

Chapter- 4
Corrosion inhibition
behaviour of Imidazolines

Nitrogen-based organic compounds are found to be effective inhibitors for mild steel corrosion in acidic solutions^{64,202-203}. The presence of lone pairs of electrons on the nitrogen atoms helps to delocalize the electrons and thus stabilizes the compound. The heterocyclic nitrogen are adsorbed to the metal surface through electrostatic interactions between the electron deficient nitrogen atom and the electron rich metal surface²⁰⁴.

Imidazolines belong to the heterocyclic compounds containing five membered ring having two nitrogen atoms. The ability of imidazolines to form cations helps it to strongly adsorb on to negatively charged surface of metals²⁰⁵. They are used as corrosion inhibitors²⁰⁶ in the oil well, oil pipeline protection and gas industry. Joseph *et al*²⁰⁷ studied the adsorption of oleic imidazoline (1-(2-aminoethyl)-2-(heptadec-8-enyl)-2-imidazoline) on mild steel surface. Imidazoline acts as a strong chemical anchor lying flat on the surface and hydrocarbon tail of oleic imidazoline acts as hydrophobic barrier between metal surface and solution and inhibits corrosion. The authors correlated the relationship between the structure of imidazolines and inhibition efficiency.

Y. Abboud *et al*²⁰⁸ focused on the efficiency of non-toxic 2,2'-bis(benzimidazole), as steel corrosion inhibitor in hydrochloric acid by electrochemical techniques. The compound possessed fairly good inhibiting property for steel corrosion in hydrochloric acid, and behaves as a mixed inhibitor. The influence of 2-methyl-imidazole and benzimidazole on the corrosion of mild steel in 1N HCl and 1N H₂SO₄ through hydrogen permeation was studied by Muralidharan *et al*⁴¹. The inhibitors were effective in both 1N HCl and 1N H₂SO₄.

D. Wang and co-workers²⁰⁹ investigated the corrosion inhibition behaviour of imidazoline derivatives with different electron releasing substituents as acid corrosion inhibitors for iron and steel. They proposed the relationship between the structure and inhibition efficiency. The electron donor substituents particularly the substituent group with conjugated system, introduced to imidazoline ring improved inhibition efficiency because it strengthens the chemical adsorption of the N atom on the metal surface.

Zhang *et al*²¹⁰ developed corrosion inhibitor containing imidazoline, non-ionic surfactant, cationic surfactant, ammonium citrate and water. The inhibitor capable of acid mist resistance and etching promotion was used in an HCl solution. They reported the inhibition efficiency 99.6% at 20°C.

This Chapter comprises the studies on the corrosion inhibiting properties of imidazoline derivatives such as 2-Undecyl-1,3 imidazoline (UDI), 2- Nonyl-1,3 imidazoline (NI) , 2- Pentadecyl-1,3 imidazoline (PDI, 2- Heptadecyl-1,3 imidazoline (HDI), 2-Heptyl-1,3 imidazoline (HI). The synthesized compounds were characterized and tested for inhibitive action on mild steel in hydrochloric acid by weight loss method, potentiodynamic polarization method and electrochemical impedance method. The observed results are presented and discussed herewith.

RESULTS AND DISCUSSION

4.1. Weight Loss Studies

The corrosion rate of mild steel in 1.0 mol dm⁻³ HCl was studied by monitoring the weight loss after a constant interval of time in the absence and presence of imidazolines. The temperature was kept constant at 30°C and the

immersion time was 3 hours. The corrosion rate and the inhibition efficiency were determined at different concentrations of imidazolines in the range from 100 to 600 ppm and are given in Table 4.1. The effect of variation in concentrations of inhibitor, solution temperature, acid concentration and immersion time on inhibition efficiency of imidazolines were studied and are presented in Figures 4.1- 4.4.

The imidazoline compounds inhibited the corrosion rate of mild steel in 1.0 mol dm^{-3} HCl solution, at different concentrations in the range 100 ppm – 600 ppm. It has been observed that the inhibition efficiency of these compounds increased with the increase in concentration of inhibitor as shown in Figure 4.1 and gave a maxima in the inhibition efficiency at 500 ppm inhibitor.

The variation of Inhibition efficiency on solution temperature is depicted in Figure 4.2. The inhibition efficiency of imidazolines increased with an increase in temperature from 30°C to 60°C . Thus the adsorption rate increases with increase in temperature and the inhibitive film formed on the metal surface becomes more protective in nature in this temperature range.

The variation of Inhibition efficiency of fatty acids imidazolines on immersion time is shown in Figure 4.3. No significant change in inhibition efficiency was observed with increase in immersion time from 3h to 24h which shows the persistency of the adsorbed fatty acid imidazolines over a longer test period on the metal surface.

The change in acid concentration from 1.0 mol dm^{-3} to 5.0 mol dm^{-3} does not cause any significant change in inhibition efficiency of these compounds as evident from the Figure 4.4. This study suggests that

imidazolines compounds behave as effective inhibitors in acid solution of these concentrations.

The value of weight loss at different initial concentrations of inhibitors in 1.0 mol dm^{-3} HCl was investigated at 30°C after 3 hour of immersion time. The data obtained from the weight loss studies were used to evaluate surface coverage (θ). The data were tested graphically by fitting to various isotherms. A straight line was obtained on plotting $\log (\theta / 1-\theta)$ versus $\log C$ (Figure 4.5) suggesting that the adsorption of the imidazolines on mild steel surface follows Langmuir's adsorption isotherm. The values of the heat of adsorption (Q) were obtained from the slope of the plots of $\log (\theta / 1-\theta)$ versus $1/T$ (Figure 4.6) for imidazolines, and the values are given in Table 4.2. The obtained values of Q obtained suggest the physical nature of adsorption.

A number of experiments were performed at different temperatures in the ranging from 30°C to 60°C at fixed concentrations of acid (1 mol dm^{-3}) and inhibitor (500 ppm). The immersion period was 3h and the corrosion rate was determined at temperatures 30°C , 40°C , 50°C and 60°C . \log (corrosion rate) versus $1/T$ was plotted (Figure 4.7) and the slope of the plot gave the values of E_a . The values of activation energy (E_a) obtained from the slope of the plot for imidazolines are given in Table 4.2. To obtain the values of ΔH and ΔS for the adsorption of imidazolines in presence of HCl on the mild steel surface, logarithm of (CR / T) was plotted against $1/T$. The slope and intercept of plot (Figure 4.8) gave the values of ΔH and ΔS respectively and the values are listed in Table 4.2.

The lower change in enthalpies, ΔH in presence of imidazolines signify the net values at rate determining step for the corrosion reactions as well as the adsorption of imidazolines at the mild steel surface. The lowering¹⁶³ in the values of ΔH in the presence of imidazolines may be due to the energy released during the adsorption of imidazolines on mild steel surface. It is evident from the fact that the presence of imidazolines reduces the corrosion rate and increases the inhibition efficiency. The values of entropy of activation ΔS in the absence and presence of imidazolines are negative and large¹⁸⁸. This indicates that the activated complex formed during the corrosion and adsorption processes is an associative in nature rather than dissociative step. Therefore, a decrease in disorderness takes place during the transformation from reactants to the activated complex¹⁸⁷.

The change in free energy of adsorption (ΔG_{ads}) were calculated¹⁹⁰ using the equations given in the experimental. The values are listed in Table 4.2. The lower values of ΔG_{ads} indicate that imidazoline of fatty acid are physically adsorbed on the metal surface¹⁹¹. It also indicate that the spontaneous nature of adsorption of inhibitor on the surface of mild steel¹⁹².

In order to determine the dependency of the corrosion rate on the activity of mild steel, a number of experiments were performed in which weight losses were monitored as a function of immersion time. The concentrations of HCl, inhibitors were kept constant at 1 mol dm⁻³ and 500 ppm, respectively at 30°C. A straight line was obtained for the plot of log (weight loss) *versus* immersion time as depicted in Figure 4.9, showing that the reaction obeyed first order kinetics. The rate constant was calculated using the first order rate equation¹⁶⁴.

The half life ($t_{1/2}$) values were calculated using following relationship:

$$t_{1/2} = 0.693 /k$$

The values of the rate constant and half life period ($t_{1/2}$) obtained in the absence and presence of imidazolines are summarized in Table 4.3. The half life ($t_{1/2}$) values indicate the durability of inhibitor film on the mild steel surface under the studied conditions¹⁹³.

4.2 Potentiodynamic Polarization Studies

The cathodic and anodic polarization curves were obtained for mild steel in 1.0 mol dm^{-3} in the absence and presence of different inhibitors at 500 ppm concentration at $30 \pm 1 \text{ }^\circ\text{C}$ and are shown in Figure 4.10.

Electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}) and inhibition efficiency (IE) were calculated from Tafel plots and these values are given in Table 4.4.

The values of I_{corr} decreased significantly in the presence of imidazolines. Maximum decrease in I_{corr} was observed for UDI. All the imidazolines did not show any significant change in E_{corr} values suggesting that these compounds behaves as mixed type inhibitors i.e., they retard the corrosion reaction by blocking both anodic and cathodic sites of the metal¹⁹⁴.

4.3. Electrochemical Impedance Studies

Table 4.5 include the results of impedance studies carried out at different concentration of UDI in 1.0 mol dm^{-3} HCl at $30 \pm 1 \text{ }^\circ\text{C}$. The results are shown in Figure 4.11 for Nyquist plots in the presence of 100, 300 and 500 ppm of UDI. The Nyquist plots are not perfect semicircles and this difference has been attributed to frequency dispersion¹⁹⁵. The values of R_t and C_{dl} were

calculated from Nyquist plots¹⁵⁷. The percentage inhibition efficiency was calculated from the following equation¹⁹⁶.

$$\% \text{ I.E.} = \frac{1/R_{t_0} - 1/R_{t_i}}{1/R_{t_0}} \times 100$$

The values of R_t , C_{dl} and inhibition efficiency are given in Table 4.5. R_t values increases with increase in inhibitor concentration (UDI) and, in turn, it leads to an increase in inhibition efficiency. The addition of UDI to 1.0 mol dm^{-3} HCl lowers the C_{dl} values, which shows that the inhibition in corrosion may be due to surface adsorption of the inhibitor¹⁹⁷.

4.4. Scanning Electron Microscopy

Scanning electron microscopy were performed for the mild steel surface after dipping it in solution containing HCl; and HCl and UDI (Figure 4.12). The surface of mild steel immersed in inhibited solution was found to be smoother than that in blank 1.0 mol dm^{-3} HCl. This observation suggest that the inhibitor is adsorbed to the metal surface, forms a protective layer and prevent the attack of acid on metal surface¹⁹⁸.

4.5. Mechanism of corrosion inhibition

Inhibition of corrosion of mild steel in the acidic solutions by the fatty acid imidazolines can be explained on the basis of molecular adsorption. The molecules of these compounds are adsorbed on the metal surface through π -electrons of aromatic ring and lone pair of electrons of N atoms and blocks the surface¹⁹⁹. The presence of long hydrophobic chain keeps the acid solution away from metal surface due to its hydrophobic nature. Thus, the surface is protected from the wetting process by aggressive solution. Among the

compounds investigated in the present study, the order of inhibition efficiency has been found to be in the following order:

UDI > NI > PDI > HDI > HI

(C₁₁) (C₉) (C₁₅) (C₁₇) (C₇)

The inhibition efficiency increased with the increase in chain length up to C₁₁ (UDI), however, a further increase in chain length (C₁₇) resulted into decreased inhibition efficiency²⁰⁰.

Table 4.1 Dependence of corrosion rate and inhibition efficiency on [Imidazolines].

Inhibitor Used	Concentration (ppm)	Weight loss (mg)	IE (%)	CR (mmpy)
UDI	0	68.1	-	25.31
	100	23.6	65.23	8.80
	200	16.7	75.12	6.29
	300	9.9	85.32	3.71
	400	6.3	90.61	2.37
	500	1.1	98.31	0.42
	600	8.5	87.46	3.17
NI	0	68.1	-	25.31
	100	24.8	63.57	9.22
	200	19.6	71.12	7.30
	300	12.0	82.27	4.48
	400	8.1	88.10	3.01
	500	2.7	96.03	1.00
	600	9.1	86.34	3.45
PDI	0	68.1	-	25.31
	100	29.3	60.10	10.91
	200	22.4	67.40	8.34
	300	14.7	78.31	5.48
	400	10.0	85.22	3.74
	500	4.0	93.99	1.52
	600	10.2	84.98	3.80
HDI	0	68.1	-	25.31
	100	27.9	59.01	10.93
	200	24.9	63.41	9.26
	300	16.8	75.20	6.27
	400	10.3	84.81	3.84
	500	6.0	90.87	2.30
	600	14.5	78.62	5.41
HI	0	68.1	-	25.31
	100	29.4	56.80	10.93
	200	27.1	60.90	10.10
	300	18.7	72.50	6.96
	400	12.3	81.93	4.57
	500	9.6	85.80	3.59
	600	16.8	75.32	6.24

[HCl] = 1.0 mol dm⁻³, Temp = 30 °C, Immersion time = 3 hour

Table 4.2. Thermodynamic activation parameters for corrosion of mild steel in the absence and presence of imidazolines.

System	E_a (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG_{ads} (kJ mol ⁻¹)	$-Q$ (kJ mol ⁻¹)
1N HCl	51.18	48.56	200.40	-	-
UDI	23.71	26.35	203.73	38.41	23.66
NI	24.76	27.40	202.20	37.12	23.04
PDI	23.77	32.42	196.75	36.25	18.08
HDI	29.75	32.39	192.43	35.81	18.62
HI	30.73	33.37	186.19	32.10	17.40

[Imidazolines] = 500 ppm; [HCl] = 1.0 mol dm⁻³

Table 4.3. Half-life values (in hours h) for the corrosion of mild steel in imidazolines.

System	$10^3 k$ (h ⁻¹)	$t_{1/2}$ (h)
HCl	32.79±0.141	21.13
HCl + UDI	3.83±0.221	180.93
HCl + NI	5.41±0.201	128.00
HCl + PDI	10.78±0.187	64.28
HCl + HDI	11.95±0.156	57.99
HCl + HI	14.83±0.134	49.89

[Imidazolines] = 500 ppm; [HCl] = 1.0 mol dm⁻³; Temp = 30° C

Table 4.4. Electrochemical polarization parameters for the corrosion of mild steel in HCl containing Imidazolines.

System	E_{corr} (mV)	I_{corr} (mA cm ⁻²)	IE (%)
HCl	-461	0.360	-
HCl + UDI	-480	0.033	90.83
HCl + NI	-476	0.037	89.72
HCl + PDI	-466	0.085	76.38
HCl + HDI	-479	0.120	66.66
HCl + HI	-493	0.150	58.33

[Imidazolines] = 500 ppm; [HCl] = 1.0 mol dm⁻³; Temp = 30° C

Table 4.5. Dependence of electrochemical impedance parameters on [UDI] for mild steel in HCl.

System	R_t (ohm cm ²)	C_{dl} (μF cm ⁻²)	IE (%)
0	36	1511.50	-
100	86.95	946.84	58.48
300	141.30	776.92	74.45
500	304.34	315.22	88.13

[HCl] = 1.0 mol dm⁻³; Temp = 30° C.

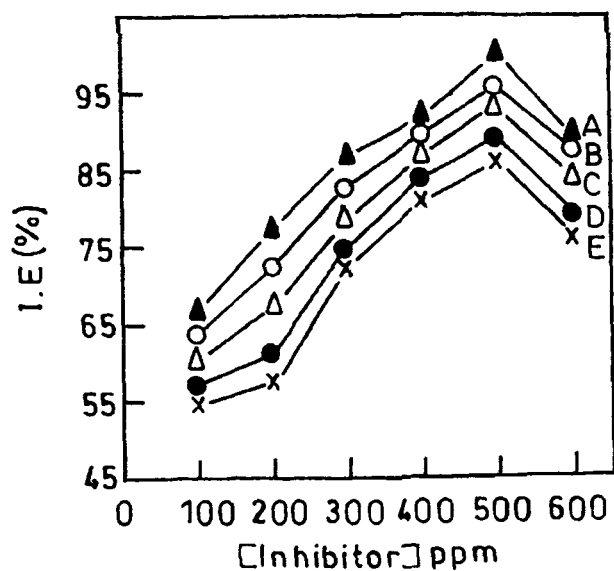


Fig 4.1. Plot of variation of inhibition efficiency on concentration for imidazolines (▲,UDI; ○, NI ; △,PDI; ●, HDI; x, HI)
Reaction conditions [HCl] =1.0 mol dm⁻³, Temp =30°C, Time =3 hours.

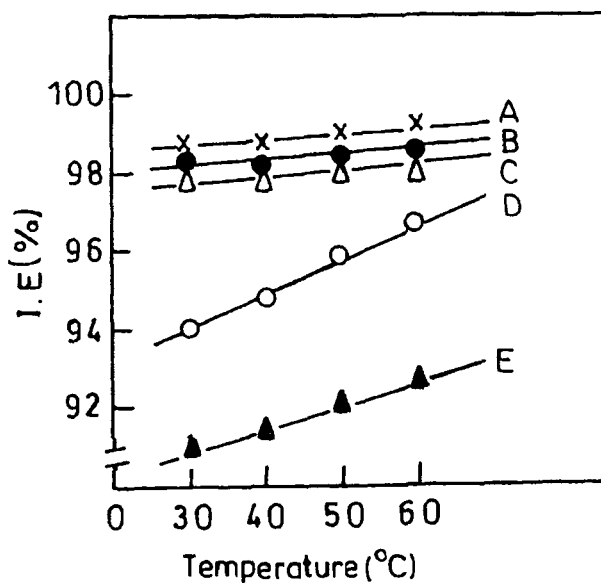


Fig 4.2. Plot of variation of inhibition efficiency on temperature for imidazolines (x,UDI; ●, NI ; △,PDI; ○, HDI; ▲, HI).
Reaction conditions [HCl] =1.0 mol dm⁻³, Time =3 hours, [inhibitor]=500 ppm.

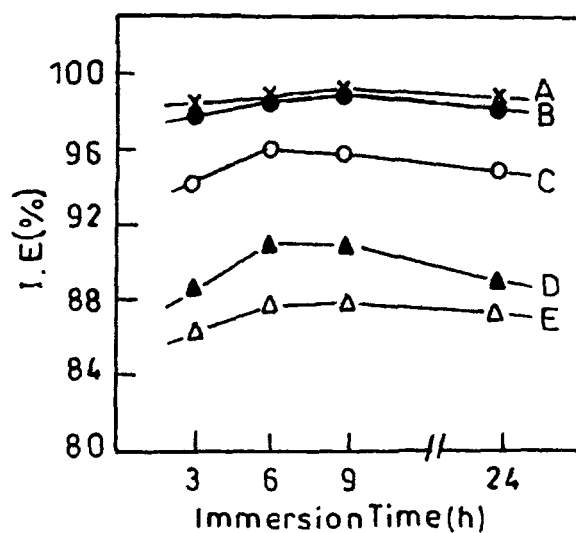


Fig 4.3. Plot of variation of inhibition efficiency on immersion time for imidazolines (x,UDI; ●, NI ; △,PDI; ○ , HDI; ▲, HI).
Reaction conditions [HCl] = 1.0 mol dm⁻³, Temp = 30°C, [inhibitor]=500 ppm.

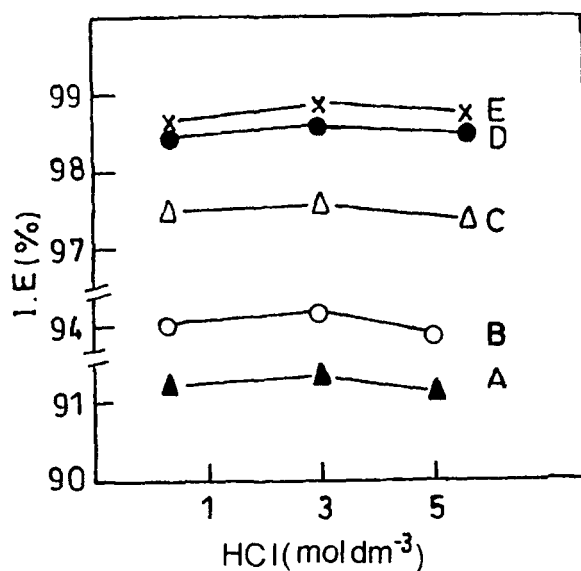


Fig 4.4. Plot of variation of inhibition efficiency on [HCl] for imidazolines (▲,UDI; ○, NI ; △, PDI; ●,HDI; x, HI).
Reaction conditions [inhibitor]=500 ppm, Temp = 30°C, Time = 3 hours

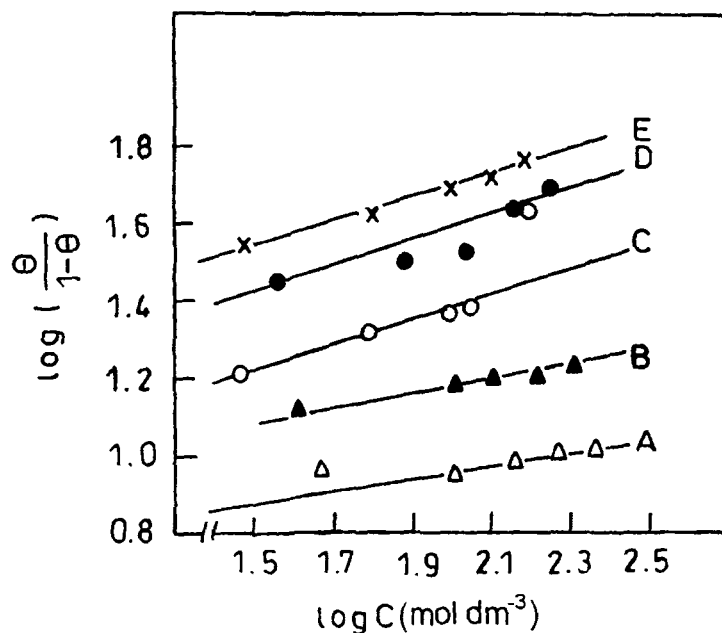


Fig 4.5. Langmuir's adsorption isotherm plots for imidazolines (Δ , UDI; \blacktriangle , NI; \circ , PDI; \bullet , HD; \times , HI)

Reaction conditions $[HCl] = 1.0 \text{ mol dm}^{-3}$, Temp = 30°C , Time = 3 hours.

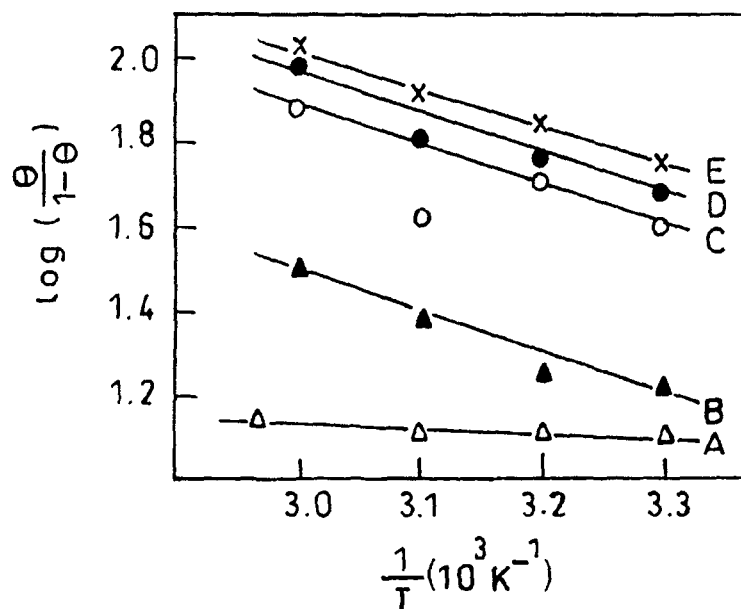


Fig 4.6. Adsorption isotherm plot for $\log(\theta / 1 - \theta)$ versus $1/T$ for imidazolines (Δ , UDI; \blacktriangle , NI; \circ , PDI; \bullet , HD; \times , HI)

Reaction conditions $[HCl] = 1.0 \text{ mol dm}^{-3}$, Time = 3 hours, [inhibitor] = 500 ppm.

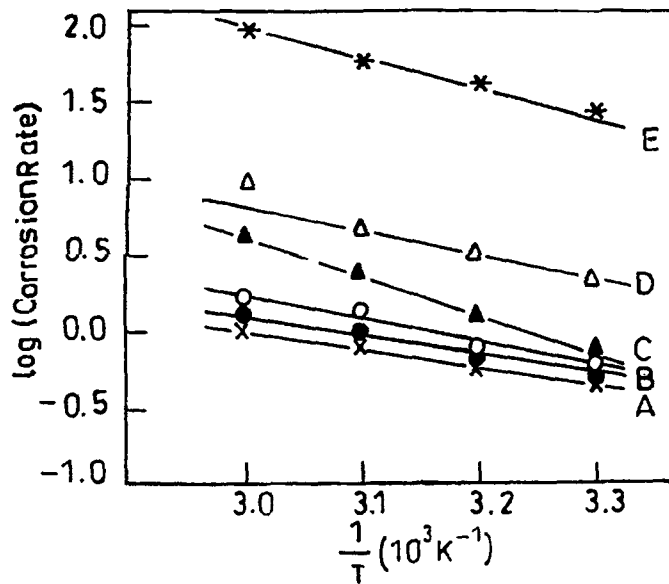


Fig 4.7. Adsorption isotherm plot for log (CR) versus 1/T for imidazolines (x ,UDI; ●, NI; ○, PDI; ▲, HD; Δ,HI; *, Blank)

Reaction conditions [HCl] = 1.0 mol dm⁻³, Time = 3 hours, [inhibitor] = 500 ppm.

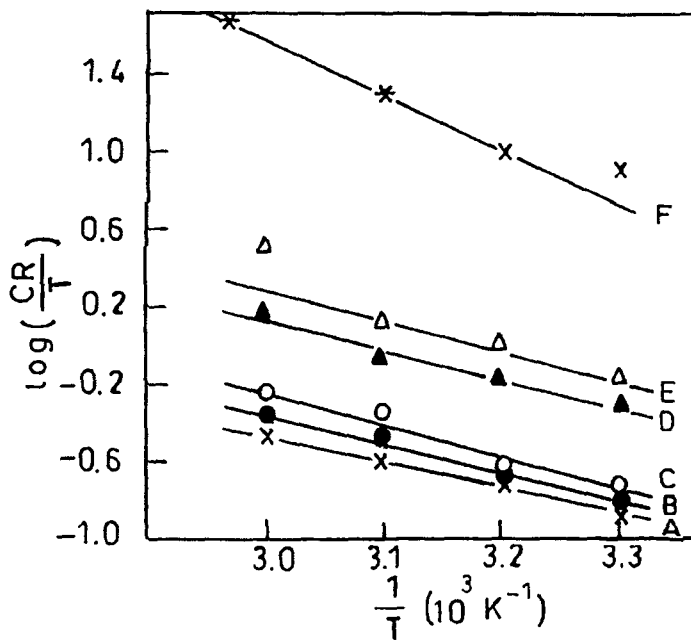


Fig 4.8. Adsorption isotherm plot for log (CR/T) versus 1/T for imidazolines (x ,UDI; ●, NI; ○, PDI; ▲, HD; Δ,HI; *, Blank)

Reaction conditions [HCl] = 1.0 mol dm⁻³, Time = 3 hours, [inhibitor] = 500 ppm.

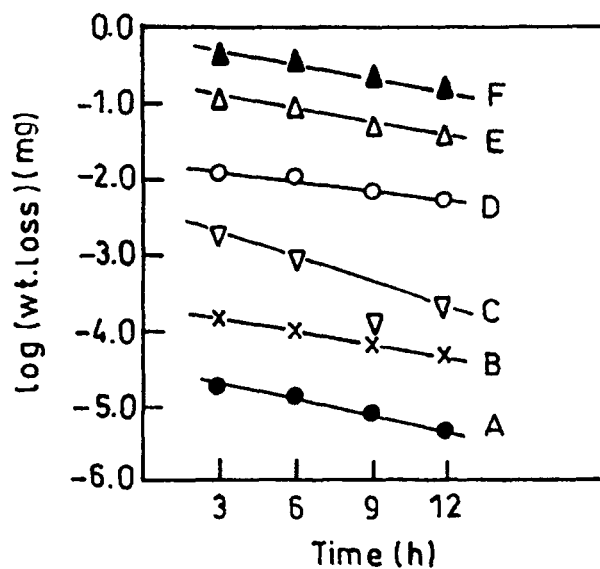


Figure 4.9. Plot of log (weight loss) versus immersion time for imidazolines (●, UDI; x, NI; ▼, PDI; ○, HD; △, HI; ▲, Blank).

Reaction conditions $[HCl] = 1.0 \text{ mol dm}^{-3}$, $[\text{inhibitor}] = 500 \text{ ppm}$, $\text{Temp} = 30^\circ\text{C}$.

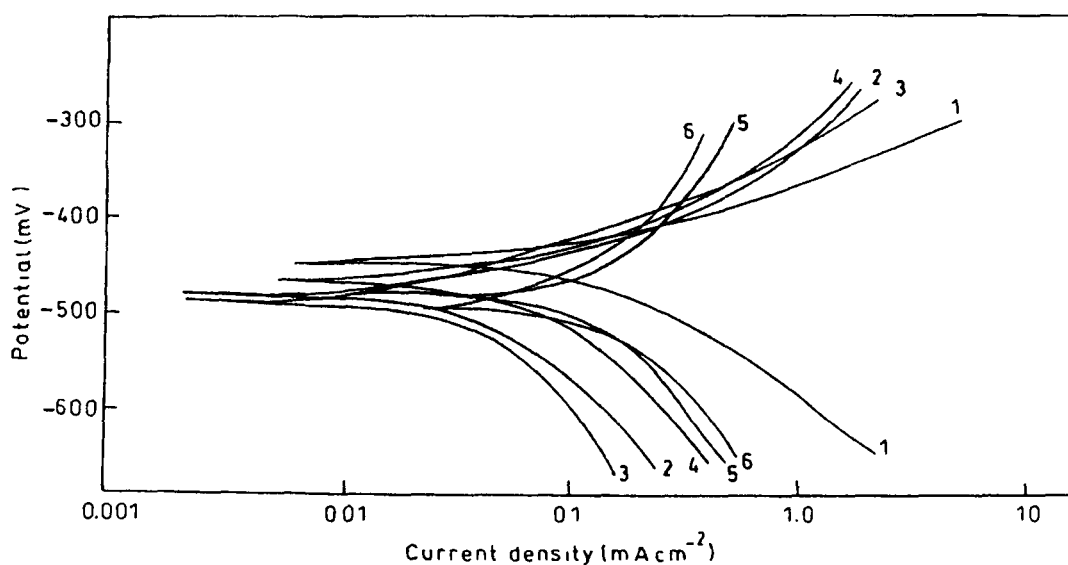


Figure 4.10. Potentiodynamic polarization curves for mild steel in presence of imidazolines (1) Blank (2) NI (3) UDI (4) PDI (5) HDI (6) HI.

Reaction conditions $[HCl] = 1.0 \text{ mol dm}^{-3}$, $\text{Temp} = 30^\circ\text{C}$.

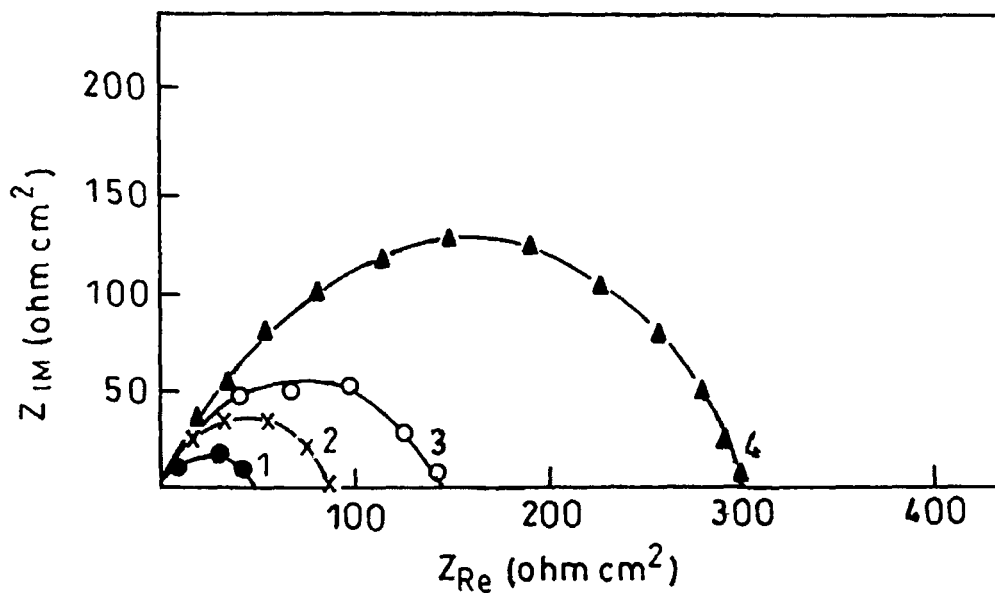
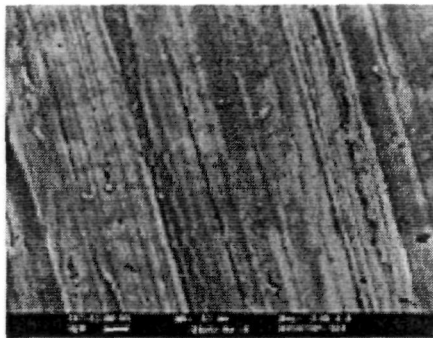


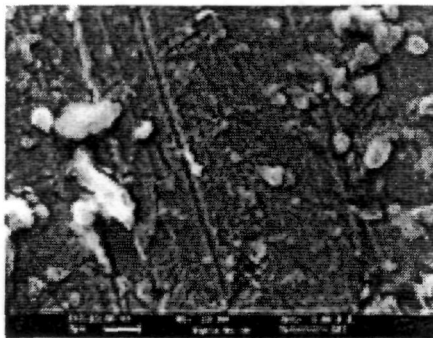
Fig 4.11. Nyquist plot of mild steel in 1.0 mol dm^{-3} HCl in the absence and presence of 100, 300 and 500 ppm of UDI (1) Blank (2) 100 ppm (3) 300 ppm (4) 500 ppm.



(a)



(b)



(c)

Figure 4.12. Scanning electron micrographs for mild steel surface in absence and presence of UDI (a) mild steel in $1.0 \text{ mol dm}^{-3} \text{ HCl}$ (b) polished mild steel and (c) mild steel in presence of UDI.