibitors for N80 steel in 15% HCl. They provide the maximum inhibition efficiency of 93.9% (ANC-1), 91.4% (ANC-2) and 85.0% (ANC-3) respectively, at 200 mgL^{-1} concentration, 6h exposure period and 308 K temperature. The inhibition efficiency of ANCs decreased with increasing the temperature and increased with increasing concentration of inhibitors. The action of ANCs inhibition towards corrosion was by adsorption over the metal surface and they follow Langmuir adsorption isotherm. The free energy of adsorption (ΔG°_{ads}) values were found to be 31.0, -29.76 and -28.98 kJ mol^{-1} for ANC-1, ANC-2 and ANC-3 respectively at 308 K. These values of $\Delta G°_{ads}$ indicate that the adsorptions of ANCs are both physisorption and chemisorption (mixed adsorption). The values of apparent activation energy (E_a) in presence of ANCs are higher than in their absence, which indicates that dissolution of N80 steel was decreased due to formation of a barrier by the adsorption of the ANCs on metal surface.

In EIS measurement studies the charge transfer resistance values were increased and the values of double layer capacitance decreased in presence of ANCs, which indicates the adsorption of ANCs at the surface of N80 steel. Potentiodynamic polarization reveals that corrosion current density was decreased in presence of ANCs and the values of E_{corr} shifts towards more negative direction with respect to blank. These ANCs are mixed type inhibitors but dominantly cathodic. SEM and EDX studies showed the adsorption of ANCs molecules on the N80 steel surface.

The quantum chemical results of ANCs are well correlated with the experimental results obtained by weight loss measurement and electrochemical methods. The values of energy gap (ΔE) are lowest in case of ANC-1 both in neutral and protonated forms and thus it is the best inhibitor among among the series.

The synthesized pyridine derivatives, 2-amino-6-(2,4-dihydroxyphenyl)-4-(4-methoxyphenyl) nicotinonitrile (ADP) and 2-amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile (AMP) are good corrosion inhibitors for N80 steel in 15% HCl and showed maximum inhibition efficiency of 90.58% and 86.76% for ADP and AMP respectively, at 200 mgL^{-1} when exposed for 6h at 308 K. The inhibition efficiency of both the inhibitors decreased as the temperature increased due to desorption of adsorbed inhibitors at higher temperature and increased with the increase in concentration. Both the inhibitors obeyed the Langmuir adsorption isotherm. The values of K_{ads} are large, which confirmed the strong adsorption of ADP and AMP on the N80 steel surface. The obtained values of $\Delta G°_{ads}$ for ADP and AMP were 30.60 and 29.88 kJ mol^{-1} respectively at 308K, suggesting mixed adsorption (physisorption as well as chemisorption) of inhibitor molecules at the surface of N80 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 N80 steel.

The result of EIS indicated that the values of C_{dl} decreased whereas values of R_{ct} and η% 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 N80 steel. The potentiodynamic study suggested that the displacement in E_{corr} is towards cathodic direction, which indicates that ADP and AMP are mixed type inhibitors favoring the cathodic side. Bode and phase plots contain only single maxima at intermediate frequency. SEM and SECM images revealed the formation of inhibitor film on the N80 steel surface.

Quantum chemical study well supports the results obtained experimentally in both the inhibitors. The value of ΔE is lower in case ADP, both in neutral and protonated forms. The protonated species are more likely to adsorb over the N80 steel surface than neutral species.

Two isatin derivatives namely 1-Benzylidene-5-(2-oxoindoline-3-ylidene) Thiocarbohydrazone (TZ-1) and 1-(4-Methylbenzylidene)-5-(2-oxoindolin-3-ylidene) Thiocarbohydrazone (TZ-2) offered substantial inhibition efficiencies for mild steel corrosion in 20% H_2SO_4. Both the inhibitors TZ-1 and TZ-2 impart maximum inhibition efficiency of 88.98 % and 99.72 %, respectively, at 300 mgL^{-1} concentration, 6 h exposure period and at 308 K. The Inhibition efficiency offered by TZs 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 both inhibitors (TZs) decreased with increasing temperature due shift of the equilibrium constant towards desorption of the inhibitors molecules. The maximum inhibition efficiency for TZ-1 and TZ-2 at the 338 K was 82.36 % and 85.47 % respectively for 6h exposed period.

The adsorption of TZs followed Langmuir adsorption isotherm. The values of free energy of adsorption were found to be -32.41 and -32.85 kJ mol^{-1} for TZ-1 and TZ-2 respectively, suggested physical as well as chemical adsorption of TZs molecules at the surface of mild steel. The values of E_a were found to be higher in presence of TZs than in their absence, indicating that the dissolution of mild steel was decreased due to formation of a barrier by the adsorption of the TZs on mild steel surface.

The result of EIS showed that the values of R_{ct} increased and the values of C_{dl} decreased when TZs 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 EDX analysis affirmed the adsorption of TZs molecules over the surface of mild steel.

Quantum chemical calculations showed that the ΔE value for TZ-2 is lower than TZ-1, indicating that TZ-2 adsorbed on the mild steel surface more strongly than TZ-1 and thus resulting its greater inhibition tendency.

Three porphyrin derivatives namely 5,10,15,20-Tetra (4-pyridyl) porphyrin (P1), 5,10,15,20-Tetraphenyl porphyrin (P2), 5,10,15,20-Tetrakis (4-hydroxyphenyl) porphyrin (P3) offered good inhibition efficiencies for J55 steel corrosion in 3.5 % NaCl saturated with CO_2. These porphyrin derivatives offered maximum inhibition efficiency of 92 % (P1), 82 % (P2) and 84 % (P3) respectively at 400 mgL^{-1} concentration, 3h exposure period and at 308 K. The inhibition efficiency of porphyrins increased with increasing concentration of inhibitors. All the three porphyrin derivatives inhibit corrosion by adsorption on the J55 steel surface and follow Langmuir adsorption isotherm. The calculated $\Delta G°_{ads}$ were -35.6 kJ mol^{-1} (P1), -34.5 kJ mol^{-1} (P2), and -34.2 (P3) kJ mol^{-1},

which probably means that both physical adsorption and chemical adsorption (comprehensive adsorption) would take place.

In EIS studies R_{ct} values increased while C_{dl} values decreased in presence of inhibitors, indicating the adsorption of inhibitors at the surface of J55 steel. There is only one phase maximum in Bode plot for the three inhibitors, indicating only one relaxation process, which would be the charge transfer process taking place at the metal-electrolyte interface. The results of potentiodynamic polarization studies revealed that as the inhibitors were added corrosion current density decreased and also 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 P1, P2 and P3 act as mixed type inhibitor but dominantly acting as anodic type. Contact Angle measurement results confirmed the formation of water repellant or hydrophobic layer on the J55 steel surface in presence of porphyrins. SECM microphotograph showed adsorption of inhibitors at the surface of J55 steel. Quantum chemical calculations showed that the ΔE value for P1 is lower than P2 and P3, indicating that P1 adsorbed on the J55 steel surface more strongly than P2 and P3 and thus resulting its greater inhibition tendency. Molecular dynamic simulations revealed the greater adsorption of P1 as compared to P2 and P3.

4.2. Conclusion

All the studied compounds were good corrosion inhibitors for respective metals and media at very low concentration. The inhibition efficiency results calculated by weight loss measurements, electrochemical impendence spectroscopy and potentiodynamic polarization methods were in good agreement. The corrosion rate of all inhibitors increased with temperature and decrease with concentration respectively. The studied inhibitors obey Langmuir adsorption isotherm. All the inhibitors followed mixed

type of adsorption i.e. physical as well as chemical. The entire inhibitors act as mixed type with predominant cathodic type except porphyrins which were anodic type. SEM, EDX and SECM studies showed the adsorption of inhibitor molecules on the metal surface. The experimental results for all the studied inhibitors were in good agreement with the quantum chemical results.

4.3. Scope for future work

1. These organic compounds were good corrosion inhibitors and therefore these compounds may be tried for other metal in acid solution.

2. In-situ analysis may be carried out in presence of these inhibitors.

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 corrosion measurements may be tried with various inhibitors above 65ºC.

5. The surface study may be done by using XPS etc. for confirming type of corrosion product.

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