Inhibiting and accelerating effects of aminophenols on the corrosion and permeation of hydrogen through mild steel in acidic solutions

S. RENGAMANI*, S. MURALIDHARAN, M. ANBU KULANDAINATHAN, S. VENKATAKRISHNA IYER

R.T. Lab, EEB Division, Central Electrochemical Research Institute, Karaikudi, Tamilnadu-623 006, India
Department of Chemistry, Sri Paramakalyani College, Alwarkurchi-627 412, India

The influence of aminophenols on the corrosion and hydrogen permeation of mild steel in 1 M HCl and 0.5 M H_2SO_4 has been studied using weight loss and gasometric measurements and various electrochemical techniques. All the isomers of aminophenol inhibit the corrosion of mild steel in 1 M HCl and accelerate it in 0.5 M H_2SO_4. They behave predominantly as cathodic inhibitors. Aminophenols, except PAP in 1 M HCl, enhance the permeation current in both the acids. The adsorption of PAP on the mild steel surface in 1 M HCl obeys the Langmuir adsorption isotherm. Surface analysis and ultraviolet spectral studies are also carried out to establish the mechanism of corrosion inhibition and acceleration of mild steel in acidic solutions.

1. Introduction

A study of the mechanism of the action of corrosion inhibitors has relevance both from the point of view of the formulation of new inhibitors and also for their effective use [1]. Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Inhibitors are generally used in these processes to control the metal dissolution as well as acid consumption. HCl and H_2SO_4 are widely used in the pickling of steel and ferrous alloys. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. Although sulphur-containing compounds are preferred for H_2SO_4, nitrogen-containing compounds function more effectively in HCl. The influence of organic compounds containing nitrogen on the corrosion of mild steel in acidic solutions has been investigated by several workers [2–4]. Aminophenols have been tried as inhibitors for the corrosion of brass in HNO_3 [5, 6], copper in trichloroacetic acid [7] and aluminium in NaOH [8]. In the present study the influence of aminophenols on the corrosion inhibition and hydrogen permeation of mild steel in acidic solutions has been studied using self corrosion and gasometric studies and various electrochemical techniques such as hydrogen permeation studies, galvanostatic polarisation and a.c. impedance measurements.

2. Experimental details

Mild steel strips containing 0.07%C, 0.08%P, 0.034%Mn, no sulphur and the remainder iron and of size 5 cm × 2 cm × 0.025 cm were used for the measurement of weight loss, gasometric and hydrogen permeation studies. Strips were mechanically polished and degreased with trichloroethylene before use. A cylindrical mild steel rod of the same composition, embedded in Araldite with an exposed area of 0.283 cm², was used for galvanostatic polarisation and impedance measurements. The electrode was polished using different grades of emery paper and degreased. AR grade HCl and H_2SO_4 were used for preparing solutions. Isomers of aminophenol (viz. ortho-(OAP), meta-(MAP), para-(PAP)) used were of high purity Loba Chemie preparation. All solutions were prepared using triple distilled water.

Weight loss and gasometric studies were carried out as described elsewhere [9, 10]. Inhibition efficiencies for different concentrations of aminophenols were calculated both from weight loss values and the volume of gas collected in the absence and presence of aminophenols at a temperature of 30 ± 2° C. In the case of OAP and PAP, concentrations of more than 20 mM could not be used, because of the very low solubility in both acids. In the case of MAP a concentration as high as 100 mM was used.

Galvanostatic polarisation experiments were carried out in the range 0.1 to 100 mA cm⁻² at a temperature of 30 ± 1° C. A platinum foil of 3 cm × 3 cm was used as the auxiliary electrode and Hg/Hg₂Cl₂/1 M HCl, Hg/Hg₂SO₄/0.5 M H_2SO_4 were used as reference electrodes. The solution was stirred using a magnetic stirrer.

The hydrogen permeation was measured using an adaptation of Devanathan and Stachurski's two-compartment cell as described elsewhere [11]. Double layer capacitance values (C_{dl}) were obtained

from impedance measurements as described elsewhere [12]. To identify the change in the nature of the inhibitor, solution analysis was carried out using u.v. spectrophotometry (Hitachi Model U-3400) for the dissolution of mild steel in 0.5 M H_2SO_4 containing OAP (20 mM). The surfaces of corroded and corrosion inhibited mild steel specimens were examined using scanning electron microscopy (JEOL-JSM-35 CF).

3. Results and discussion

Table 1 gives values of the inhibition efficiency obtained from the weight loss and gasometric measurements for different concentrations of aminophenols in 1 M HCl and 0.5 M H_2SO_4. Aminophenols inhibit the corrosion of mild steel in 1 M HCl, whereas they accelerate corrosion in 0.5 M H_2SO_4. It is observed that they give more inhibition efficiency than aniline in 1 M HCl [13]. This enhanced efficiency may be due to the introduction of an electron releasing –OH group in the benzene ring. In 1 M HCl, for a concentration of 20 mM, aminophenols show corrosion inhibition in the following order: PAP (89%) > MAP (59%) > OAP (42%). The very low value of inhibition obtained for OAP may be due to the fact that it undergoes intermolecular hydrogen bonding, which may lead to a change in its adsorption and consequent inhibitive capacity.

From Table 1 it can be seen that inhibition efficiencies obtained from the two methods for OAP show a considerable difference, in spite of the fact that they were carried out under the same conditions. Higher values of inhibition efficiency are obtained for OAP from gasometric measurements at all concentrations of OAP. This may be due to a decrease in the volume of hydrogen gas collected and may arise from the loss of the gas by dissolution

in HCl containing OAP. It may also be due to the permeation of some hydrogen through the steel membrane.

Aminophenols accelerate the corrosion of mild steel in 0.5 M H_2SO_4 at all concentrations, as is clearly evident from both self corrosion and gasometric experiments. The acceleration of corrosion is greater at lower concentrations and is found to decrease with increase in aminophenol concentrations. The acceleration by aminophenols in 0.5 M H_2SO_4 may be attributed to the following factors: (i) the lowering of overpotential for the cathodic process; (ii) catalytic action of the adsorbed compound on the evolution of hydrogen; and (iii) the formation of readily soluble complexes which lower the overpotential of the cathodic process [14]. Cathodic stimulation may be caused by the ability of amines to produce a catalytic path of lowered activation energy for hydrogen discharge [15]. According to Donahue and Nobe [16] an organic compound may interact with the metal surface in the following ways: (i) through chemisorption on the electrode surface; (ii) through the formation of a more or less stable complex with an intermediate of chemical reaction such as $Fe(OH)_{ads}$, thus definitely removing the intermediate from the dissolution sequence; and (iii) through the formation of a complex having definite oxidative tendency. The corrosion acceleration in the presence of an organic compound is related to oxidative tendency of surface chelates. It takes place until the chelate is adsorbed. If charge transfer occurs with the desorption of a complex ion, the inhibitor will function as a stimulator.

Figure 1 shows the u.v.–visible spectra in the region 200–700 nm with respect to H_2SO_4 as a solvent containing 20 mM OAP (Fig. 1(a)) and H_2SO_4 containing dissolved iron (Fe^{2+}) and OAP (Fig. 1(b)). The spectrum for the solution containing Fe^{2+} is found

Table 1. Inhibition efficiencies for various concentrations of isomers of aminophenol in 1 M HCl and 0.5 M H_2SO_4 from weight loss and gasometric measurements

| *Inhibitor concentration* /mM	*Inhibition efficiency/%*			
	1 M HCl		*0.5 M H_2SO_4*	
	Weight loss	*Gasometric*	*Weight loss*	*Gasometric*
(i) *o*-Aminophenol				
3.3	68.4	74.7	—	—
5.0	73.9	76.4	−98.5	−93.2
10.0	62.9	79.3	−55.0	−37.3
20.0	41.8	74.7	−54.2	−27.1
(ii) *m*-Aminophenol				
20	59.1	58.1	−245.4	−253.4
50	78.9	79.3	−164.6	−169.5
75	80.7	83.3	−137.6	−138.1
100	82.3	81.8	−45.0	−44.1
(iii) *p*-Aminophenol				
3.3	77.7	76.2	—	—
5.0	81.4	81.8	−177.3	−181.4
10.0	84.3	84.5	−133.5	−131.4
20.0	89.3	88.9	−105.0	−93.2
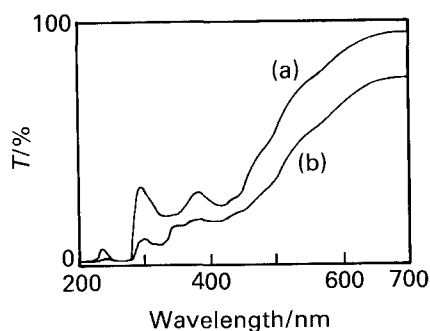
Fig. 1. U.v.-visible spectra for (a) 20 mM OAP in H_2SO_4 and (b) 20 mM OAP in H_2SO_4 containing Fe^{2+}.

to be different from that in the absence of Fe^{2+} in the following respects: (i) the percentage transmission in the solution containing Fe^{2+} is less; and (ii) the ratio of peak height varies in the two spectra.

It is known that OAP in H_2SO_4 exists in the protonated form and its spectrum with H_2SO_4 as reference shown in Fig. 1(a) indicates the characteristic peaks of OAP. Figure 1(b) does not retain these characteristic features (relative ratios) and also shows additional peaks around 350 nm, thereby indicating the formation of new species. The change in the optical density in Fig. 1(b) indicates the consumption of OAP either by a possible reduction or a chemical reaction with Fe^{2+}. The observed fall of transmission at 700 nm is due to the presence of Fe^{2+} in solution. Thus, there is a possibility of chemical involvement of OAP with the metal (Fe^{2+}) in the H_2SO_4 medium.

The better performance of aminophenols in 1 M HCl can be explained in the following way. In aqueous acidic solutions amines exist either as neutral molecules or in the form of cations. Amines may be adsorbed on the metal surface in the form of neutral molecules through a chemisorption mechanism, involving the displacement of water molecules from the metal surface and sharing of electrons between the nitrogen atom and the metal surface [17]. Amines may also adsorb through

electrostatic interactions between the positively charged amine cation and the negatively charged metal surface [18]. In addition, in the case of aromatic amines, π-electron interaction between the aromatic nucleus and the positively charged metal surface may also play a role [19]. It has already been observed that the extent of adsorption of the amine is also influenced by the nature of anions in acidic solutions [20]. The specific adsorption of anions is expected to be more pronounced with anions having a smaller degree of hydration, such as chloride ions. Being specifically adsorbed they create an excess negative charge towards the solution phase, and favours more adsorption of amine cations leading to more adsorption and inhibition of corrosion [21]. There is also a point of view that strong adsorption of organic molecules is not always a direct combination of the organic molecule with the metal surface [22]. In some cases the adsorption occurs through the already adsorbed chloride or sulphate ions which interfere with the adsorbed organic molecules. The lesser interference by sulphate ions may lead to lower adsorption and inhibition of corrosion.

Table 2 gives values of i_{corr}, E_{corr}, b_c and b_a for different concentrations of aminophenols in both the acids, obtained from galvanostatic polarisation studies. The b_c values for different concentrations of aminophenols are enhanced considerably whereas the b_a values do not show much change. An increase in the b_c values indicates an increase in the energy barrier for proton discharge, leading to less gas evolution. The inhibition of corrosion of mild steel in 1 M HCl is under cathodic control and aminophenols act as cathodic inhibitors in 1 M HCl. But, in the case of H_2SO_4, the b_c values do not change although b_a values are found to be less in the presence of aminophenols. So the stimulation of corrosion in the presence of aminophenols may be due to a decrease in b_a which may lead to a decrease in the energy barrier for anodic dissolution.

Table 2. Electrochemical polarization parameters for mild steel in 1 M HCl and 0.5 M H_2SO_4 in the presence of different concentration of isomers of aminophenol

Inhibitor concentration/mM	1 M HCl				0.5 M H_2SO_4			
	E_{corr}/mV	b_c/mV	b_a/mV	$I_{corr}/mA\,cm^{-2}$	E_{corr}/mV	b_c/mV	b_a/mV	$I_{corr}/mA\,cm^{-2}$
Blank	−525	120	60	3.5	−925	130	80	2.6
o-Aminophenol								
5	−520	130	65	2.1	−938	130	65	2.9
10	−530	130	70	2.0	−926	130	65	2.8
20	−528	130	55	1.3	−930	130	65	2.8
m-Aminophenol								
20	−530	150	70	1.6	−930	130	62	3.0
50	−515	160	70	1.1	−924	130	60	2.9
100	−510	140	80	0.9	−920	130	60	2.8
p-Aminophenol								
5	−520	160	65	1.2	−920	130	50	3.2
10	−518	150	70	1.0	−920	130	50	2.9
20	−510	170	70	0.7	−918	130	50	3.0

Table 3. Polarization overvoltage for mild steel in 1 M HCl and 0.5 M H_2SO_4 containing different concentration of aminophenols

Concentration/mM	1 M HCl		0.5 M H_2SO_4	
	Cathodic (η_c)/mV	Anodic (η_a)/mV	Cathodic (η_c)/mV	Anodic (η_a)/mV
Blank	16	12	22	18
o-Aminophenol				
5	64	46	26	18
10	75	54	32	17
20	104	59	26	13
m-Aminophenol				
20	118	81	32	17
50	119	56	30	13
100	148	65	28	16
p-Aminophenol				
5	118	32	26	16
10	151	30	28	18
20	167	51	25	13

The effect of aminophenols on anodic and cathodic overvoltages, when the mild steel is polarised to $10\,mA\,cm^{-2}$ in 1 M HCl and 0.5 M H_2SO_4 is given in Table 3. Aminophenols are found to enhance the cathodic overvoltage (η_c) to a greater extent than the anodic overvoltage (η_a) in 1 M HCl. The observed increase in η_c is due in a large measure to an increase in the cathodic Tafel slope (b_c). So aminophenols serve as cathodic inhibitors in 1 M HCl. The cathodic overvoltage for aminophenols for a concentration of 20 mM follows the order PAP (167) > MAP (118) > OAP (104), which is exactly the same as that for inhibition of corrosion in 1 M HCl. Thus there is a correlation between the overvoltage, hydrogen evolution and corrosion inhibition efficiency. But in 0.5 M H_2SO_4 cathodic overvoltages are enhanced to a lesser extent and this may lead to lesser inhibition of corrosion and, in fact, to more corrosion in the presence of different concentrations of aminophenols.

Hydrogen permeation current against time curves for steel in 1 M HCl and 0.5 M H_2SO_4 in the presence of 20 mM aminophenol are shown in Figs 2 and 3. The permeation current is greater for mild steel in 1 M HCl, because of the more corrosive nature of chloride ions. In the presence of aminophenols (20 mM), only PAP reduces the permeation current, whereas OAP and MAP increase the permeation current. It is seen from the self corrosion studies that all the isomers of aminophenol inhibit corrosion in HCl. So PAP, which shows maximum inhibition of corrosion, reduces the permeation. OAP and MAP, however, which are less inhibitive, enhance the permeation. This may be due to the fact that the –OH group present in the ortho and meta position favours a vertical orientation of the molecule on the
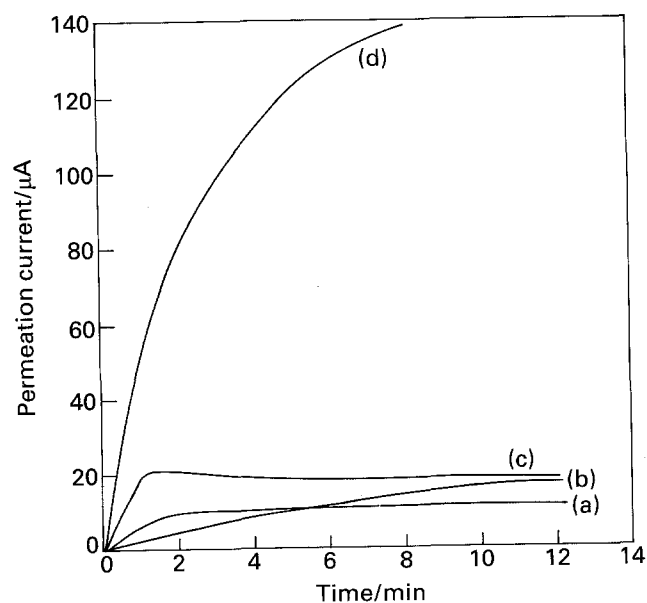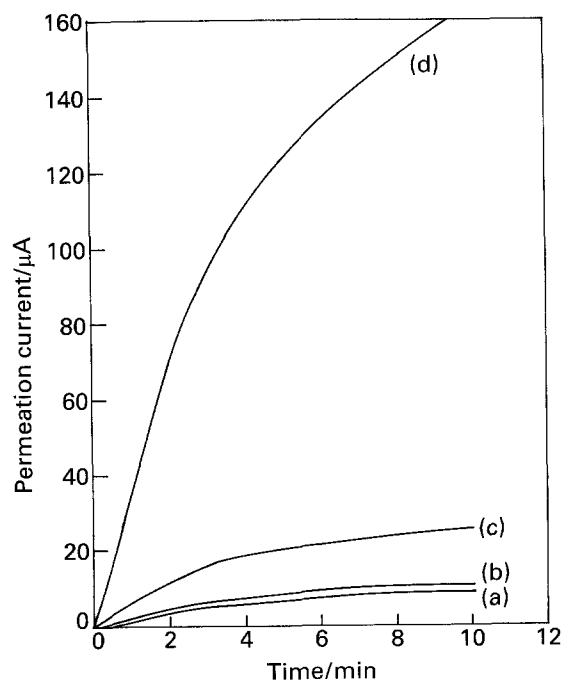

Fig. 2. Hydrogen permeation current against time for mild steel in 1 M HCl containing isomers of aminophenol: (a) 1 M HCl, (b) 1 M HCl + 20 mM PAP, (c) 1 M HCl + 20 mM MAP and (d) 1 M HCl + 20 mM OAP.

Fig. 3. Hydrogen permeation current against time for mild steel in 1 M H_2SO_4 containing isomers of aminophenol: (a) 0.5 M H_2SO_4, (b) 0.5 M H_2SO_4 + 20 mM PAP (c) 0.5 M H_2SO_4 + 20 mM MAP and (d) 0.5 M H_2SO_4 + 20 mM OAP.

Table 4. A comparison of volume of hydrogen (V) collected, cathodic overvoltage (η_c), cathodic Tafel slope (b_c) and hydrogen permeation current (I_p) for mild steel in 1 M HCl and 0.5 M H_2SO_4 containing 20 mM concentration of isomers of aminophenol

System	1 M HCl				0.5 M H_2SO_4			
	V/ml	b_c/mV	η_c/mV	$I_p/\mu A\,cm^{-2}$	V/ml	b_c/mV	η_c/mV	$I_p/\mu A\,cm^{-2}$
Blank	19.8	120	16	18.0	11.8	130	22	8.6
OAP	8.0	130	118	—	15.0	130	26	—
MAP	5.3	150	104	19.8	17.0	130	32	25.0
PAP	2.2	170	167	11.7	22.8	130	25	12.0

metal surface, leading to lower coverage of the metal surface by the molecule. This, in turn, may lead to more permeation of hydrogen through the metal and also less corrosion inhibition. It is seen from Table 4 that more hydrogen is evolved in the case of OAP and MAP and considerably less in the case of PAP. Thus, the presence of OAP and MAP, which are less inhibitive, may lead to the evolution of more hydrogen. By contrast, PAP which is more inhibitive, gives rise to less gas evolution and less permeation current. In this case, then, a definite correlation is observed between the inhibition efficiency and the amount of hydrogen permeated through steel. In 0.5 M H_2SO_4 the presence of all the isomers of aminophenol enhance the permeation current. It has already been observed that aminophenols enhances the corrosion of mild steel in 0.5 M H_2SO_4. This leads to greater evolution of hydrogen, which in turn leads to more permeation of hydrogen through the steel.

Impedance diagrams obtained for the frequency range 10 mHz to 10 kHz at the open circuit potential for mild steel in both the acids are shown in Figs 4 and 5. The impedance diagrams are not perfect semicircles and the difference has been attributed to frequency dispersion [23]. The charge transfer resistance, R_t, values are calculated from the differences in impedance at lower and higher frequencies as suggested by Haruyama and Tsuru [24]. These values of R_t have been substituted in the Stern–Geary equation to obtain the corrosion current.

$$I_{corr} = \frac{(b_a b_c)}{2.303 R_t (b_a + b_c)} \qquad (1)$$

To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum ($-Z''$ max) is found and C_{dl}

values are obtained from the equation

$$f(-Z'' \text{max}) = \frac{1}{2\pi C_{dl} R_t} \qquad (2)$$

Table 5 gives values of R_t, i_{corr} and C_{dl} for mild steel in 1 M HCl and 0.5 M H_2SO_4, alone and in the presence of isomers of aminophenol (20 mM). i_{corr} values are greater for HCl than for H_2SO_4. It is also found that the values of i_{corr} for 1 M HCl in the presence of aminophenols follows the order ortho > meta > para, which is in agreement with that obtained from polarization measurements. Very high values of C_{dl} are obtained for 0.5 M H_2SO_4 in the presence of aminophenols (20 mM) due to the acceleration of corrosion and are not reported here. The corrosion accelerating effect of aminophenols in 0.5 M H_2SO_4 has not been revealed from the values of i_{corr} given in this Table. This observed discrepancy can be explained as follows. The corrosion rate of mild steel in 0.5 M H_2SO_4 increases gradually over longer periods of immersion even in the presence of inhibitors. Prolonged immersion of mild steel in the acid, allows the cathodic hydrogen evolution to increase, presumably, as more cathodic sites are exposed to the corrosion process. This may be the possible reason why such electrochemical techniques such as impedance studies in which measurements are taken in a short time fails to reveal the acceleration of corrosion. However in other techniques such as weight loss, gasometry and polarization studies longer periods of immersion allow the cathodic hydrogen evolution kinetics to increase and more cathodic sites are exposed to the corrosion process.

To establish whether the inhibition is due to the formation of a phenolic film on the metal surface, through chemisorption, scanning electron photographs were taken. It was found that an adsorbed
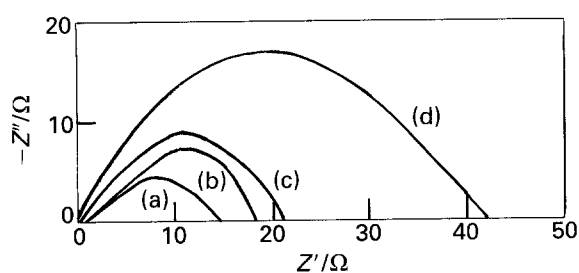

Fig. 4. Impedance diagrams for mild steel in 1 M HCl in the presence of isomers of aminophenol: (a) 1 M HCl, (b) 1 M HCl+ 20 mM OAP, (c) 1 M HCl + 20 mM MAP and (d) 1 M HCl + 20 mM PAP.
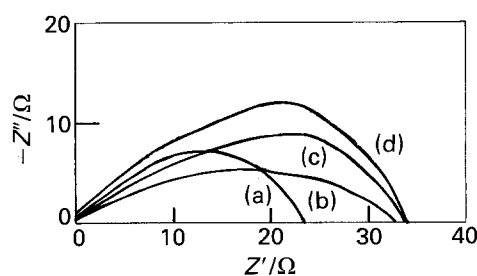

Fig. 5. Impedance diagrams for mild steel in 0.5 M H_2SO_4 in the presence of isomers of aminophenol: (a) 0.5 M H_2SO_4, (b) 0.5 M H_2SO_4 + 20 mM OAP, (c) 0.5 M H_2SO_4 + 20 mM MAP and (d) 0.5 M H_2SO_4 + 20 mM PAP.

Table 5. Impedance measurements for mild steel in 1 M HCl and 0.5 M H₂SO₄ with and without the isomers of aminophenol (20 mM)

System	1 M HCl			0.5 M H₂SO₄		
	$R_t/\Omega\,cm^2$	$I_{corr}/mA\,cm^{-2}$	$C_{dl}/\mu F\,cm^{-2}$	$R_t/\Omega\,cm^2$	$I_{corr}/mA\,cm^{-2}$	$C_{dl}/\mu F\,cm^{-2}$
Blank	4.10	4.35	314	6.5	3.30	244
OAP	5.20	3.40	274	8.8	2.40	—
MAP	5.90	2.90	153	9.6	2.43	—
PAP	12.00	0.70	80	9.6	2.53	—

phenolic layer is formed on mild steel both from 1 M HCl and 0.5 M H₂SO₄ solutions which inhibit the corrosion of mild steel in acid. The protective activity of PAP for mild steel in HCl solutions was retained, when specimens dipped in inhibited acids, were transferred into fresh acid without inhibitor. This observation clearly proves that the inhibition is due to the formation of an insoluble stable phenolic film through the process of chemisorption on the metal surface.

The surface coverage (θ) for different concentrations of PAP in 1 M HCl has been evaluated from weight loss and impedance measurements using the equations.

$$\theta = 1 - \frac{W_{inh}}{W} \tag{3}$$

$$\theta = 1 - \frac{C_{dl(inh)}}{C_{dl}} \tag{4}$$

The data were tested graphically for fitting a suitable isotherm. Values of θ obtained using Equation 3 were used, in the plot of c/θ against c. Similarly θ against $(1 - (I_{corr(inh)}/I_{corr}))$ graph was plotted using θ values obtained from Equation 4. In both cases a straight line was observed clearly proving that the adsorption of PAP from HCl solutions on the mild steel surface obeys a Langmuir adsorption isotherm.

4. Conclusion

The following points can now be made:
(i) Aminophenols inhibit the corrosion of mild steel in 1 M HCl, but accelerate it in 0.5 M H₂SO₄.
(ii) They behave as cathodic inhibitors in HCl.
(iii) With the exception of the para isomer in 1 M HCl aminophenols enhance the permeation of hydrogen through mild steel.
(iv) The inhibition of corrosion of mild steel in HCl solutions by PAP may be due to the formation of a chemisorbed phenolic film on the metal surface.
(v) The adsorption of the PAP from 1 M HCl on the mild steel surface obeys a Langmuir adsorption isotherm.

References

[1]   G. Trabanelli, *Corrosion* **47** (1991) 410.
[2]   G. Schmitt, *Br. Corros. J.* **19** (1984) 165.
[3]   J. M. Sykes, *ibid.* **25** (1990) 175.
[4]   P. Chatterjee, M. K. Banerjee and K. P. Mukherjee, *Indian J. Technol.* **29** (1991) 191.
[5]   M. N. Desai, M. K. Gandhi and J. S. Joshi, *Trans. SAEST* **9** (1974) 173.
[6]   M. N. Desai, B. C. Thacker and P. M. Chhaya, *J. Indian Chem. Soc.* **52** (1975) 930.
[7]   N. K. Patel, A. B. Patel and J. C. Vora, *Trans. SAEST* **8** (1973) 3.
[8]   J. D. Patel and R. H. Modi, *Br. Corros. J.* **14** (1979) 109.
[9]   N. Subramanyan, S. Venkatakrishna Iyer and V. Kapali, *Trans. SAEST* **15** (1980) 251.
[10] P. B. Mathur and T. Vasudevan, *Corrosion* **38** (1982) 17.
[11] M. A. V. Devanathan and Z. Stachurski, *Proc. Roy. Soc., A* **270** (1962) 90.
[12] M. Natesan and S. Venkatakrishna Iyer, Proc. 5th Asian Pacific Corrosion Control Conference, Australia, Vol. 1 (1987) p. 351.
[13] S. Rengamani, Ph.D Thesis, Madurai-Kamaraj University (1987) Tamilnadu, India.
[14] A. Frignani, G. Trabanelli and F. Zucchi, Proc. 4th European Symposium on Corrosion Inhibitors, Ann. Univ. Ferrara, Italy (1975) p. 652.
[15] T. P. Hoar and R. P. Khera, Comptes Rendus du Symposium Européen sur les Inhibit de Corros, Ann. Univ. Ferrara, Italy, N.S. sez. V, suppl. N3 (1961) p. 73.
[16] F. M. Donahue and K. Nobe, *J. Electrochem. Soc.* **114** (1967) 1012.
[17] N. Hackerman and A. C. Makrides, *J. Phys. Chem.* **59** (1955) 707.
[18] C. A. Mann, *Trans. Electrochem. Soc.* **69** (1936) 105.
[19] M. A. Gerovich and G. F. Rybalchenko, *Zh. Fiz. Khim.* **32** (1958) 109.
[20] Z. A. Foroulis, Proc. 6th European Symposium on Corrosion Inhibitors, Ann. Univ. Ferrara, Italy, N. S., sez. V, Suppl. N.8 (1985) p. 130.
[21] Z. A. Iofa and G. N. Tomashov, *Zh. Fiz. Khim.* **34** (1960) 1036.
[22] T. Murakawa and N. Hackerman, *Corros. Sci.* **4** (1964) 387.
[23] F. Mansfeld, *Corrosion* **37** (1981) 301; *ibid.* **38** (1982) 570.
[24] T. Tsuru and S. Haruyama, *Boshoku Gijutsu*, (*J. Japan Soc. Corros. Engng*) **27** (1978) 573.