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Eco – Friendly Corrosion Inhibitors for N80 Steel in Hydrochloric Acid

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Abstract

An important method of protecting metallic materials against deterioration due to corrosion is by the use of corrosion inhibitors. In the present investigation, corrosion inhibition study of two amino acid compounds, 2-amino-*N*-decyl-3-phenyl propionamide (Inh I) and 2-amino-*N*-decylacetamide (Inh II) have been performed for N80 steel in 15% HCl using weight loss, electrochemical polarization, AC impedance and SEM techniques. The inhibition efficiencies of the inhibitors follow the sequence, Inh I > Inh II. The results showed that inhibition efficiency of all inhibitors increased with increase in inhibitors concentration. Both inhibitors act as mixed inhibitors and obey the Langmuir adsorption isotherm. Corrosion inhibition mechanism take place through adsorption phenomenon.

Keywords: Amino acid compounds; N80 steel; 15% HCl ; Corrosion inhibition.

1. Introduction

Mild steel is one of the frequently used structural materials for storage tanks, reaction vessels, pipelines etc., in chemical and allied industries. During certain operations like cleaning, pickling, descaling or even transportation it may come in the contact with sulfuric acid and get severely corroded. Several organic compounds as inhibitors have been reported for mild steel corrosion in acidic environments [1-11]. Acidization of a petroleum oil well is one of the important stimulation techniques for enhancing oil production. It is commonly brought about by forcing a solution of 15% to 28% hydrochloric acid into the well to open up near bore channels in the formation and hence to increase the flow of oil. To reduce the aggressive attack of the acid on tubing and casing materials (N-80 steel), inhibitors are added to the acid solution during the acidifying process. The effective acidizing inhibitors that are usually found in commercial formulations are acetylenic alcohols, alkenyl phenones, aromatic aldehydes, nitrogen-containing heterocyclics, quaternary salts and condensation products of carbonyls and amines[12-17]. However, these inhibitors suffer from drawbacks , they are effective only at high concentrations and they are harmful to the environment due to their toxicity, so it is important to search for new nontoxic and effective organic corrosion inhibitors for N-80 steel – 15% hydrochloric acid system. In this regard, amino acid compounds have a promising alternative for the design of eco-friendly corrosion inhibitors which will satisfy the environmental requirements.

Thus, it was considered interesting to prepare amino acid compounds like 2-amino-*N*-decyl-3-phenyl propionamide (Inh I) and 2-amino-*N*-decylacetamide (Inh II) and to assess their inhibitive properties for oil-well tubular steel (N-80) in 15% hydrochloric acid.

2. Experimental Procedure

2.1. Materials

The working electrode and specimens for weight loss experiments were prepared from oil-well N-80 steel sheets having the following percentage composition:

C	Mn	Si	P	S	Cr	Fe
0.31	0.92	0.19	0.01	0.008	0.20	**Remainder**

2.2. Weight measurements

The specimens for the weight loss experiments were of the size 3cm x 3cm and those for electrochemical studies the size of the electrodes was 1cm x 1cm with a 4 cm long tag for electrochemical contact. Both sides of the specimens were exposed for both the techniques. The specimens were mechanically polished successively with 1/0, 2/0, 3/0 and 4/0 grade emery papers. After polishing with the paper of each grade, the surface was thoroughly washed with soap, running tap water, distilled water and finally was degreased with acetone. The samples were dried and stored in a vacuum dessicator before immersing in the test solution. For weight loss experiments 300 mL of 15% hydrochloric acid was taken in 500 mL glass beakers with lids. The inhibition efficiencies were evaluated after a pre-optimized time interval of 6 h using 20, 50, 100, 150 and 200 ppm of inhibitors. The specimens were removed from the electrolyte, washed thoroughly with distilled water, dried and weighed. The inhibition efficiencies were evaluated using the formula

$$\%\,\mathrm{IE} = \frac{w - w_i}{w} \times 100$$

where, w is weight loss in absence of inhibitor and w_i is weight loss in presence of inhibitor.

2.3. Electrochemical measurements

The electrochemical experiments were carried out in a three necked glass assembly containing 150 mL of the electrolyte with different concentrations of inhibitors (from 20 ppm to 200 ppm by weight) dissolved in it. The potentiodynamic polarization studies were carried out with N80 steel strips having an exposed area of $1\mathrm{cm}^2$. A conventional three electrode cell consisting of N80 steel as working electrode, Platinum as counter electrode and a saturated calomel electrode as reference electrode was used. Polarisation studies were carried out using VoltaLab 10 electrochemical analyser and data was analysed using Voltamaster 4.0 software. The potential sweep rate was 10 mVs^{-1}. All experiments were performed at 25 ± 0.2°C in an electronically controlled air thermostat. For calculating %IE by electrochemical polarization method we use the formula-

$$\%\ \mathrm{IE} = \frac{I_0 - I_{inh}}{I_0} \times 100$$

Where, I_0 = Corrosion current in absence of inhibitor

I_{inh} = Corrosion current in presence of inhibitor

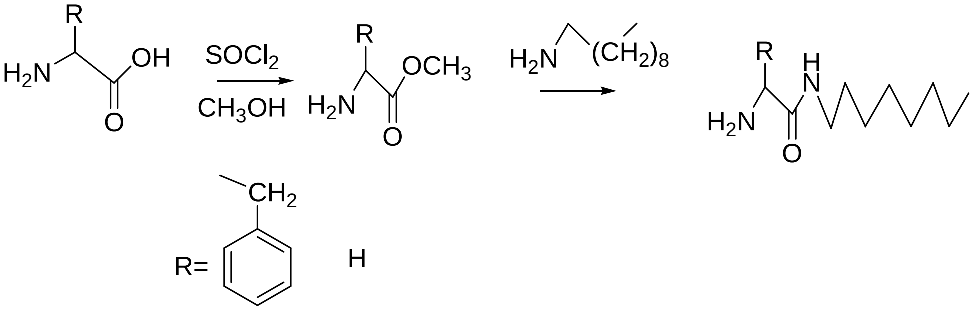
- AC-impedance studies were carried out in a three electrode cell assembly using computer controlled VoltaLab 10 electrochemical analyser, using N80 steel as the working electrode, platinum as counter electrode and saturated calomel as reference electrode.The data were analysed using Voltamaster 4.0 software. The electrochemical impedance spectra (EIS) were aquared in the frequency range 10 kHz to 1mHz at the rest potential by applying 5mV sine wave AC voltage. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were determined from Nyquist plots. The inhibition efficiencies were calculated from charge transfer resistance values by using the following formula:

$$\%\,\mathrm{IE} = \frac{R_{ct(Inh)} - R_{ct}}{R_{ct(Inh)}} \times 100$$

Where R_{ct} = charge transfer resistance in absence of inhibitor; $R_{ct(Inh)}$ = charge transfer resistance in presence of inhibitor

2.4. Synthesis of inhibitors

The inhibitors were synthesized in the laboratory by amidation of methyl esters of amino acids with alkyl amine without solvents [18].

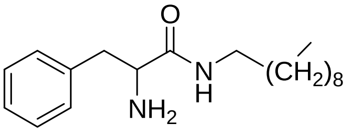


3. Results and Discussion

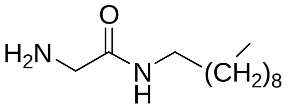
3.1. Weight loss study

The percentage inhibition efficiencies (% IEs) of 20, 50, 100, 150 and 200 ppm Inh I and Inh II have been evaluated by weight loss technique at 25^{0}C and the results are summarized in Table 1.

It is evident from these values that both the inhibitors are significantly effective even at low concentrations like 10 ppm and there is a linear increase in %IE in the whole range of concentrations studied. The structure of the inhibitors are given below :



Inh-1



Inh-2

Table 1: Percentage inhibition efficiency (% IE) values calculated by weight loss technique for Inh I and Inh II at 25^{o}C

Concentration	Inh I (%IE)	Inh II (%IE)
0	-	-
20	63.12	55.00
50	70.68	64.09
100	81.45	72.96
150	85.12	80.91
200	89.36	83.00

On the basis of observed IE values the inhibitors follow the order :

Inh I > Inh II

The above order may be explained well considering adsorption of the inhibitor molecules on the metal surface through the probable sites of adsorption, N, S, O and phenyl ring. The participation of phenyl ring during the adsorption of the inhibitor may be shown by higher IE values in case of Inh I.

3.2. Electrochemical studies

Electrochemical polarisation behaviour of Inh I and Inh II for N80 steel in 15% hydrochloric acid at 25^{o}C is shown in figure 1(a, b) and various parameters obtained are given in tables 2 and 3.

The curves in figure 1(a, b) illustrate that the nature of the curve remains almost same even after the addition of the inhibitors and also on increasing the concentration of the inhibitor. However, on increasing the concentration of the inhibitor the curves are gradually shifted towards lower current density. The corrosion potential also slightly shifted towards negative direction on increasing the concentration of the inhibitors.

It is realized from these observations that the inhibitors molecules retard the corrosion process without changing the mechanism of corrosion process in the medium of investigation. The magnitude of the shift in current density is directly proportional to the concentration of the inhibitors, indicating that the inhibitive property of the inhibitor is concentration dependent.

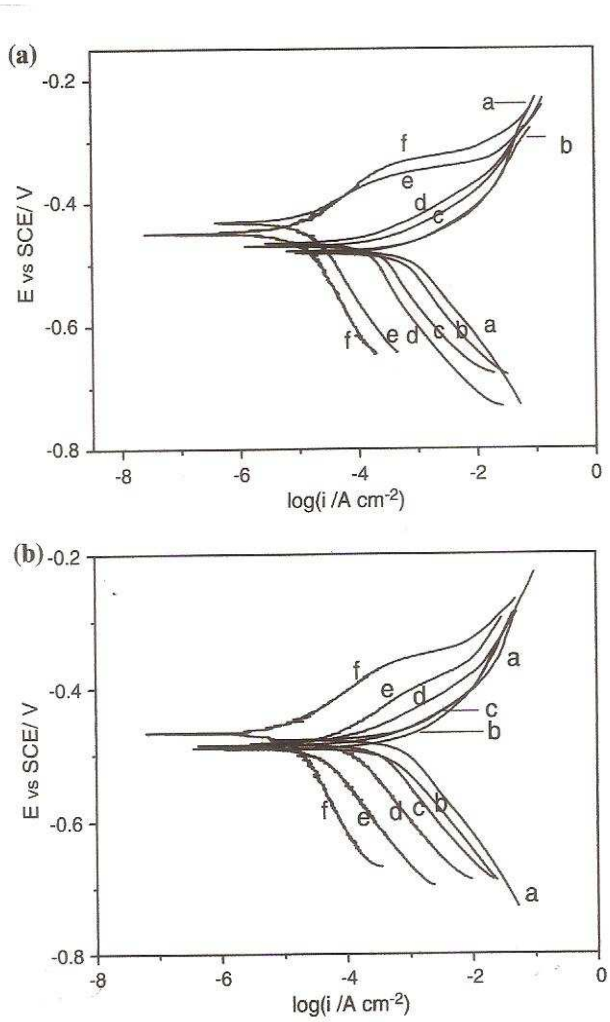


Figure 1: Electrochemical polarization curves for N80 steel in 15% hydrochloric acid with different concentrations of **(a)** InhI and **(b)** InhII : a,Blank, b 20 ppm , c 50 ppm , d 100 ppm e 150 ppm and f 200 ppm of inhibitors at 25^{o}C.

It is clear from the polarization curves of the inhibitors that the shift in current density towards lower current density for anodic as well as cathodic curve increases on increasing the concentration of the inhibitor.

The positive shift in the E_{corr} in presence of inhibitors on increasing the concentration of the inhibitors is due to the decrease in the rate of anodic reaction. Moreover, the increase in the cathodic and anodic Tafel slopes (β_c and β_a) is related to the decrease in both the cathodic and anodic currents. Both the inhibitors affect both, the anodic as well as cathodic sites, so these are mixed inhibitors.

To get further information concerning the inhibition process and to confirm the polarization experiments, electrochemical impedance spectroscopic investigations of N80 steel in absence and presence of inhibitors in 15% HCl solution were carried out. Electrochemical impedance is a powerful tool in the investigation of the corrosion and adsorption phenomenon. The impedance data of N80 steel, recorded in presence of 20,50, 100 and 150 ppm of the inhibitor Inh I in 15% HCl solution at 25^{o}C as Nyquist plots are shown in fig. 2. The Nyquist plots show depressed circular shape with their centres below the real axis. This behaviour is typical for solid metal electrodes that show frequency dispersion of the impedance data.

For a simple equivalent circuit consisting of parallel combination of a capacitor C_{dl}, and a charge transfer resister R_{ct}, in series with a solution resister R_s, the electrode impedance (Z) in this case is represented by the mathematical formula :

$$Z = R_s + \frac{R_{ct}}{1 + (2\pi f\, R_{ct}\, C_{dl})^{\alpha}}$$

where α denotes an empirical parameter (0 ≤ α ≤ 1) and f is the frequency in Hz.

Table 2 : Corrosion parameters obtained from polarisation curves shown in Fig. 1(a) for N80 steel in 15% hydrochloric acid in the absence and presence of inhibitor Inh I.

Concentration (ppm)	**E_{corr} (mV)**	**I_{corr} (μA cm^{-2})**	**β_c (mV dec^{-1})**	**β_a (mV dec^{-1})**	**% IE**
0	- 470	575	150	130	-
20	- 468	219	167	153	62.12
50	- 466	161	171	157	71.68
100	- 464	109	173	159	80.45
150	- 463	81	174	162	86.12
200	- 460	69	175	161	88.36

Table 3 : Corrosion parameters obtained from polarisation curves shown in Fig. 1(b) for N80 steel in 15% hydrochloric acid in the absence and presence of inhibitor Inh II.

Concentration (ppm)	**E_{corr} (mV)**	**I_{corr} ($\mu A\ cm^{-2}$)**	**β_c (mV dec^{-1})**	**β_a (mV dec^{-1})**	**% IE**
0	- 470	575	150	130	-
20	- 467	253	165	156	56.00
50	- 466	195	167	158	66.09
100	- 464	144	170	160	74.96
150	- 462	104	171	162	81.91
200	- 460	92	172	164	84.00

The impedance spectra obtained experimentally were analysed using software provided with the electrochemical analyser. The impedance data of the N80 steel electrode in presence of 20,50, 100 and 150 ppm of the inhibitor was analysed using the equivalent circuit shown in fig. 3. The calculated equivalent circuit parameters for N80 steel in 15% HCl solution at 25^{o}C in presence of 20,50 100 and 150 ppm of the inhibitor is presented in Table 4. From the data in Table 4, it is clear that the value of R_{ct} increases on increasing the concentration of the inhibitor, indicating that the corrosion rate decreases in presence of the inhibitor. It is also clear that the value of C_{dl} decreases on addition of inhibitor, indicating a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that the inhibitor molecule function by formation of the protective layer at the metal surface.

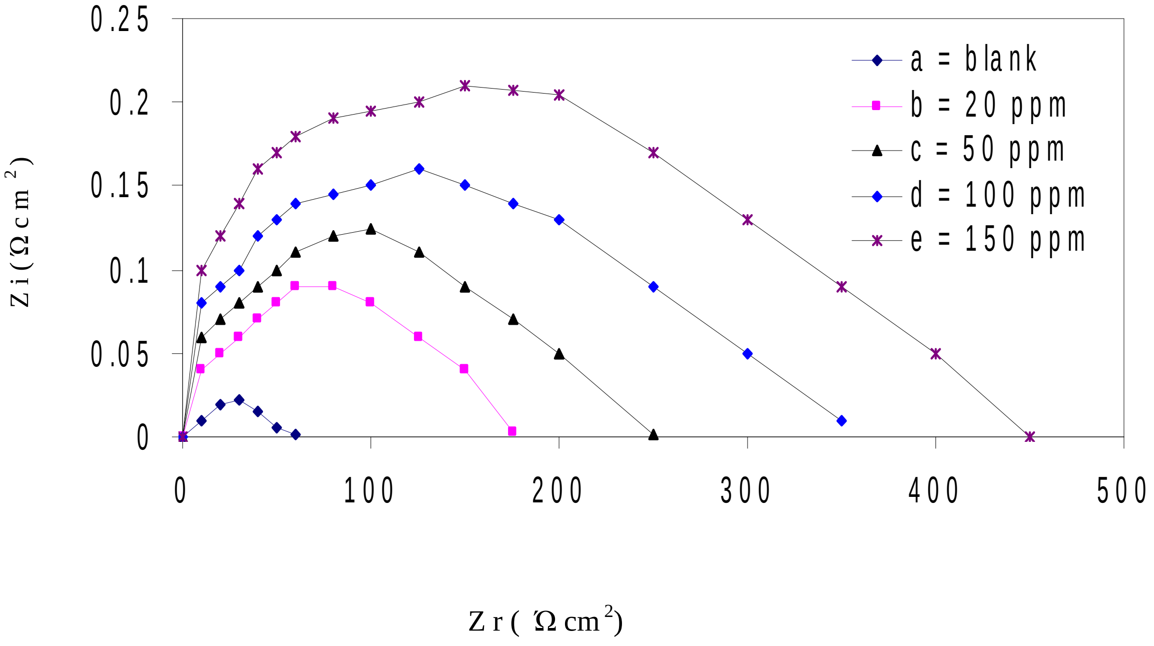


Fig. 2: Nyquist plot for N80 steel in 15% HCl acid in presence and absence of Inh I at 25^{0}C.

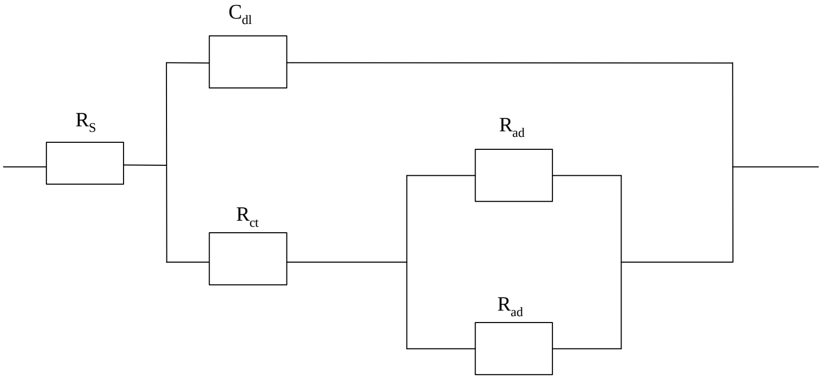


Fig**. 3**: Equivalent circuit model used in the fitting of the impedance data of N80 steel in 15%HCl acid at 25^{o}C

Where,
R_s = Sodium resistance
R_{ct} = Charge transfer resistance
C_{dl} = Constant phase element of the double layer
C_{ad} = Constant phase element of the adsorbed layer
R_{ad} = Adsorbed layer resistance

Table 4: Equivalent circuit parameters and inhibition efficiency for N80 steel in 15% HCl acid in presence of 150 ppm of Inh I at 25^{o}C

Concentration	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	%IE
0	68	480	-
20 ppm	179	212	62.18
50 ppm	234	182	71.36
100 ppm	358	148	81.24
150 ppm	453	128	85.48

In order to confirm the potentiodynamic results, the corrosion inhibition efficiency (IEs) in presence of 20,50 100 and 150 ppm concentration of the inhibitor Inh I in 15% HCl acid at 25^{o}C was also calculated from the corresponding electrochemical impedance data according to :

$$\%\,IE = \frac{R_{ct(Inh)} - R_{ct}}{R_{ct(Inh)}} \times 100$$

where R_{ct} is the charge transfer resistance of the metal in absence of inhibitor and $R_{ct(Inh)}$ is the charge transfer resistance in presence of inhibitor. The inhibition efficiencies calculated from impedance data are in good agreement with those obtained from electrochemical polarization and weight loss measurement.

3.3. Adsorption Isotherms

The adsorption of inhibitor molecules on the surface of the corroding metal has been considered as the root cause of corrosion inhibition. Assuming that the percentage area covered by the inhibitors is directly proportional to retardation in the corrosion rate, the compounds should obey Langmuir adsorption isotherm[19.

Langmuir isotherm may be written as :

$$\log \frac{\theta}{1-\theta} = \log A + \log C - \frac{Q}{2.3RT}$$

where A and Q are temperature independent constant and heat of adsorption respectively. The validity of Langmuir isotherm is confirmed from the linearity of the $\log\frac{\theta}{1-\theta}$ vs log C plot having the slope value to be unity. The plots of $\log \frac{\theta}{1-\theta}$ vs log C for the investigated inhibitors at 25^{0}C are shown in Fig. 4. It is observed that although these plots are linear, the gradient are never unity, contrary to what is expected for the ideal Langmuir adsorption isotherm equation. The departure in the values of the slopes of Langmuir plots from unity may be advocated to be due to the mutual interaction between adsorbed molecules in close vicinity [20]. Organic molecules and metal complexes having polar atoms or groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction and hence may affect the heat of adsorption. All the inhibitors follow the Langmuir adsorption isotherm, indicating that the adsorption of inhibitors at the surface of N-80 is the root cause of corrosion inhibition.

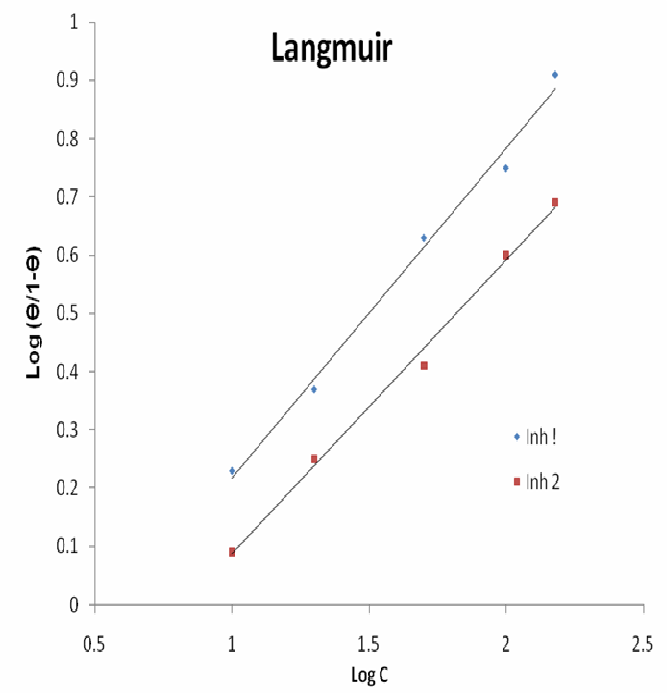
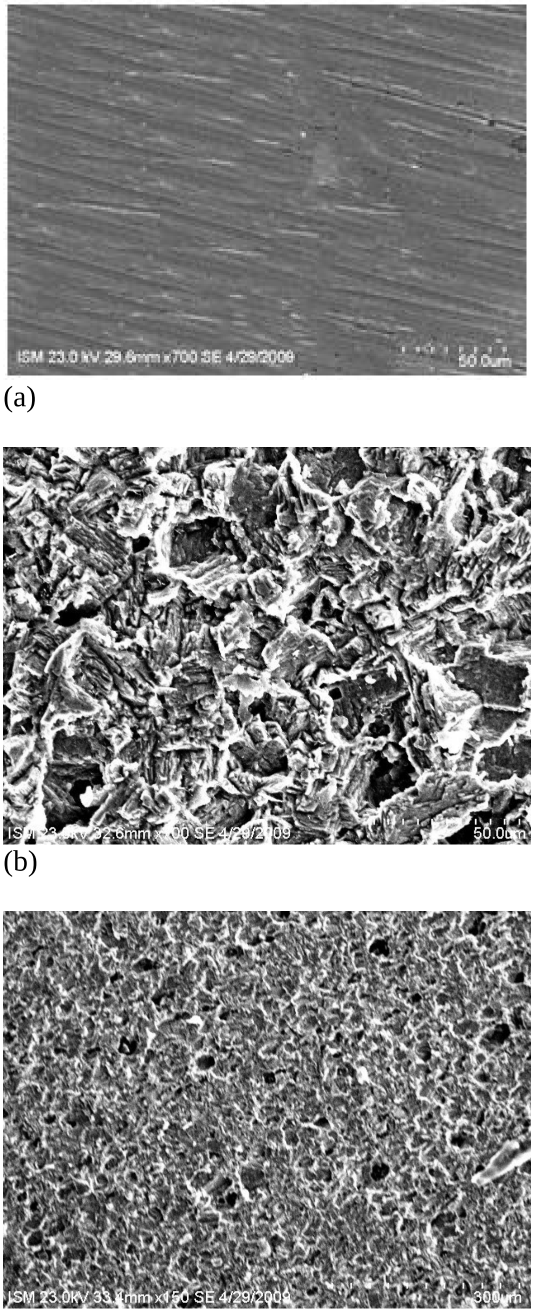


Fig.4 : Langmuir plots

3.4. *Microscopic Study*

Figure 5 (a, b, c,) show the microphotographs for N80 steel in 15% hydrochloric acid in the absence and presence of 150 ppm of Inh I at 200 X magnification. On comparing these micrographs, it appears that in the presence of inhibitor, the surface of the test material has improved remarkably with respect to its smoothness. The smoothening of the surface would have been caused by the deposition of inhibitor molecules on it and thus, the surface is fully covered.



(a)

(b)

(c)

Fig. 5: SEM of (a) Polished sample (b) Sample in presence of 15 % hydrochloric acid (c) Sample in presence of 150ppm of Inh I.

Conclusion

(i) Both the inhibitors Inh I and Inh II act as efficient corrosion inhibitor for N-80 steel in 15% HCl solution.
(ii) Inh I shows appreciably higher efficiency than the Inh II due to presence of more number of active

centres and larger size as compared to the inhibitor Inh II.

(iii) Both the the inhibitors act as mixed inhibitors.

(iv) It is suggested from the results obtained from SEM and Langmuir adsorption isotherm that the mechanism of corrosion inhibition is occurring through adsorption process.

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