

Corrosion inhibition of aluminium by 2-chloronicotinic acid in HCl medium

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The inhibiting effect of 2-chloronicotinic acid on the dissolution of aluminium in various concentrations of HCl has been studied using weight loss and polarization measurements. The inhibition efficiency was found to increase with increasing concentration of the inhibitor. The effect of temperature on corrosion inhibition was investigated. The results indicate the decreased inhibition efficiency for the increase in temperature. The inhibitor was found to be adsorbed on aluminium surface probably following Langmuir adsorption isotherm at higher concentrations of HCl.

Keywords: Corrosion inhibition, Aluminium, 2-Chloronicotinic acid, Weight loss method, Polarisation method

The corrosion of a metal or a material is a global scientific problem as it affects, different walks of life especially in metallurgical, chemical, materials and oil industries^{1,2}. Aluminium is widely used in various industrial operations because of its light weight and relatively high mechanical strength. Therefore, the study of corrosion inhibition of Al is of much interest and has gained great importance in recent years³⁻⁵.

There exists a large volume of literature on the use of organic compounds with nitrogen, sulphur or oxygen containing functional groups acting as inhibitors⁶⁻⁸ for corrosion of Al⁹⁻¹¹, iron¹², and copper¹³. The increased interest in the manufacture of HCl has created the need for the study on the corrosion resistance of Al to HCl attack. Problem and magnitude of corrosion depends on the nature of the material and the environment. In the present work the effect of 2-chloronicotinic acid as corrosion inhibitor for Al in 1 M HCl, 1.5M HCl and 2M HCl was studied by weight loss and polarization measurements and presented.

Experimental Procedure

Materials and methods

Aluminium metal of the type Al- 63400 obtained from Pushpa Agencies, Mangalore was used as such for investigation. The chemical composition of Al-63400 is as follows: Cu, 0.1; Mg, 0.4-0.9; Si, 0.3-0.7; Fe, 0.6; Mn, 0.3; Zn, 0.2; Cr, 0.2; Ti or other grain refining elements, 0.1, and Al remainder. Each sheet was 1/16 inch in thickness, and was cut into 1 inch×0.5 inch coupons. They were polished with

emery paper number 80, degreased with acetone, washed, dried and weighed. All the experimental solutions were prepared using double distilled water and A.R grade chemicals.

Weight – loss method

In weight loss experiment, clean Al coupons were weighed and immersed completely in the corrodent in the presence and absence of inhibitor. The specimens were dipped in 2 M HCl for 2 h, 1.5 M HCl for 3 h, 1 M HCl for 24 h, 0.5 M HCl for 360 h and 0.1 M HCl for 600 h in the absence and presence of 2.5, 5.0, 10.0, 50.0, 100.0, 250.0 and 500.0 ppm of the inhibitor. The coupons were retrieved at specific time intervals, washed, dried and weighed. The differences in weight of the coupons were taken as weight loss. Three trials were performed in each case and average value was considered.

The corrosion rate was calculated¹⁴ using the equation:

$$CR = \frac{534W}{dAT} \quad \dots (1)$$

where W is the weight loss in mg, d is the density in g/cm^3 , A is the area of the specimen in $inch^2$ and T is the exposure time in h.

The inhibition efficiency was calculated using following relation¹⁵:

$$I.E = \frac{(W_o - W_i)}{W_o} \times 100 \quad \dots (2)$$

where W_o is the weight loss in uninhibited solution, W_i is the weight loss in inhibited solution.

Polarization studies

For polarization method, a conventional three electrode compartment cell consisting of Al specimen as working electrode of 1 cm² area, saturated calomel electrode as reference electrode and Pt electrode as auxiliary electrode was used. The anodic and cathodic polarizations were performed manually, galvanostatically using potentiometer (model- EQ-601). I_{corr} , E_{corr} and I.E were obtained by extrapolating cathodic and anodic polarization curves. Inhibition efficiency was then calculated, using the following Eq. (3)¹⁶,

$$IE = \frac{I_{\text{free}} - I_{\text{inhi}}}{I_{\text{free}}} \times 100 \quad \dots (3)$$

where I_{free} and I_{inhi} are corrosion current in the absence and presence of the inhibitor.

Results and Discussion

Weight-loss measurements

The inhibition efficiency (I.E) of the inhibitor on Al specimen was determined by weight loss method as explained earlier. The weight loss data obtained are shown in Fig. 1, indicating the variation of corrosion inhibition efficiency against concentration of the test inhibitor. Inhibition efficiency increased with the increase in the concentration of the inhibitor for all acid concentrations, indicating that 2-chloronicotinic acid acted as good inhibitor. The I.E increased for 2 M HCl, 1.5 M and 1 M HCl upto 250 ppm inhibitor concentration, thereafter it was found to decrease slightly or remained almost constant, which might be due to the interaction between adsorbed molecules at surface sites. Probably adsorbed molecules formed a

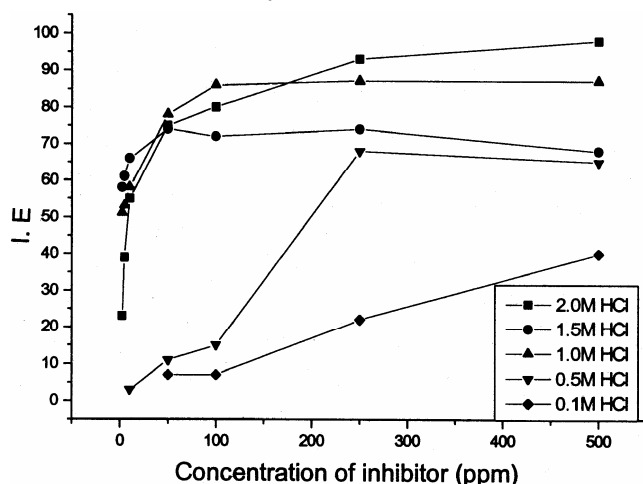


Fig. 1—Plot of influence of inhibitor concentration on corrosion inhibition of Al

layer on the surface and it did not allow further adsorption and hence no notable effect on the I.E proposing the Langmuir adsorption isotherm was more suited in this environment to the system. Therefore, in the case of 0.5 M and 0.1 M concentration of the HCl, inhibition efficiency was significant only at 250 ppm. From Fig. 1 it is clear that the inhibition efficiency increased with increase in the concentration of the inhibitor upto 250 ppm and does not show any effect above that concentration. At the same time it was also found that inhibition efficiency was maximum in 2 M HCl.

Polarization measurements

Figure 2(a-d) shows the cathodic and anodic polarization curves for Al in 1.5 M, 1 M, 0.5 M and 0.1 M HCl in absence and presence of the various concentrations of inhibitor at 300 K. From these Figures it is evident that inhibitor was comparatively more interactive at cathodic sites than at anodic site. The Figures also showed the decrease in corrosion current (I_{corr}) with increase in the concentration of the inhibitor. The I.E obtained were almost in agreement with those of weight loss measurements. As could be seen from Fig. 2, I_{corr} marginally decreased with increase in the inhibitor concentration, whereas I.E increases with increase in concentration of the inhibitor. The I.E and I_{corr} decreased with decrease in concentration of HCl indicating efficiency of the inhibitor increased with increase in concentration of HCl which was in accordance with the results obtained by weight loss method.

Effect of temperature on inhibition efficiency

The inhibition efficiency was evaluated, by weight loss method, in 2 M and 1.5 M HCl by dipping the specimen for 2 and 3 h respectively, at temperatures 301 K, 308 K, 313 K, 318 K and 323 K at different inhibitor concentrations ranging from 2.5-50 ppm (Fig. 3a and 3b).

Figure 4(a) and 4(b) shows the Arrhenius plots¹⁷ for 1.5 M and 2 M HCl based on Arrhenius Eq. (4) at various temperatures. It was found that for both 1.5 M HCl and 2 M HCl, inhibition efficiency decreased with increase in the temperature. The thermodynamic parameters for the dissolution of Al in 2 M and 1.5 M HCl in the absence and presence of the various concentration of the inhibitor were obtained¹⁷ by Eq. (4) and transition state values from Eq. (5) respectively.

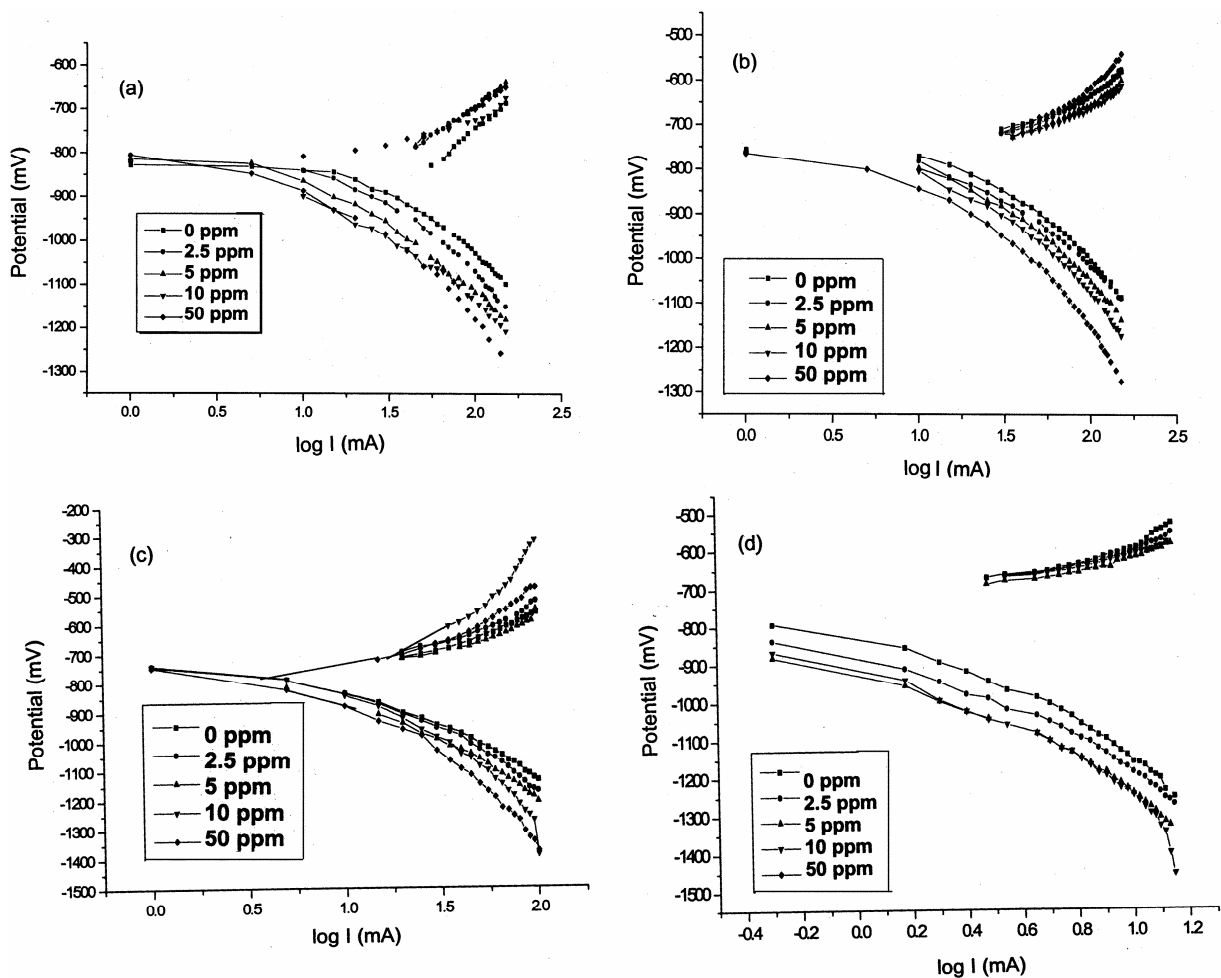


Fig. 2–Polarization curves for aluminium in absence and presence of various concentrations of the inhibitor (a) 1.5 M HCl, (b) 1.0 M HCl, (c) 0.5 M HCl and (d) 0.1 M HCl

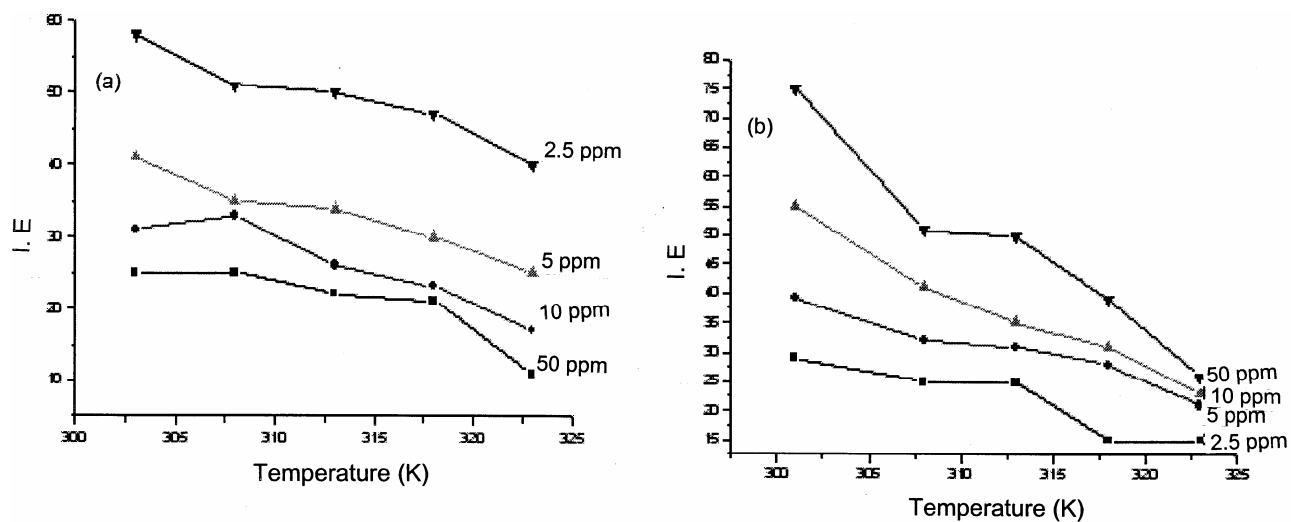


Fig. 3–Plot of I.E versus temperature for the corrosion inhibition of Al by 2-chloronicotinic acid in, (a) 1.5 M and (b) 2 M HCl

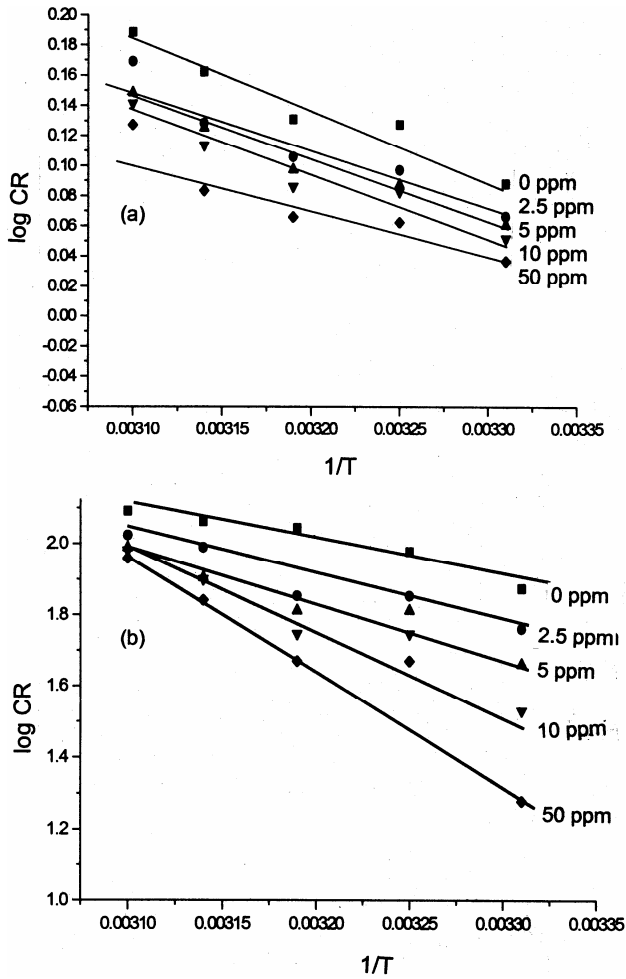


Fig. 4–Plot of log CR versus 1/T for the corrosion inhibition of Al by 2-chloronicotinic acid in (a) 1.5 M HCl and (b) 2 M HCl

$$\text{Log CR} = -\frac{E_a}{1.303 RT} + \log A \quad \dots (4)$$

$$\log \frac{\text{CR}}{T} = \log \frac{R}{Nh} + \frac{\Delta S^\ddagger}{2.303R} - \frac{\Delta H^\ddagger}{2.303RT} \quad \dots (5)$$

where CR is the corrosion rate, E_a is energy of activation, ΔS^\ddagger is entropy of activation, ΔH^\ddagger is enthalpy of activation, h is Planks constant, N is Avogadro number. According to Eq. (4) energy of activation can be obtained from the slope of the plot log CR versus 1/T (Fig. 4a and 4b), and ΔH^\ddagger and ΔS^\ddagger from the slope and intercepts¹⁷ of the plot of log CR/T versus 1/T (Fig. 5a and 5b), since slope = $(\Delta H^\ddagger/2.303R)$ and intercept = $\log R/Nh + (\Delta S^\ddagger /2.303R)$ [using Eq. (5)] (Table 1). The free energy of activation, ΔG^\ddagger was calculated from the Eq. $\Delta G^\ddagger = - RT \log CR$ (Table 2).

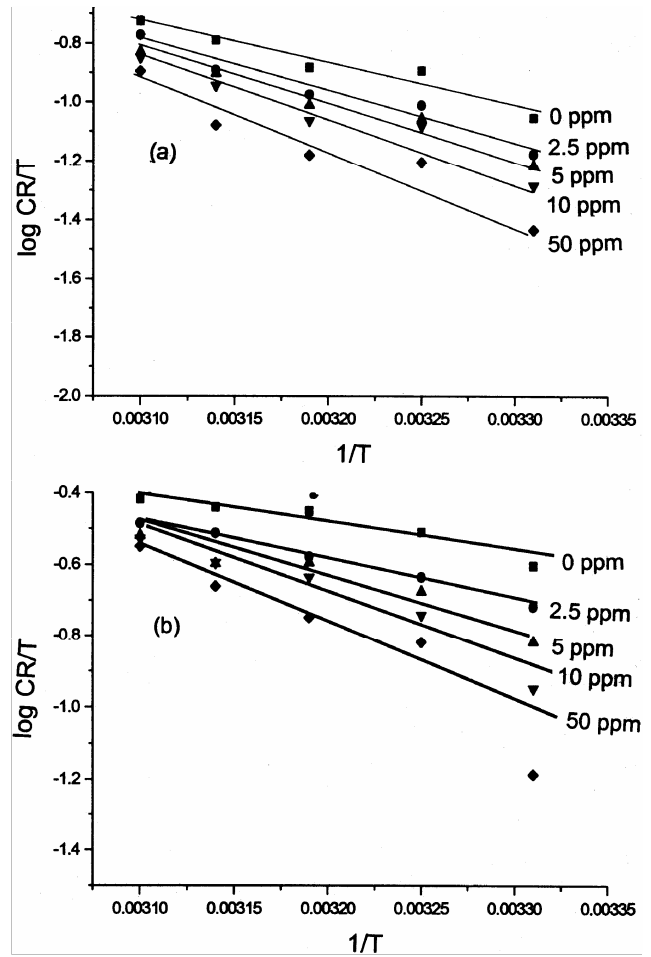


Fig. 5–Plot of log CR/T versus 1/T for the corrosion inhibition of Al by 2-chloronicotinic acid in (a) 1.5 M HCl and (b) 2 M

Table 1–Values of activation energy (E_a), enthalpy of activation (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) for corrosion of Al in HCl. at various inhibitor concentrations

[Inhibitor] (ppm)	E_a (KJ/mole)	ΔH^\ddagger (KJ/mole)	$-\Delta S^\ddagger$ (J/K/mole)
1.5 M HCl			
0.0	28.60	27.59	125.89
2.5	34.17	33.47	108.92
5.0	36.52	33.64	109.07
10.0	37.22	36.28	101.41
50.0	40.47	43.12	81.79
2.0 M HCl			
0.0	19.07	16.33	154.53
2.5	23.68	21.32	140.52
5.0	26.77	24.55	31.27
10.0	37.91	36.09	95.27
50.0	55.54	52.24	45.6

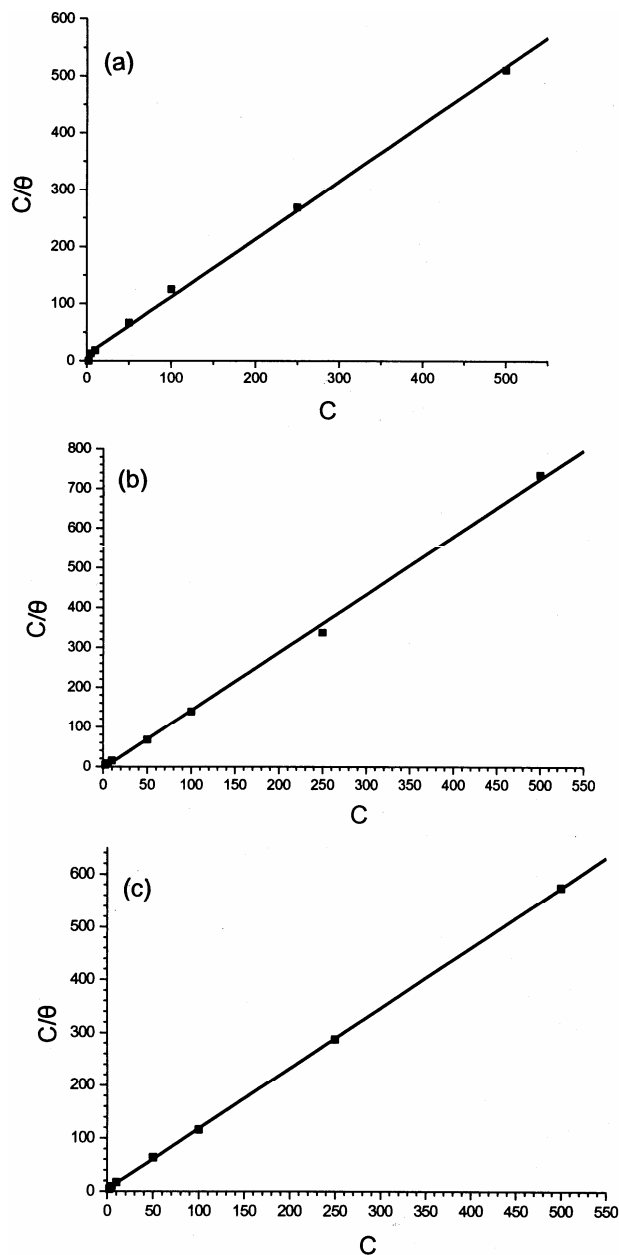
Table 2—Values of free energy of activation (ΔG^\ddagger) for corrosion of Al in HCl at various inhibitor concentrations

[Inhibitor] (ppm)	$-\Delta G^\ddagger$ (KJ/mole)				
	301 K	308	313 K	318 K	323 K
1.5 M HCl					
0.0	8.2	9.4	9.7	10.4	10.9
2.5	7.5	8.7	9.1	9.8	10.6
5.0	7.3	8.3	8.9	9.7	10.4
10.0	6.9	8.3	8.6	9.5	10.1
50.0	6.0	7.6	7.9	8.7	9.5
2.0 M HCl					
0.0	10.79	11.658	12.24	12.55	12.731
2.5	10.14	10.921	11.48	12.106	12.316
5.0	9.585	10.681	11.38	11.589	12.106
10.0	8.819	10.298	11.138	11.564	12.057
50.0	7.367	9.843	10.465	11.205	11.923

From the above data it is clear that the energy of activation for inhibited solution was greater than that of uninhibited solution. Energy of activation increased with increase in the concentration of the inhibitor. This indicated a physical adsorption of the inhibitor molecules on the surface of the metal¹⁵. Further, it was found that enthalpy of activation (ΔH^\ddagger) was low in the absence of the inhibitor and increased with increase in the concentration of the inhibitor. The entropy of activation (ΔS^\ddagger) in the presence and absence of the inhibitor was highly negative that could lead to infer that, activated complex represented association rather than dissociation, i.e. increase in the disorder takes place on going from reactants to activated complex¹⁸. Free energy of activation (ΔG^\ddagger) was negative and decreased with increase in the concentration of the inhibitor depicting decrease in CR. Similarly with increase in the temperature, ΔG^\ddagger value became more negative showing increase in CR, which supported Arrhenius relationship of temperature and reaction rate.

Adsorption isotherms

The plot of concentration of the inhibitor (C) versus C/θ , was found to be linear (Fig. 6a-6c) suggesting the fact that inhibition followed Langmuir adsorption isotherm as stated earlier in case of 2 M HCl, 1.5 M HCl and 1 M HCl, whereas further decrease in the concentration of HCl found to deviate from Langmuir adsorption isotherm (Fig. not shown). Further, the volume of the species required to occupy the surface by one molecular depth, V_m was calculated from the slope of the plot and from which number of molecules used to cover the surface by one molecular depth was calculated¹⁹ (Table 3).

Fig. 6—Plot of C/θ versus C for corrosion inhibition of Al by 2-chloronicotinic acid in HCl; (a) 2 M HCl, (b) 1.5 M HCl and (c) 1 M HClTable 3—Values of V_m and number of molecules covering the surface area

[HCl] (M)	V_m	No. of molecules covering surface area of one molecular depth
2	0.9896	2.66×10^{19}
1.5	0.6868	1.8463×10^{19}
1	0.7162	1.9254×10^{19}
0.5	1.7959	4.828×10^{19}
0.1	1.7863	4.8022×10^{19}

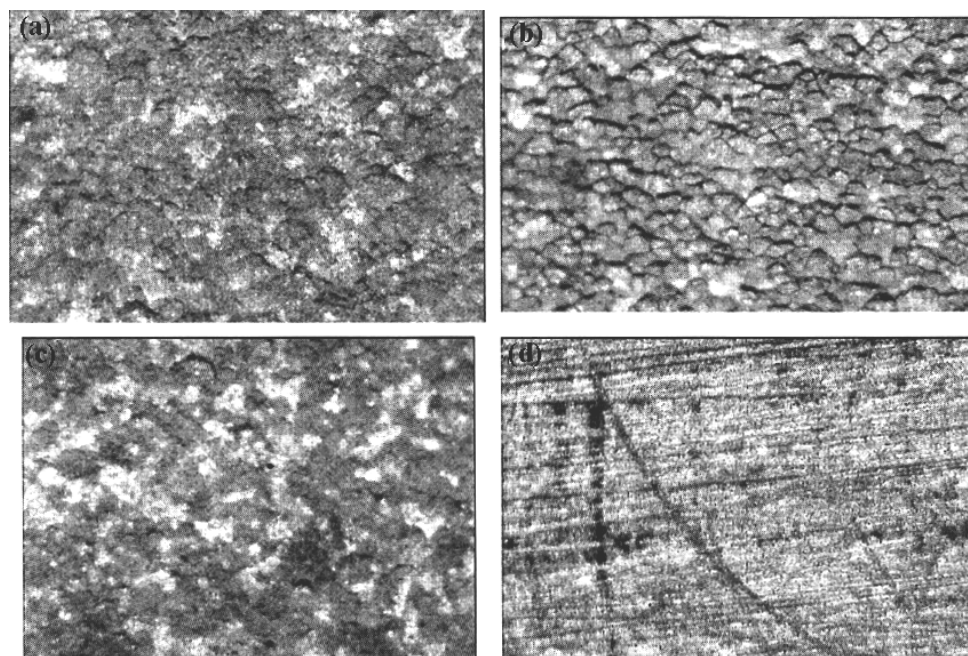


Fig. 7–Motic images of aluminium coupon in: (a) 1 M HCl (b) 1 M HCl containing 50 ppm of the inhibitor; (c) 1.5 M HCl (d) 1.5 M HCl containing 500 ppm of the inhibitor

Microphotographs

The microphotographs of the aluminium coupons were taken after corrosion in the presence of the inhibitor and in the absence of the inhibitor using motic system (magnification-40 \times) (Fig. 7). From the photographs it is clear that, surface of Al remains in good condition in presence of the inhibitor than in the absence of the inhibitor. Thus confirmed the inhibiting ability of the used inhibitor.

Conclusion

The 2-chloronicotinic acid acts as an efficient inhibitor for corrosion of Al in hydrochloric acid medium. The inhibition efficiency increased with increase in the concentration of the inhibitor, but decreased with increase in temperature. The increase in concentration of the inhibitor decreased corrosion current indicating increase in corrosion inhibition. The inhibitor was adsorbed on the surface of the metal and adsorption followed Langmuir adsorption isotherm at higher concentration of the acid. The values of thermodynamic parameters (E_a , $\Delta H^\#$, $\Delta S^\#$, $\Delta G^\#$) also support the observed trend.

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