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# Co-adsorption effect of polyaniline and halide ions on the corrosion of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions

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#### Abstract

The synergistic effect of halide ions on the inhibition of corrosion of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions by polyaniline has been studied by polarization and impedance methods. Addition of  $0.5 \times 10^{-3}$  M I<sup>-</sup> ions enhanced the inhibition efficiency of polyaniline at 10 ppm from 53% to 90%. However in the case of bromide and chloride ions, the inhibition efficiency of polyaniline at 50 ppm has been increased from 71% to 90%. The synergism parameter in all cases is found to be greater than 1. The synergistic effect is attributed to enhanced adsorption of polyaniline by the adsorbed halide ions. © 2005 Elsevier B.V. All rights reserved.

Keywords: Iron; Inhibition; Polyaniline; Synergistic effect; Halide ions

## 1. Introduction

Acid solutions are widely used in many industries for pickling, acid cleaning of boilers, descaling and oil well acidizing. To control the undesirable base metal corrosion by these cleaning acids, corrosion inhibitors are employed. The selection of appropriate inhibitors mainly depends on the type of acid, its concentration, temperature, velocity, presence of dissolved solids and the type of metallic materials involved. Organic compounds containing N, O and S groups and compounds with unsaturated  $\pi$  bonds are reported to be most efficient corrosion inhibitors [1-4]. Presence of functional groups such as =NH, -N=N-, -CHO, R-OH, R=R, etc. in the inhibitor molecule [5,6] and also the steric factors, aromaticity, electron density at the donor atoms are found to influence the adsorption of the inhibitor molecule over corroding electrode surface. The role of

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molecular area [7] and molecular weight [8] of the organic molecule on its inhibition efficiency is also reported.

The important prerequisites for a compound to be an efficient inhibitor are: (i) it should form a defect free, compact barrier film, (ii) it should chemisorb on to the metal surface, (iii) it should be polymeric or polymerise in situ on the metal and (iv) the barrier thus formed should increase the inner layer thickness.

Co-adsorption of two or more molecules otherwise called the synergistic effects of the inhibitors describe the enhancement of the performance of a corrosion inhibitor in the presence of another substance in small quantity in the corrosive medium. This phenomenon can be thought of as an effective method of getting better performance or to decrease the amount of usage of the inhibitor.

The synergistic effect between quaternary ammonium cations such as tetra butyl ammonium cation  $(TBA)^+$  and hexadecyl pyridinium cation  $(HDP)^+$  and  $SCN^-$  or  $Cl^-$ ,  $I^-$  on the corrosion of steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> was studied by Zou et al. [9]. Synergistic effects of halide ions with furfuraldehyde have been found to be in the order  $Br^- > I^- > Cl^-$  and it is stated that furfuraldehyde is

adsorbed through ion pair attraction with halide ions [10]. Similar synergistic effects between inorganic anions and organic amines or ammonium salts [11-13] and phosphonium salts [14–16] for the corrosion inhibition of iron in acid solutions have been studied. The synergistic effect of amines such as n-hexylamine, di-n-hexylamine with KI on the corrosion of pure iron in deaerated 1N H<sub>2</sub>SO<sub>4</sub> [17], iodide ions on the corrosion of carbon steel in 25% H<sub>2</sub>SO<sub>4</sub>, with mono, di and tributylamine for corrosion of iron in dilute H<sub>2</sub>SO<sub>4</sub> [18], quinoline and chloride ions [19] for carbon steel in 0.25 M H<sub>2</sub>SO<sub>4</sub>, halide ions and ethylenediamine for mild steel in H<sub>2</sub>SO<sub>4</sub>, mono, di and triethylamine and Br<sup>-</sup> or propionate ions for the corrosion of iron in  $HClO_4$  [20], benzyl amine with halides on the corrosion of steel in dilute H<sub>2</sub>SO<sub>4</sub> [21], dicyclohexylamine with  $I^-$  ions [22], dodecylamine with  $CI^-$  ions on the corrosion of iron in  $H_2SO_4$  [23], N,N-dipropynoxymethylaine acetate with Cl<sup>-</sup> ions on corrosion of pure iron in  $H_2SO_4$  [24] and more recently the synergistic influence of iodide ions on the inhibition of corrosion of carbon steel in sulphuric acid by some aliphatic amines [25] and between surfactant OP and NaCl for cold-rolled steel in phosphoric acid [26] has been studied.

Polymers such as poly(ethoxy)aniline [27], poly(methoxy)aniline [28], polyaniline [29], polyaminoquione [30] because of the their bulky structure and very efficient attachments to their backbone are found to inhibit iron corrosion effectively. It is also reported that halide ions are found to inhibit the corrosion of iron in acidic solutions [31–33]. However, the report about synergism between a polymer and halide ions on the metal corrosion in sulphuric acid medium is very rare. In this work, the synergistic inhibition between polyaniline and halide ions on the corrosion of pure iron in 0.5 M  $H_2SO_4$  solutions has been investigated and possible synergistic mechanism has been proposed.

# 2. Experimental

## 2.1. Synthesis of water soluble polyaniline

Reagent grade aniline was purified by distillation in the presence of small amount of zinc dust. Sodium salt of dodecyl benzene sulphonic acid (0.1 M) was used as dopant and was neutralized with conc. HCl. To this solution, 0.1 M of freshly distilled aniline dissolved in 0.1 M HCl was added and precooled. To this reaction mixture, freshly prepared solution of 0.1 M ammonium persulphate kept at a temperature of 5–10 °C was slowly added with constant stirring for 2 h [34]. Finally a dark green solution of polyaniline was obtained and the efficiency of polymerization was about 50%. The unreacted aniline was recovered by distillation. The poly(aniline) was characterized by UV–Vis (HITACHI – U3400), FTIR (PERKIN ELMER – PARAGON 500) spectroscopy. The average molecular weight  $(M_w)$  was determined by GPC method (Shimadzu, Japan) and found to be 16,260.

# 2.2. Electrochemical studies

Experiments were made using a conventional three electrode cell assembly. The working electrode was a pure iron (Johnson Mattey Ltd., UK) sample of one cm<sup>2</sup> area with the rest being covered with araldite epoxy and a rectangular platinum foil of  $6 \text{ cm}^2$  was used as counter electrode and saturated calomel electrode as reference electrode. The working electrode was polished with 1/0, 2/0, 3/0 and 4/0 grade emery papers, washed with distilled water and degreased with trichloroethylene. The solutions were deaerated by purging purified nitrogen gas for 30 min before the start of the experiment. Studies have been made with polyaniline in the concentration range of 10-100 ppm in the presence of  $0.5 \times 10^{-3}$  M KI,  $1 \times 10^{-3}$  M KBr and  $1 \times 10^{-3}$  M KCl. The low concentration of KI  $(0.5 \times 10^{-3} \text{ M})$  has been chosen since its inhibition efficiency is higher even at this concentration in comparison with other halide ions of concentration of  $1 \times 10^{-3}$  M. Further, the low concentration of halide ions has been chosen in order to find out the effectiveness of synergistic effect since at higher halide ions concentration, their inhibitive effect will be predominant [35]. Solatron Electrochemical analyzer (Model 1280B) interfaced with an IBM computer was used for measurements. The polarization studies were made at the end of 30 min of immersion at  $28 \pm 1$  °C. The polarization was carried out using a Corware software from a cathodic potential of -0.2 V to an anodic potential of +0.2 V with respect to the corrosion potential at a sweep rate of  $0.5 \,\mathrm{mV/s}$  in order to see the effect of inhibitors on corrosion. The linear Tafel segments of the anodic and cathodic curves (-0.2 to)+0.2 V vs corrosion potential) were extrapolated to corrosion potential to obtain the corrosion current densities. The inhibition efficiency was evaluated from the measured  $i_{corr}$  values using the relationship

$$\text{I.E.\%} = \left\{ \frac{i_{\text{corr}} - i'_{\text{corr}}}{i_{\text{corr}}} \right\} \times 100,$$

where  $i_{corr}$  and  $i'_{corr}$  are the corrosion current values without and with the addition of various concentrations of inhibitor.

For linear polarization measurements, a sweep from -0.02 to +0.02 V vs open circuit potential at a sweep rate of 0.5 mV/s was used and the polarization resistance ( $R_p$ ) was measured from the slope of  $\eta$ vs *i* curve in the vicinity of corrosion potential. From the measured polarization resistance values, the inhibition efficiency has been calculated using the relationship,

I.E.% = 
$$\left\{\frac{R'_{\rm p} - R_{\rm p}}{R'_{\rm p}}\right\} \times 100,$$

where  $R_p$  and  $R'_p$  are the polarization resistance values without and with the addition of inhibitors.

Z plot software was used for data acquisition and analysis of interfacial impedance. AC signals of 10 mV amplitude and a frequency spectrum from 100 KHz to 0.01 Hz was impressed and the Nyquist representations of the impedance data were analysed with Zview software. The charge transfer resistance ( $R_{ct}$ ), is obtained from the diameter of the semicircle in Nyquist representation. The inhibition efficiency of the inhibitor has been found out from the relationship,

I.E.% = 
$$\left\{\frac{R'_{\rm ct} - R_{\rm ct}}{R'_{\rm ct}}\right\} \times 100,$$

where  $R_{ct}$  and  $R'_{ct}$  are the charge transfer resistance values in the absence and presence of inhibitors.

The interfacial double layer capacitance has been estimated from the impedance value of the frequency having maximum imaginary component in the Nyquist plot by using the following equation,

$$C_{\rm dl} = \frac{1}{2\pi f_{\rm max} R_{\rm ct}}$$

and the surface coverage  $\theta$  by the inhibitor molecule is given by [24,25]

$$\theta = \frac{C_{\rm dl} - C'_{\rm dl}}{C_{\rm dl}},$$

where  $C_{dl}$  and  $C'_{dl}$  are the double layer capacitance values in the absence and presence of inhibitors.

# 3. Results and discussion

#### 3.1. Characterisation of polyaniline

The adsorption peak of polyaniline at 336 nm shows the  $\pi$ - $\pi$ \* transition in the benzenoid ring and 578 nm shows the donor-acceptor interaction of quinonoid ring (Fig. 1). The well known cation radicals and localized po-



Fig. 1. UV-Vis spectrum of poly(aniline).



Fig. 2. FTIR spectrum of poly(aniline).

laron peaks were observed at 449 and 775 nm. The major IR adsorption bands (Fig. 2) at 1555 and 1453 cm<sup>-1</sup> are the characteristics band due to nitrogen–quinoid ring structure and peaks for poly(aniline) observed at 1632 cm<sup>-1</sup>, for N–H bending, 1555 and 1494 cm<sup>-1</sup> for nitrogen benzenoid–quinonoid ring structure, the other IR characteristics are observed at 1126 and 1036 cm<sup>-1</sup>. The structure of poly(aniline) is shown as follows:



#### 3.2. Inhibition effect of polyaniline

Conjugated polymers have attracted a great deal of research interest because of their high electrical conductivity, electrochemical and optical properties. Their use in corrosion resistant coatings and as inhibitors is also reported [36-38]. The Nyquist representation of the complex impedance of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with the addition of various concentrations of polyaniline (Fig. 3) shows the presence of depressed semicircles indicating the activation controlled nature of the reaction process with micro roughness at the interface. The charge transfer resistance  $R_{ct}$ , interfacial double layer capacitance  $C_{\rm dl}$  and the surface coverage  $\theta$  derived from these figures are given in Table 1. The  $R_{ct}$  values increase from 33 to 110  $\Omega$  cm<sup>2</sup> with a corresponding decrease in C<sub>dl</sub> values from 2244 to 267  $\mu$ F cm<sup>-2</sup> for the added polyaniline concentrations. The  $\theta$  value is increased to 0.90 with 100 ppm of poly(aniline). From the LPR studies too, it has been found that the polarisation resistance  $(R_p)$  values increase (Table 1) from  $34 \,\Omega \,\text{cm}^2$  of that of blank to  $125 \,\Omega \,\mathrm{cm}^2$  with the highest concentration of inhibitor added indicating the good inhibition character of the

added polyaniline. Fig. 4 shows the Tafel polarization curves for iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with the addition of various concentrations of poly(aniline). The important corrosion parameters obtained from these curves are presented in Table 2. It is evident from the table that the corrosion current values ( $i_{\rm corr}$ ) decrease from 410 µA cm<sup>-2</sup> of that of blank to 67 µA cm<sup>-2</sup> with the addition of highest concentration of polyaniline (100 ppm). The addition of poly(aniline) does not alter the values of  $E_{\rm corr}$ ,  $b_{\rm a}$  and  $b_{\rm c}$  significantly indicating the mixed type inhibiting behaviour of polyaniline.

Poly(aniline) is one of the most promising and most widely studied conducting polymers due to its stability and lower cost. Earlier studies showed the inhibitive properties of substituted poly(aniline) for mild steel in acid chloride solutions [27,28]. The inhibitive property of poly(aniline) can mainly be attributed to the presence of plenty of  $\pi$ -electron clouds coexisting with quaternary nitrogen atom. The larger molecular size ensures the greater coverage of the metallic surface and lesser adsorption of  $SO_4^{2-}$  ions on the metal surface leaving more and more space for the organic molecules to get adsorbed [39].

addition of polyaniline: ---- Blank; ..... 10 ppm; ---- 50 ppm; -

# 3.3. Synergism of polyaniline with halide ions

#### 3.3.1. Iodide ions

100 ppm.

Fig. 5 shows the impedance behaviour of steel in  $0.5 \text{ M H}_2\text{SO}_4$  containing  $0.5 \times 10^{-3} \text{ M I}^-$  ions along with various concentrations of polyaniline. The charge transfer resistance and the double layer capacitance values deduced from these figures are presented in Table 3. The results show that the addition of  $0.5 \times 10^{-3} \text{ M I}^-$  ions has increased the values of  $R_{ct}$  from the blank value of 33 to 440  $\Omega$  cm<sup>2</sup> corresponding to an inhibition efficiency of 93% at 75 ppm of polyaniline. This may be compared to the bare polyaniline addition at this concentration yielding only 70% of inhibition efficiency. Similarly iodide ions alone gave 78% of efficiency. The double layer capacitance values also decrease to a low value of 53  $\mu$ F cm<sup>-2</sup> as compared to that of blank (2244  $\mu$ F cm<sup>-2</sup>). This resulted



-150

-100

-50

Z" (ohm)

Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with poly(aniline)

Concentration of polyaniline (ppm)	Impedance m	nethod	LPR method			
	$R_{\rm ct}~(\Omega~{\rm cm}^2)$	$C_{\rm dl}~(\mu{\rm F~cm^{-2}})$	Inhibition efficiency (%)	Surface coverage, $\theta$	$R_{\rm p}~(\Omega~{\rm cm}^2)$	Inhibition efficiency (%)
Blank	33	2244	_	_	34	_
10	55	600	40	0.82	57	40
25	57	365	42	0.84	68	50
50	74	305	55	0.86	80	58
75	111	267	70	0.90	125	73
100	110	267	70	0.90	122	72

Fig. 3. Nyquist plot of iron in 0.5 M  $H_2SO_4$  with the addition of polyaniline: — Blank;  $\cdot$  10 ppm;  $\bullet$  25 ppm;  $\Box$  50 ppm;  $\circ$  75 ppm;  $\blacksquare$  100 ppm.

Z' (ohm)

100

150

50

-0.2 -0.3 -0.4 E (V vs SCE) -0.5 -0.6 -0.7 -0.8 10<sup>-4</sup> 10<sup>-2</sup> 10<sup>-7</sup> 10-6 10-5 10<sup>-3</sup> 10<sup>-1</sup> I (A/cm<sup>2</sup>) Fig. 4. Polarisation behaviour of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with the

Table 2Corrosion kinetic parameters of pure iron in 0.5 M H2SO4 with poly(aniline)

Concentration of polyaniline (ppm)	E <sub>corr</sub> (mV vs SCE)	$b_{\rm a}$ (mV/dec)	$b_{\rm c}$ (mV/dec)	$i_{\rm corr}~(\mu {\rm A/cm^2})$	Inhibition efficiency (%)
Blank	-508	76	109	410	_
10	-521	50	113	191	53
25	-487	48	100	158	61
50	-491	48	96	120	71
75	-493	50	93	70	83
100	-488	50	95	67	84



Fig. 5. Nyquist plot of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with the addition of polyaniline in the presence of  $0.5 \times 10^{-3}$  M I<sup>-</sup> ions: — Blank; 10 ppm;  $\Box$  25 ppm;  $\blacksquare$  50 ppm;  $\bigcirc$  75 ppm;  $\blacklozenge$  100 ppm.

in an enhanced surface coverage  $\theta$  of 0.98 compared to iodide free value of 0.90.

From the linear polarization studies, it is observed that the polarization resistance  $R_p$  values increase from 34 to 533  $\Omega$  cm<sup>2</sup> with increase in polyaniline concentration in presence of iodide ions.

The co-adsorption effect of iodide ions on the polarization behaviour of steel in presence of various concentrations of polyaniline for steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> is shown in Fig. 6. The corrosion kinetic parameters obtained from these curves are tabulated in Table 4. The  $i_{corr}$ values decrease from 410 to 19 µA cm<sup>-2</sup> and the maximum inhibition efficiency is observed at 75 ppm of poly-



Fig. 6. Polarisation behaviour of iron in  $0.5 \text{ M H}_2\text{SO}_4$  with the addition of polyaniline in the presence of  $0.5 \times 10^{-3} \text{ M I}^-$  ions: — Blank; ……… 10 ppm; ---- 50 ppm; — 100 ppm.

aniline. The Tafel constants  $b_a$  and  $b_c$  are in the range of 43–76 and 82–109 mV/dec, respectively.

## 3.4. Bromide ions

Addition of bromide ions improves the inhibitive property of polyaniline at all concentrations as is evinced by Fig. 7 showing the impedance behaviour of steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The charge transfer resistance  $R_{\rm ct}$  is increased from 33 to 250  $\Omega$  cm<sup>2</sup>, the double layer capacitance  $C_{\rm dl}$  is decreased from 2244 to 98 µF cm<sup>-2</sup> as shown in Table 5. The surface coverage also increased to 0.96. The polarization resistance  $R_{\rm p}$  obtained from

Table 3

Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M  $H_2SO_4$  with poly(aniline) and  $0.5 \times 10^{-3}$  M I<sup>-</sup> ions

Concentration of polyaniline (ppm)	Impedance m	nethod	LPR method			
	$R_{\rm ct} (\Omega {\rm cm}^2)$	$C_{\rm dl}~(\mu {\rm F~cm^{-2}})$	Inhibition efficiency (%)	Surface coverage, $\theta$	$R_{\rm p}~(\Omega~{\rm cm}^2)$	Inhibition efficiency (%)
Nil	67	731	50	0.61	100	66
10	293	82	89	0.96	400	91.5
25	383	77	81	0.97	432	92.1
50	410	71	92	0.97	474	92.8
75	440	53	93	0.98	533	93.6
100	424	70	92	0.97	516	93.4

Table 4 Polarisation parameters for pure iron in 0.5 M  $H_2SO_4$  with polyaniline and  $0.5 \times 10^{-3}$  M  $I^-$  ions

*	-					
Concentration of polyaniline (ppm)	Corrosion potential, $E_{corr}$ (mV vs SCE)	Corrosion current density, $i_{corr}$ ( $\mu$ A/cm <sup>2</sup> )	$b_{\rm a}$ (mV/dec)	$b_{\rm c}  ({\rm mV/dec})$	Inhibition efficiency (%)	Synergism parameter, S
Nil	-503	89	53	95	78	_
10	-510	30	60	95	92	1.2925
25	-500	27	52	91	93	1.2257
50	-493	23	43	95	94	1.0633
75	-503	19	71	82	95	0.7480
100	-491	24	56	93	94	0.5866



Fig. 7. Nyquist plot of iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with the addition of polyaniline in the presence of  $1.0 \times 10^{-3}$  M Br<sup>-</sup> ions: — Blank; **I** 10 ppm;  $\Box$  25 ppm; **I** 50 ppm;  $\bigcirc$  75 ppm; **I** 100 ppm.

linear polarization resistance method is increased from  $34 \,\Omega \,\text{cm}^2$  corresponding to blank to  $315 \,\Omega \,\text{cm}^2$  with highest concentration of polyaniline.

Fig. 8 shows the polarization behaviour of iron in the presence of bromide ions along with polyaniline. The  $i_{\rm corr}$  value is decreased from 410 to 30  $\mu$ A cm<sup>-2</sup> and the maximum inhibition efficiency is observed at 100 ppm of polyaniline (Table 6). The Tafel constants  $b_{\rm a}$  and  $b_{\rm c}$  are in the range of 45–76 and 88–109 mV/ dec, respectively.

# 3.5. Chloride ions

The increase of charge transfer resistance value from 33 to  $316 \,\Omega \,\text{cm}^2$  as shown in Table 7 deduced from the



Fig. 8. Polarisation behaviour of iron in  $0.5 \text{ M H}_2\text{SO}_4$  with the addition of polyaniline in the presence of  $1.0 \times 10^{-3} \text{ M Br}^-$  ions: — Blank; ……… 10 ppm; ----- 50 ppm; — 100 ppm.

Nyquist plots (Fig. 9) resulting in 90% of inhibition efficiency has conveyed the synergistic action of chloride anions along with polyaniline on iron in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The double layer capacitance  $C_{dl}$  is decreased to 108 µF cm<sup>-2</sup> and the surface coverage is increased to a maximum of 0.90. The polarization resistance  $R_p$  obtained from linear polarization studies and the corrosion current density  $i_{corr}$  obtained from Tafel polarization method also showed similar behaviour.

The polarization curves for iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing various concentrations of polyaniline along with  $1.0 \times 10^{-3}$  M Cl<sup>-</sup> are shown in Fig. 10. The corrosion current density is decreased from 410 to 29 µA cm<sup>-2</sup> yielding 92% of inhibition efficiency (Table 8). This

Table 5

Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M  $H_2SO_4$  with poly(aniline) and  $1.0 \times 10^{-3}$  M  $Br^-$  ions

Concentration of polyaniline (ppm)	Impedance r	nethod	LPR method			
	$R_{\rm ct} (\Omega {\rm cm}^2)$	$C_{\rm dl}~(\mu {\rm F~cm}^{-2})$	Inhibition efficiency (%)	Surface coverage, $\theta$	$R_{\rm p} (\Omega {\rm cm}^2)$	Inhibition efficiency (%)
Nil	45	1178	26	_	46	26
10	175	221	80	0.90	210	84
25	187	229	82	0.90	229	85
50	195	180	83	0.92	221	84.6
75	215	126	85	0.94	232	85.3
100	250	98	87	0.96	315	89

Polarisation parame	ters for pure from in 0.5 N	$\pi_{2}$ $30_{4}$ with polyannine and $\pi_{2}$	.0 × 10 IVI DI	IOIIS		
Concentration of polyaniline (ppm)	Corrosion potential, $E_{\rm corr}$ (mV vs SCE)	Corrosion current density, $i_{corr}$ ( $\mu$ A/cm <sup>2</sup> )	$b_{\rm a}$ (mV/dec)	$b_{\rm c} ({\rm mV/dec})$	Inhibition efficiency (%)	Synergism parameter, S
Nil	-540	2296	49	100	28	_
10	-485	75	53	107	82	1.8800
25	-510	45	52	93	89	2.5500
50	-520	36	60	97	91	2.3200
75	-496	33	43	88	92	1.5300
100	-497	30	45	109	93	1.6500

Table 7

Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M  $H_2SO_4$  with poly(aniline) and  $1.0 \times 10^{-3}$  M  $Cl^-$  ions

Concentration of polyaniline (ppm)	Impedance me	ethod	LPR method			
	$\overline{R_{\rm ct}~(\Omega~{\rm cm}^2)}$	$C_{\rm dl}~(\mu {\rm F~cm}^{-2})$	Inhibition efficiency (%)	Surface coverage, $\theta$	$R_{\rm p}~(\Omega~{\rm cm}^2)$	Inhibition efficiency (%)
Nil	38	1066	13	_	42	19
10	102	233	68	0.90	114	70
25	149	157	78	0.93	152	78
50	327	93	90	0.96	420	92
75	527	63	94	0.97	720	95
100	316	108	90	0.95	384	91



Fig. 9. Nyquist plot of iron in  $0.5 \text{ M H}_2\text{SO}_4$  with the addition of polyaniline in the presence of  $1.0 \times 10^{-3} \text{ M Cl}^-$  ions: — Blank; 10 ppm;  $\Box$  25 ppm;  $\blacksquare$  50 ppm;  $\bigcirc$  75 ppm;  $\blacklozenge$  100 ppm.

may be compared with the chloride ion alone case where the corrosion current density is  $347 \ \mu A \ cm^{-2}$ .

# 3.6. Synergism parameter

All the experimental results have suggested that the addition of halide ions to the inhibited solution increases the inhibition efficiency and the degree of surface coverage ( $\theta$ ). This behaviour is attributed to the synergistic effect between added halide ions and polyaniline.

Schmitt and Bedhur [40] have considered the synergistic effect by proposing two types of co-adsorption namely competitive and co-operative. In competitive adsorption the anion and cation are adsorbed at differ-



Fig. 10. Polarisation behaviour of iron in  $0.5 \text{ M H}_2\text{SO}_4$  with the addition of polyaniline in the presence of  $1.0 \times 10^{-3} \text{ M Cl}^-$  ions: — Blank; ……… 10 ppm; ---- 50 ppm; — 100 ppm.

ent sites on the metal surface. In co-operative adsorption, the anion is chemisorbed on the surface and the cation is adsorbed on a layer of the anion.

The extent of synergism between halide ions and polyaniline has been analysed by estimating the synergism parameter obtained from the inhibition efficiency (from Tafel polarization method) according to Aramaki and Hackerman [41] as

$$S_I = \frac{(1 - I_{1+2})}{(1 - I'_{1+2})},$$

where  $I_{1+2} = (I_1 + I_2) - (I_1I_2)$ ;  $I_1 =$  Inhibition efficiency in the presence of synergistic halide ions;  $I_2 =$  Inhibition

Table 6 Pelorisation memory for more in 0.5 M H SO, with reductiling and  $1.0 \times 10^{-3}$  M  $Pe^{-1}$  is

Table 8 Polarisation parameters for pure iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> with polyaniline and  $1.0 \times 10^{-3}$  M Cl<sup>-</sup> ions

hibition Synergism ficiency (%) parameter, S						
- -						
2.1026						
2.0719						
4.1083						
3.6125						
1.7000						

efficiency of polyaniline;  $I'_{1+2}$  = measured inhibition efficiency of synergistic ions in combination with polyaniline.

Tables 4, 6 and 8 give the computed  $S_I$  values and the values are found to be more than unity in most of the cases suggesting the synergistic action of halide ions with the polyaniline.

Amines in aqueous acid media may exist as either neutral or in the form of cations [42] depending on the concentration of H<sup>+</sup> ions in the solutions. In acidic solutions, they predominantly exist as cations and adsorb through electrostatic interaction onto the halide covered surface through their hydrogen ion [43]. The synergistic effect is due to the co-adsorption of halide ions on the surface which forms oriented dipoles with their negative ends toward the solution, thus increasing adsorption of organic molecules [44]. Besides, the nature of anions present in the acidic solutions plays a significant role in influencing the extent of adsorption. This in turn may favour more adsorption of cations on the surface and resulting in more inhibition [45]. The corrosion inhibition of medium sized polymer-polymethyleneimine and its synergistic effect with iodide ions has been studied by Aramaki et al. [41] and it is found that anions in acidic solutions play a significant role in influencing the inhibitive ability of the organic compound [46]. Fouda et al. [25] in their study on synergistic influence of iodide ions with some aliphatic amines on the inhibition of corrosion of carbon steel in sulphuric acid has suggested that the chemisorbed of iodide ions on the metal surface as the sole responsible factor for the synergism effect of the protonated cations of the inhibitors. The cations of the inhibitors are adsorbed by coulombic attraction on the metal surface where iodide ions are already adsorbed (co-operative adsorption).

In this study, the halide ions show synergism with polyaniline. The increase in inhibition efficiency and synergism factor show that the mechanism of synergic action is due to the co-adsorption of halides and polyaniline. The synergistic effect is found to be greater in the presence of  $Cl^-$  ions than that of  $Br^-$  and  $I^-$  ions, since the chloride ions provide more sites for adsorption of polyaniline than do  $Br^-$  and  $I^-$  ions of same concentration [20,45]. Based on the synergism parameter, the order of synergism of halide ions with polyaniline is

found to be  $Cl^- > Br^- > I^-$ . Earlier study [10] with fufuraldehyde, has shown that the synergism order with halide ions is  $Br^- > I^- > Cl^-$ . The difference in synergism order may be due to the purity of iron used in the studies since, inhibitor performance, the corrosion rate and the amount of adsorption of inhibitor are dependent on the purity of the iron sample [47]. Further study to find out the nature of interaction of halide ions and polyaniline on iron surface by surface analytical techniques will be highly useful.

## 4. Conclusions

Polyaniline is found to inhibit corrosion of iron in  $0.5 \text{ M } H_2\text{SO}_4$  to an extent of 80% at 100 ppm. In the presence of halide ions concentration of 0.5 to  $1.0 \times 10^{-3} \text{ M}$ , the inhibition efficiency of polyaniline is enhanced to more than 90% in the presence of lower concentration of polyaniline. The synergistic effect of halide ions is attributed to the enhanced adsorption of polyaniline over the halide ions covered iron surface. Based on the synergism parameter, the synergistic effect of halide ions is found to be in the order Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>.

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