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Influence of anions on the performance of isomers of aminobenzoic acid on the corrosion inhibition and hydrogen permeation through mild steel in acidic solutions

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The influence of aminobenzoic acids on the corrosion and hydrogen permeation through 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 three isomers of aminobenzoic acid inhibit the corrosion of mild steel both in HCl and H_2SO_4 in the order ortho > meta > para. It is observed that the inhibition is greater in HCl than in H_2SO_4. The predominant behaviour is in the cathodic inhibitor mode. These compounds reduce the permeation current in 1 M HCl and enhance it in 0.5 M H_2SO_4. The adsorption of these compounds on mild steel in 1 M HCl and 0.5 M H_2SO_4 obeys Langmuir's adsorption isotherm.

1. Introduction

HCl and H_2SO_4 are widely used for pickling ferrous alloys and steel. Inhibitors are generally used in industrial processes to control both metal dissolution and acid consumption. The influence of organic compounds containing nitrogen on the corrosion of mild steel in acidic solutions has been studied by several workers [1–5]. Aminobenzoic acids have been tried as inhibitors for the corrosion of iron in HNO_3 [6], brass in HNO_3 [7], iron in aerated sodium sulfate aqueous solution [8] and iron in HCl [9]. In the present study the influence of aminobenzoic acids on corrosion inhibition and hydrogen permeation through mild steel in acidic solutions was studied using self corrosion and gasometric studies and various electrochemical techniques such as hydrogen permeation, galvanostatic polarization 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 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 cm^2 was used for galvanostatic polarization and impedance measurements. The electrode was polished using different grades of emery paper and degreased. AR grade HCl and H_2SO_4 was used for preparing solutions. All the solutions were prepared using triple distilled water.

Ortho aminobenzoic acid (OAB), meta aminobenzoic acid (MAB) and para aminobenzoic acid (PAB) were of Riedel make (Germany), Sisco research lab (Bombay) and BDH grade (London), respectively. The structural formulae for the isomers of aminobenzoic acid are given in Table 1.

Weight loss and gasometric studies were carried out as described elsewhere [10] and a brief description of the gasometric set up is as follows. The gasometric instrument consists of three parts. The first part consists of a thermostatic bath to maintain the system at a constant temperature. The second part consists of the reaction cell with provision for inserting test specimens into the solution. The third part consists of a gas collector vertical column tubes made up of standard capacity graduated burettes. Inhibition efficiencies for different concentrations of aminobenzoic acids were calculated both from weight loss values and the volume of gas collected in the absence and presence of aminobenzoic acids at a temperature of 30 ± 1 °C. In the case of meta and para isomers, a concentration more than 75 mM could not be used for studies using 0.5 M H_2SO_4, because of solubility limits.

Galvanostatic polarization 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 dimensions 3 cm × 3 cm was used as the auxiliary electrode and $Hg/Hg_2Cl_2/1$ M HCl and $Hg/Hg_2SO_4/0.5$ M H_2SO_4

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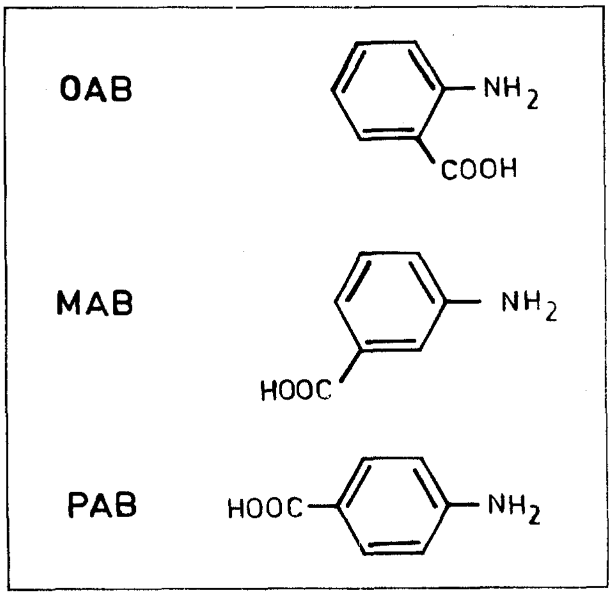
Table 1. Structural formulae for isomers of aminobenzoic acid



were used as reference electrodes. The solution was stirred using a magnetic stirrer.

The hydrogen permeation current was measured using an adaptation of a Devanathan and Stachurski's two compartment cell as described elsewhere [11]. Charge transfer resistance (R_t) and double layer capacitance values (C_{dl}) were obtained from impedance measurements as described elsewhere [12].

3. Results and discussion

Table 2 gives the values of inhibition efficiency obtained from weight loss and gasometric measurements and also from electrochemical methods such as polarization and impedance techniques for different concentrations of aminobenzoic acids in 1 M HCl and 0.5 M H_2SO_4. All the isomers inhibit the corrosion of mild steel in both acids. The inhibition of corrosion is greater in HCl than H_2SO_4 are reported earlier [5, 13]. The better performance of aminobenzoic acids in 1 M HCl can be explained as follows. In aqueous acidic solutions, amino compounds exist either as neutral molecules or in the form of cations. Amines can be considered to 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 [14]. Amines can also adsorb through electrostatic interaction between the positively charged amine cation and the negatively charged metal surface. In addition, in the case of aromatic amines, π-electron interaction between the aromatic molecules and the positively charged metal surface may also play a role [15]. The extent of adsorption of the amine is influenced by the nature of the anions in acidic solutions [5, 13]. 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 favour more adsorption of amine cations, leading to greater inhibition [16]. It is also possible that stronger adsorption of organic molecules is not always a direct combination of organic molecules with the metal surface [17]. In some cases the adsorption occurs through the already adsorbed chloride or sulfate ions which interfere with adsorbed organic molecules. The lesser interference by sulfate ions results in lower adsorption and inhibition of corrosion.

The difference in the extent of inhibition shown by isomers can be explained as follows. The tendency to form amine cations in acidic solutions is enhanced by the electron withdrawing effect of the carboxylic

Table 2. Inhibition efficiencies for various concentrations of isomers of aminobenzoic acid in 1 M HCl and 0.5 M H_2SO_4 from different techniques

Inhibitor conc.	*Inhibition efficiency/%*							
	1 M HCl				*0.5 M H_2SO_4*			
/mM	*Weight loss*	*Gasometric*	*Polarization*	*EIS*	*Weight loss*	*Gasometric*	*Polarization*	*EIS*
OAB								
20	70.5	70.7	71.4	71.1	48.8	50.8	46.2	45.5
50	76.6	75.8	77.1	75.5	70.0	67.0	62.0	63.6
75	82.5	79.3	–	–	74.2	76.2	–	–
100	88.4	87.9	83.0	80.0	76.9	78.8	77.0	69.7
MAB								
20	67.3	67.3	65.7	64.4	39.5	39.7	34.6	*
50	72.3	71.8	74.3	71.1	59.2	60.9	57.8	48.5
75	80.7	78.8	–	–	72.7	72.7	73.1	57.5
100	86.8	86.4	77.0	73.3	–	–	–	–
PAB								
20	30.9	30.8	35.5	35.2	34.3	34.9	23.1	*
50	57.9	58.1	62.8	60.0	54.6	56.2	50.0	36.4
75	76.8	75.8	–	–	68.5	70.3	69.2	54.5
100	79.5	79.3	74.3	71.1	–	–	–	–

* acceleration

Table 3. 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 aminobenzoic acid

Inhibitor conc. /mM	*1 M HCl* E_{corr} /mV	b_c /mV	b_a /mV	I_{corr} /mA cm^{-2}	*0.5 M H_2SO_4* 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
OAB								
20	−526	110	80	1.0	−916	150	75	1.4
50	−520	120	80	0.8	−904	160	75	1.0
100	−520	138	80	0.6	−890	165	80	0.6
MAB								
20	−520	100	60	1.2	−920	140	78	1.7
50	−510	110	60	0.9	−906	145	80	1.1
75	–	–	–	–	−902	150	80	0.7
100	−500	125	60	0.8	–	–	–	–
PAB								
20	−518	100	60	2.3	−918	130	70	2.0
50	−512	105	60	1.3	−912	140	70	1.3
75	–	–	–	–	−912	145	75	0.8
100	−500	115	60	0.9	–	–	–	–

substituent present in aminobenzoic acids. Ortho aminobenzoic acid gives rise to the amine cation more easily than meta and para isomers, due to the well known 'ortho effect' in the ortho isomer [18, 19]. This leads to more adsorption of the ortho isomer followed by meta and para isomers in decreasing order. Electrocapillary studies on mercury have clearly shown that the extent of adsorption of aminobenzoic acids follows the order: ortho > meta > para [20].

The corrosion kinetic parameters such as I_{corr}, E_{corr}, b_{c} and b_{a} derived from galvanostatic polarization curves for different concentrations of aminobenzoic acids in both acids are given in Table 3. The addition of aminobenzoic acids to acidic solutions shifts E_{corr} to more positive values, indicating that these amines cause anodic polarization. It is also found that values of b_{c} are altered in the presence of different concentrations of isomers in HCl. Anodic Tafel slopes (b_{a}) remain almost unaffected. In H_2SO_4, there is only a small change in the anodic Tafel slope, but the cathodic Tafel slope is considerably enhanced. The

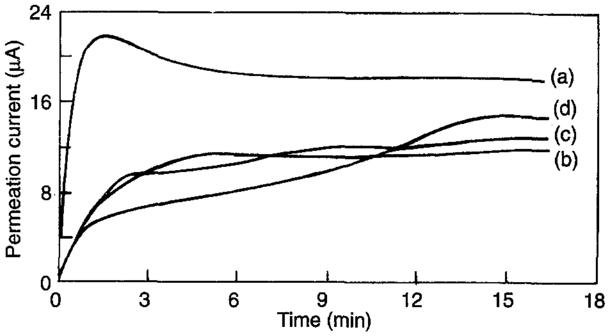


Fig. 1. Hydrogen permeation current against time graphs for mild steel in 1 M HCl containing isomers of aminobenzoic acid. Concentrations: (a) 1 M HCl, (b) 1 M HCl+20 mM OAB, (c) 1 M HCl+20 mM MAB, and (d) 1 M HCl+20 mM PAB.

Table 4. Polarization overvoltage for mild steel in 1 M HCl and 0.5 M H_2SO_4 containing different concentration of aminobenzoic acid at a constant current density

Inhibitor conc. /mM	*1 M HCl* Cathodic (η_c) /mV	Anodic (η_a) /mV	*0.5 M H_2SO_4* Cathodic (η_c) /mV	Anodic (η_a) /mV
Blank	16	12	22	18
OAB				
20	55	37	128	48
50	88	62	178	59
100	93	61	204	70
MAB				
20	26	15	79	39
50	63	39	110	48
75	–	–	126	53
100	95	75	–	–
PAB				
20	21	16	73	33
50	41	20	86	42
75	–	–	112	51
100	59	40	–	–

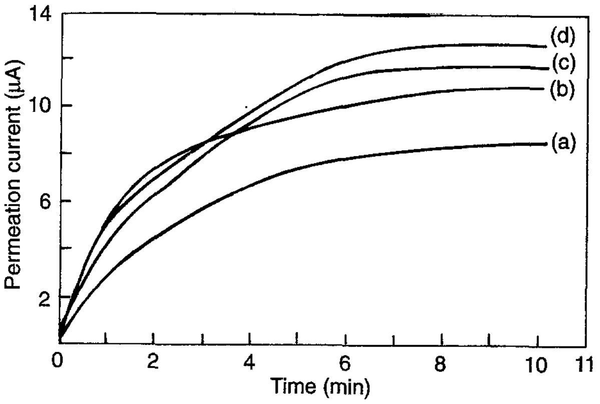


Fig. 2. Hydrogen permeation current against time graphs for mild steel in 0.5 M H_2SO_4 containing isomers of aminobenzoic acid. Concentrations: (a) 0.5 M H_2SO_4, (b) 0.5 M H_2SO_4 + 20 mM OAB, (c) 0.5 M H_2SO_4 + 20 mM MAB, and (d) 0.5 M H_2SO_4 + 20 mM PAB.

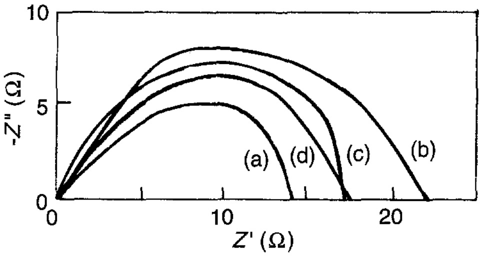


Fig. 3. Impedance diagrams for mild steel in 1 M HCl in the presence of isomers of aminobenzoic acid. Concentrations: (a) 1 M HCl, (b) 1 M HCl + 20 mM OAB, (c) 1 M HCl + 20 mM MAB, and (d) 1 M HCl + 20 mM PAB.

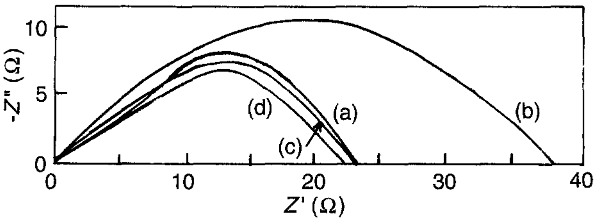


Fig. 4. Impedance diagrams for mild steel in 0.5 M H_2SO_4 in the presence of isomers of aminobenzoic acid. Concentrations: (a) 0.5 M H_2SO_4, (b) 0.5 M H_2SO_4 + 20 mM OAB, (c) 0.5 M H_2SO_4 + 20 mM MAB, and (d) 0.5 M H_2SO_4 + 20 mM PAB.

presence of aminobenzoic acids reduces I_{corr} in both acids in the order: ortho > meta > para.

The effect of aminobenzoic acids on anodic and cathodic overvoltages when mild steel is polarized to 10 mA cm^{-2} in 1 M HCl and 0.5 M H_2SO_4 is given in Table 4. An increasing concentration of aminobenzoic acids enhances the cathodic overvoltage (η_c) to a greater extent than the anodic overvoltage (η_a) in both acids. This shows that aminobenzoic acids serve as cathodic inhibitors in both acids and the values of overvoltage follow the order: ortho > meta > para. This order is in agreement with that of the inhibition efficiency values.

Hydrogen permeation current against time curves for mild steel in 1 M HCl and 0.5 M H_2SO_4 in the presence of 20 mM aminobenzoic acids are shown in Figs 1 and 2. The permeation current is greater for mild steel in 1 M HCl, because of the more corrosive nature of chloride ions. Aminobenzoic acids reduce the permeation current in 1 M HCl. The reduction in permeation current follows the order: ortho > meta > para, in agreement with that obtained for values of inhibition efficiency.

In the case of 0.5 M H_2SO_4, aminobenzoic acids enhance the permeation current. Maximum enhancement of permeation current is shown by para, followed by meta and ortho in decreasing order. Thus the ortho compound which gives maximum inhibition in 0.5 M H_2SO_4 shows least enhancement of permeation current and the para isomer, which shows less inhibition, shows maximum enhancement of permeation current. The meta isomer exhibits intermediate behaviour, both in corrosion inhibition and permeation current enhancement.

Impedance diagrams for the frequency range 10 mHz to 10 kHz at the open circuit potential for mild steel in both acids are shown in Figs 3 and 4. The impedance diagrams are of almost semicircular appearance, but are not perfect semicircles. This difference has been attributed to frequency dispersion [21].

Table 5 gives the values of C_{dl}, R_t and I_{corr} of mild steel in 1 M HCl and 0.5 M H_2SO_4 alone and in the presence of different concentrations of aminobenzoic acids. I_{corr} values are greater for HCl than H_2SO_4 as already observed. The values of I_{corr} for 1 M HCl in the presence of aminobenzoic acids follow the order: ortho > meta > para, which is in agreement with that obtained from polarization experiments. In 0.5 M H_2SO_4, I_{corr} values decrease at all concentrations in the presence of ortho isomers and there is a slight enhancement of I_{corr} values in the presence of meta and para isomers at 20 mM concentrations. But at concentrations more than 20 mM, there is a reduction in I_{corr} values. The difference between I_{corr} values

Table 5. Impedance parameters for mild steel in 1 M HCl and 0.5 M H_2SO_4 with and without the isomers of aminobenzoic acid (20 mM)

System	*1 M HCl*			*0.5 M H_2SO_4*		
	R_t /Ω cm^2	I_{corr} /mA cm^{-2}	C_{dl} /μF cm^{-2}	R_t /Ω cm^2	I_{corr} /mA cm^{-2}	C_{dl} /μF cm^{-2}
Blank	4.1	4.5	314	6.5	3.3	244
OAB						
20	15.4	1.3	142	12.0	1.8	180
50	18.9	1.1	138	18.5	1.2	172
75	22.1	0.9	125	23.4	1.0	160
MAB						
20	10.2	1.6	180	6.4	3.4	248
50	13.0	1.3	165	13.1	1.7	220
75	–	–	–	16.2	1.4	205
100	14.7	1.2	160	–	–	–
PAB						
20	5.6	2.9	221	5.7	3.5	253
50	9.2	1.8	200	9.6	2.1	228
75	–	–	–	14.3	1.5	210
100	13.0	1.3	195	–	–	–

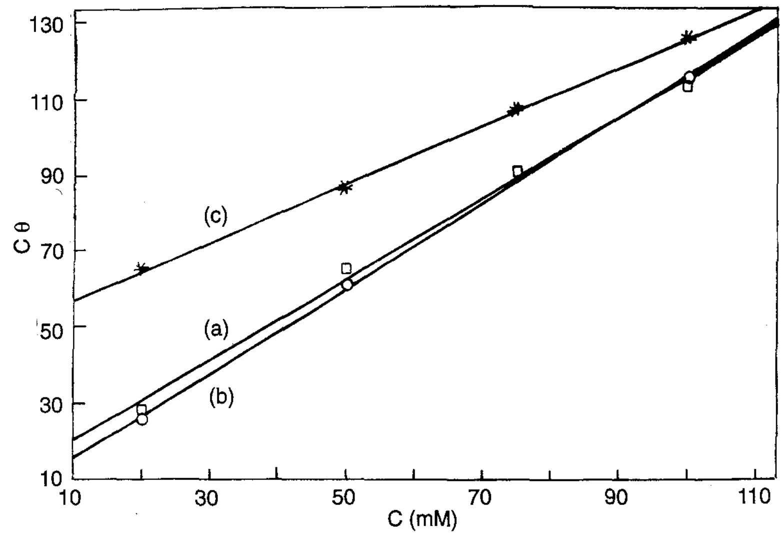


Fig. 5. Langmuir adsorption isotherm plots for mild steel in 1 M HCl containing isomers of aminobenzoic acid: (a) OAB, (b) MAB and (c) PAB.

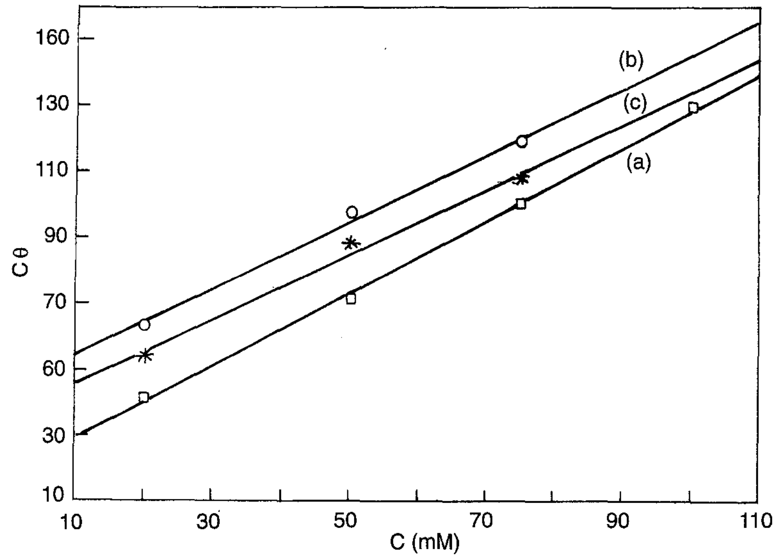


Fig. 6. Langmuir adsorption isotherm plots for mild steel in 0.5 M H_2SO_4 containing isomers of aminobenzoic acid: (a) OAB, (b) MAB and (c) PAB.

obtained by electrochemical techniques may be due to the polarization signal amplitude. The inhibition efficiencies for different concentrations of isomers obtained from impedence techniques are given in Table 2, which show good agreement among the values obtained from different techniques in 1 M HCl; no agreement is observed in 0.5 M H_2SO_4.

The surface coverage (θ) values for different concentrations of aminobenzoic acids, both in 1 M HCl and 0.5 M H_2SO_4, was calculated [10] and these values were graphically tested for fitting a suitable adsorption isotherm. The plot of c/θ against c yields a straight line (Figs 5 and 6) clearly suggesting that the adsorption of aminobenzoic acids from both acids obeys Langmuir's adsorption isotherm.

4. Conclusion

The following conclusions can be made:

(i) Aminobenzoic acids are found to perform well in both HCl and H_2SO_4, with a better performance in 1 M HCl.
(ii) Aminobenzoic acids behave as cathodic inhibitors in both acids.
(iii) They reduce the hydrogen permeation through mild steel in 1 M HCl, but enhance it in 0.5 M H_2SO_4.
(iv) The adsorption of the isomers on mild steel obeys Langmuir's adsorption isotherm.

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