

# INHIBITION OF CORROSION OF MILD STEEL BY AMMONIUM PYRROLIDENE DITHIOCARBAMATE IN 1 M HYDROCHLORIC ACID

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**Inhibition of corrosion of mild steel in 1 M hydrochloric acid solution by Ammonium pyrrolidene dithiocarbamate (APDC) was evaluated using weight loss, polarisation and electrochemical impedance techniques. Results obtained through the above mentioned techniques indicated that inhibition efficiency (IE) increased with concentration of inhibitor, thus reaching a maximum efficiency of 95% at  $1 \times 10^{-2}$  M. The rise in temperature did not alter the corrosion rate of mild steel drastically at higher inhibitor concentration. The adsorption of inhibition followed Langmuir isotherm. The activation energies generally increased with concentration revealing chemisorption of inhibitor on the mild steel surface. Surface analysis by XRD and UV-luminescence emission spectra were also carried out to establish the mechanism of corrosion inhibition.**

**Keywords:** Chemisorption, inhibitors, polarisation, ammonium pyrrolidene dithiocarbamate, surface characterization.

## INTRODUCTION

Organic additives are commonly used to reduce the corrosion of metals in acidic media [1-8]. Many nitrogen containing heterocyclic compounds with polar groups and/or  $\pi$ -electrons are employed as good corrosion inhibitors for mild steel in acidic media [9]. Inhibition by these molecules are due to the adsorption of molecules and ions on the metal surface. The adsorption depends on the chemical structure of inhibitors, type of the aggressive acid and the nature and the surface charge on the metal.

The objective of the present work is to study the inhibition effect of APDC on the corrosion process of mild steel in 1 M hydrochloric acid. The inhibition efficiencies have been evaluated by weight loss, polarisation and electrochemical impedance spectroscopy (EIS) techniques. Surface analysis have also been carried out to find out the mechanism of corrosion inhibition of mild steel in acidic medium.

## EXPERIMENTAL

Experiments were conducted with mild steel having the following composition: (0.02-0.03% S, 0.3-0.8% P, 0.4-0.5%

Mn, 0.1-0.2% C and rest Fe). Mild steel specimens with dimensions 1.0 x 4.0 x 0.2 cm were used for weight loss measurements. The same specimens were also used for surface analysis. Electrochemical measurements were carried out with specimens of 1 cm<sup>2</sup> surface area. The surface of the specimens was polished successively with 1/0 to 4/0 emery papers and degreased with trichloroethylene.

Mild steel specimens in triplicate were immersed in 1 M hydrochloric acid solution for 2 hours. Changes in weight were followed to an accuracy of  $\pm 5\%$ . The percentage inhibition efficiency was calculated by

$$\%IE = \frac{W_1 - W_2}{W_1} \times 100$$

where  $W_1$  and  $W_2$  are weight loss of mild steel in uninhibited and inhibited acid chloride solutions.

Electrochemical measurements were carried out in a conventional three-electrode cell assembly. The working electrode was mild steel specimen of 1 cm<sup>2</sup> area. A saturated calomel electrode (SCE) and a platinum (Pt) foil were used as reference and counter electrodes respectively. The temperature was controlled thermostatically at  $303 \pm 1$  K.

The potentiostatic polarisation studies were carried out using the potentiostat (EG&G173) Universal programmer (EG&G175) and the X-Y recorder (Rikadenki) at a sweep rate of 1 mV/s.

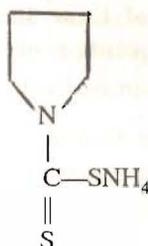
A.C. impedance measurement was carried out by using electrochemical impedance analyser (EG&G model 6310) in the frequency range of 0.1 mHz to 100 Hz.

To establish that the inhibition is due to the chemisorption of APDC on the metal surface, X-ray diffraction technique and UV-luminescence emission spectral studies were carried out.

XRD patterns were recorded by using a computer controlled X-ray powder diffractometer, JEOL JDX 8030 with CuK $\alpha$  (Ni filtered) radiation ( $\lambda = 1.5418^{\circ}$ ) at a rating of 40 kV; 20 mA. The scan rate was 0.05-20 $^{\circ}$  per step and the measuring time was 1 s/step.

UV-Luminescence emission spectra were recorded using Hitachi 650-10S fluorescence spectrophotometer equipped with a 150 W xenon lamp and a Hamamatsu R929 F photomultiplier tube. The emission spectra were corrected for beam intensity variation and the spectra response of the photomultiplier tube used.

The aggressive solutions (1 M HCl) were prepared by dilution of analytical grade 37% HCl with double distilled water. Analytical grade (Merck) APDC was used for this study. Its structure is as follows



## RESULTS AND DISCUSSION

### Weight loss measurements

The loss in weight of the mild steel specimens in the absence and presence of various concentrations of the inhibitor ( $10^{-4}$  to  $10^{-2}$  M) was determined and given in Table I. The corrosion rate was found to decrease with increase in APDC concentration. Thus the inhibition efficiency attained a maximum of 95% at  $10^{-2}$  M of APDC. These weight loss measurement data were in good agreement with the data obtained from electrochemical methods.

### Polarisation measurements

Typical potentiostatic polarisation curves for mild steel in HCl containing various inhibitor concentrations are shown in Fig. 1. The electrochemical parameters derived from the polarisation curves are listed in Table II. From this study, it is clear that  $I_{corr}$  decreases with increasing inhibitor concentrations and that inhibition efficiency reaches a maximum value of 96% at  $10^{-2}$  M APDC.

It is obvious from Table II that the Tafel constants  $b_a$  and  $b_c$  do not change significantly. The apparently constant values of the Tafel slopes (near to 60 mV/decade for  $b_c$  and 55 mV/decade for  $b_a$ ) suggest that the inhibition mechanism for all these molecules involves a simple blocking of reaction sites [10]. It is also observed from the Tafel curve that the inhibitor is of mixed type. The constancy of the cathodic

TABLE I: Corrosion rates of mild steel in 1 M HCl acid solution in presence and absence of APDC of various concentrations at different temperatures

T (K)	Concentration (M)	W (mg/cm <sup>2</sup> /h)	IE (%)
303	0	1.2188	--
	$1.0 \times 10^{-4}$	0.6438	47
	$1.0 \times 10^{-3}$	0.2713	78
	$2.5 \times 10^{-3}$	0.2000	84
	$5.0 \times 10^{-3}$	0.1164	90
	$7.5 \times 10^{-3}$	0.685	94
	$1.0 \times 10^{-2}$	0.0373	97
313	0	3.1250	--
	$1.0 \times 10^{-4}$	1.7563	44
	$1.0 \times 10^{-3}$	0.9563	69
	$2.5 \times 10^{-3}$	0.5688	82
	$5.0 \times 10^{-3}$	0.3563	89
	$7.5 \times 10^{-3}$	0.1875	94
	$1.0 \times 10^{-2}$	0.1500	95
323	0	10.4375	--
	$1.0 \times 10^{-4}$	6.2063	41
	$1.0 \times 10^{-3}$	3.6750	65
	$2.5 \times 10^{-3}$	2.3813	77
	$5.0 \times 10^{-3}$	1.3000	88
	$7.5 \times 10^{-3}$	0.7008	93
	$1.0 \times 10^{-2}$	0.5487	95
333	0	23.1000	--
	$1.0 \times 10^{-4}$	14.2875	38
	$1.0 \times 10^{-3}$	8.6125	63
	$2.5 \times 10^{-3}$	6.5063	72
	$5.0 \times 10^{-3}$	3.5000	85
	$7.5 \times 10^{-3}$	1.9188	92
	$1.0 \times 10^{-2}$	1.5000	94

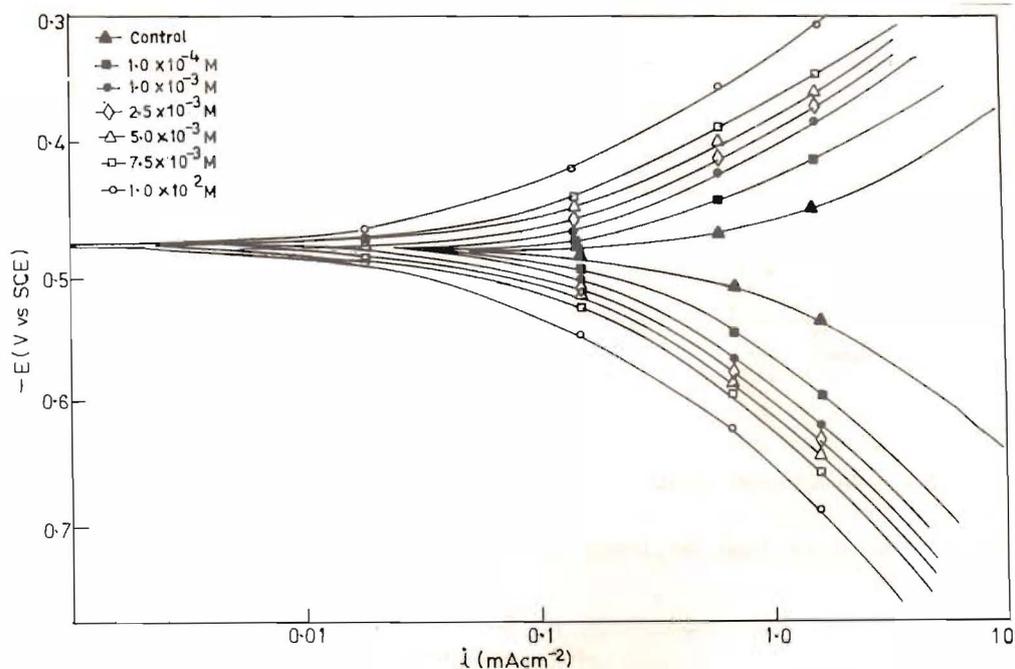


Fig. 1: Potentiostatic polarisation curves of mild steel in 1 M HCl with and without APDC

Tafel slope ( $b_c$ ) in lower concentrations (ie  $10^{-4}$  and  $10^{-3}$  M) indicates that the mechanism of hydrogen evolution reaction is the same either in absence or presence of APDC. But at higher concentration, the increase in  $b_c$  values indicates that the hydrogen evolution is suppressed due to the blocking of inhibitor molecules on the metal surface.

The plot of  $\log(\theta/1-\theta)$  vs  $\log C$  (Fig. 2) was found to be a straight line which shows that the adsorption of the inhibition follows Langmuir isotherm. From Fig. 2 it is also obvious that the % IE values are in good agreement with weight loss studies.

TABLE II: Electrochemical parameters from tafel curves for mild steel in 1 M HCl without and with addition of various concentrations of APDC

Concn (M)	$E_{corr}$ (mV/SCE)	$I_{corr}$ (mA/cm <sup>2</sup> )	$b_a$ (mV/decade)	$b_c$ (mV/decade)	IE (%)
0	-490	0.410	50	52	--
$1.0 \times 10^{-4}$	-478	0.278	52	54	32
$1.0 \times 10^{-3}$	-476	0.128	64	58	69
$2.5 \times 10^{-3}$	-475	0.091	54	56	78
$5.0 \times 10^{-3}$	-480	0.069	60	56	83
$7.5 \times 10^{-3}$	-485	0.055	56	60	87
$1.0 \times 10^{-2}$	-490	0.046	74	72	89

**Electrochemical impedance measurements**

The parameters derived from the Nyquist plots (Fig. 3) with and without the addition of inhibitor are given in Table III. The charge transfer resistance ( $R_{ct}$ ) increases with increase in inhibitor concentration. The double layer capacitance ( $C_{dl}$ ) values obtained from Fig. 3 are given in Table III. The

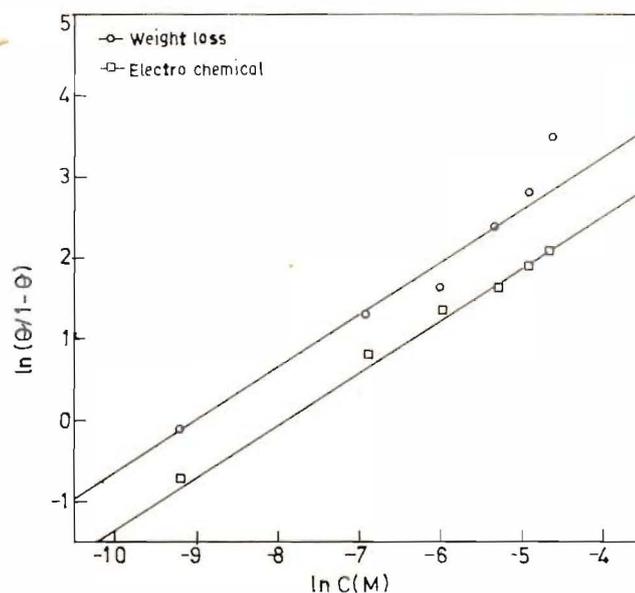


Fig. 2: Langmuir adsorption isotherm model of APDC on the surface of mild steel in 1 M HCl

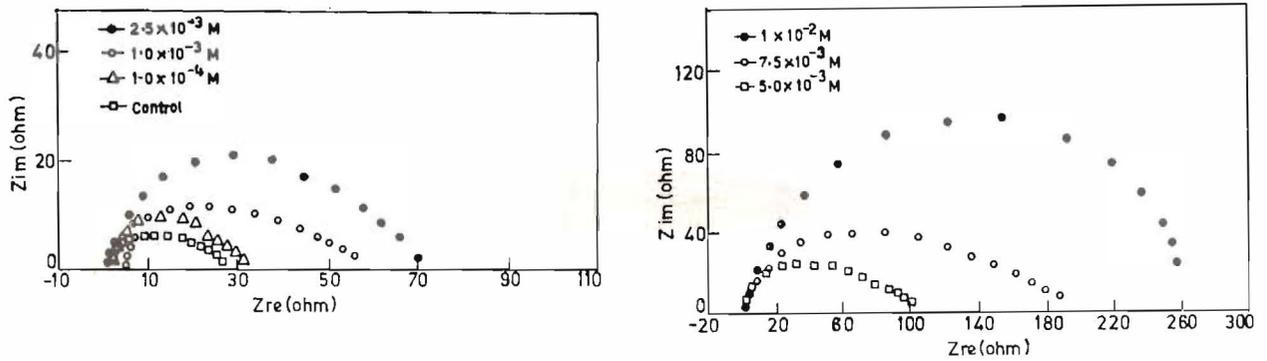


Fig. 3: Nyquist plots of mild steel immersed in 1 M HCl with and without APDC.

surface coverage  $\theta$  was calculated from the following equation:

$$\theta = 1 - \frac{C_{dli}}{C_{dl}}$$

where  $C_{dli}$  is the double layer capacitance with inhibitor and  $C_{dl}$  is the double layer capacitance without inhibitor. These capacitance calculations show a surface coverage of 0.85 for inhibitor system. The degree of coverage ( $\theta$ ) was found to increase with inhibitor concentration.

**Effect of temperature**

To verify the nature of adsorption, the effect of temperature (303 K to 333 K) on the corrosion behaviour of mild steel in 1 M HCl in the absence and presence of APDC was studied using the weight loss technique. Results given in Table I indicate that the rate of corrosion was not drastically changed with rise in temperature. The behaviour showed that APDC was an efficient inhibitor in the range of temperature

studied. The activation energies ( $E_a$ ) for the corrosion process in the absence and presence of the inhibitor are estimated from the slopes of the lines of the Arrhenius plot (Fig. 4) and given in Table IV.

With decrease in inhibitor concentration, the apparent activation energy decreases. Reduction in  $E_a$  may be attributed to chemisorption of APDC on the mild steel surface.

**TABLE III: Electrochemical parameters from Nyquist plots for mild steel in 1 M HCl without and with addition of various concentrations of APDC**

Concn (M)	$R_{ct}$ (K.ohm/cm <sup>2</sup> )	$C_{dl}$ ( $\mu$ F/cm <sup>2</sup> ) 10 <sup>-2</sup>	Surface coverage	IE (%)
0	0.025	6.37	--	--
1.0 x 10 <sup>-4</sup>	0.035	4.55	0.29	29
1.0 x 10 <sup>-3</sup>	0.072	3.50	0.45	65
2.5 x 10 <sup>-3</sup>	0.105	2.40	0.62	76
5.0 x 10 <sup>-3</sup>	0.130	1.94	0.70	81
7.5 x 10 <sup>-3</sup>	0.180	1.40	0.78	86
1.0 x 10 <sup>-2</sup>	0.260	0.97	0.85	90

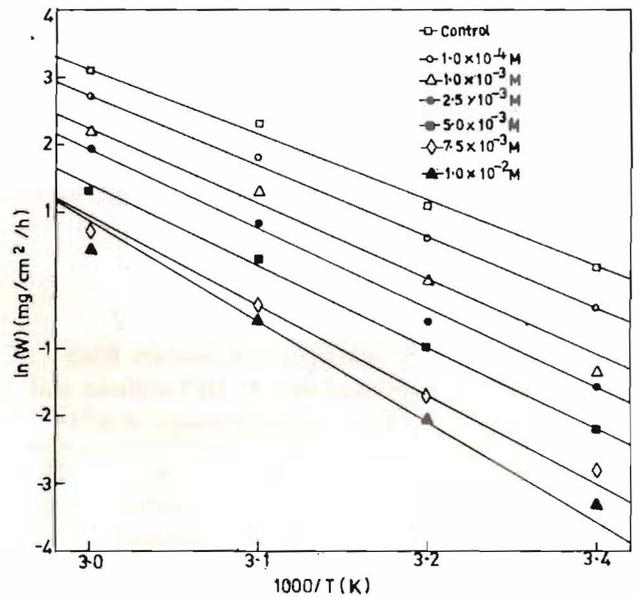


Fig. 4: Arrhenius plots related to the corrosion rate of mild steel for various concentrations of APDC.

**TABLE IV: The activation energy ( $E_a$ ) kJ/mole of the dissolution reaction at various concentrations of APDC in temperature range 303 to 323 K**

Concn of APDC (M)	Activation energy ( $E_a$ )
0	9.62
$1.0 \times 10^{-4}$	10.42
$1.0 \times 10^{-3}$	11.11
$2.5 \times 10^{-3}$	11.54
$5.0 \times 10^{-3}$	11.96
$7.5 \times 10^{-3}$	13.33
$1.0 \times 10^{-2}$	14.64

**Surface analysis**

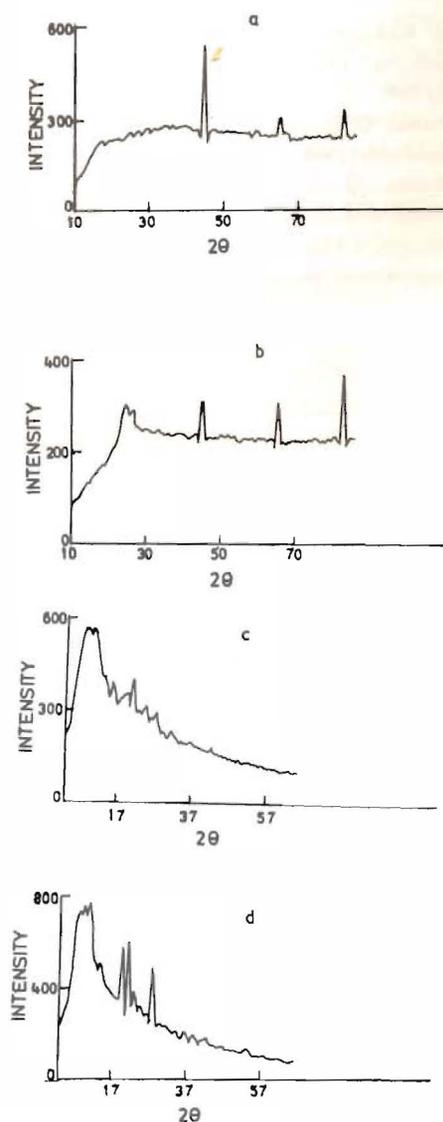
**X-ray diffraction pattern**

The XRD patterns of the mild steel specimens immersed in test solutions with and without inhibitors are shown in Fig. 5. The specimens immersed in 1 M HCl solution show only iron peaks corresponding to the  $2\theta$  values  $44^\circ$ ,  $65^\circ$  and  $82^\circ$ . But in the case of specimens immersed in system 1 M HCl containing APDC a broad organic peak [11] is noticed at lower angles in addition to the iron peaks. But the intensity of the iron peaks is found to be low when compared to the above system. It is concluded that a chemisorbed organic layer is formed on the metal surface in 1 M HCl solution which inhibits the corrosion of mild steel.

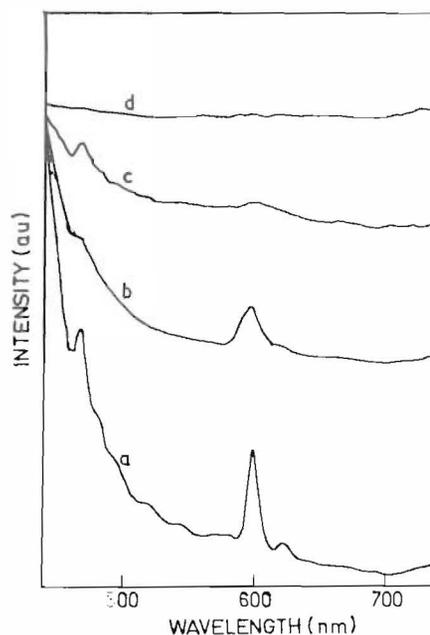
Further, the XRD patterns of APDC and the complex of APDC+ $Fe^{2+}$  ion are also taken and shown in Fig. 5. The XRD patterns confirm that the protection of mild steel is due to the chemisorption of APDC on the metal surface and not the adsorbed layer of APDC on the metal surface.

**UV-Luminescence emission spectra**

The UV-Luminescence emission spectra of mild steel surface immersed in 1 M HCl without and with various combinations of inhibitors are shown in Fig. 6. The emission spectra were taken at  $\lambda = 404$  nm. The mild steel specimens immersed



**Fig. 5: XRD patterns of mild steel surface immersed in (a) 1 M HCl (b) 1 M HCl + APDC XRD patterns of (c) APDC +  $Fe^{2+}$  complex and (d) APDC.**



**Fig. 6: Luminescence spectra of mild steel surface immersed in (a) 1 M HCl (b) 1 M HCl + APDC Luminescence spectra of (c) APDC +  $Fe^{2+}$  complex and (d) APDC.**

in 1M HCl, shows peak at 600 nm, whereas the peak intensity decreases with increase in the concentration of inhibitor. This is confirmed by the spectra of the  $\text{Fe}^{2+}$ +APDC and  $\text{Fe}^{3+}$ +APDC complex prepared in the laboratory and shown in Fig. 6. Since the complex is not fluorescence active and it does not give any peak it confirms the formation of an organic film on the metal surface due to the chemisorption of APDC.

### CONCLUSIONS

Inhibition efficiency increases with increasing inhibitor concentration as indicated by results of weight loss, polarisation and impedance spectroscopy calculations. Temperature does not alter the corrosion rate of mild steel in 1 M hydrochloric acid at higher inhibitor concentration. APDC acts as a mixed inhibitor and the inhibition efficiency attains a maximum of  $10^{-2}$  M concentration. The activation energy  $E_a$  decreases with decrease in inhibitor concentration suggesting chemisorption of the inhibitor molecule. The chemisorption of APDC on mild steel surface follows Langmuir isotherm. The surface analysis technique confirms

the formation of chemisorbed organic film on the metal surface.

### REFERENCES

1. G Schmitt, *Brit Corros J*, **19** (1984) 165
2. G Banerjee, S N Malhotra, *Corrosion*, **48** (1992) 10
3. B Donnely, T C Downie, R Grzeskowiak, H R Hambourg and D Short, *Corros Sci*, **18** (1991) 109
4. J Uhrea and K Aramaki, *J Electrochem Soc*, **138** (1991) 3245
5. F B Crowcock and V Lopp, *Corros Sci*, **28** (1988) 397
6. N Eldakar and K Nobe, *Corrosion*, **32** (1976) 238
7. J O'M Bockris and B Yang, *J Electrochem Soc*, **138** (1991) 2237
8. Adam Rauscher, Gyorgy Kutsan, Zoltan Lukacs, Tibor Horvath and Eriksman, *ACH-Models in Chemistry*, **132** (1995) 589
9. G Moretti, G Quartarone, A Tatsan and A Zingales, *Brit Corros J*, **31** (1996) 49
10. G Moretti, G Quartarone, A Tatsan and A Zingales, *Werkstoffe und Korrosion*, **45** (1994) 5
11. S Mohanan, S Maruthamuthu, A Mani and G Venkatachari, *Anticorr method material*, **43** (1996) 2