

Influence of halide ions on the adsorption of diphenylamine on iron in 0.5 M H₂SO₄ solutions

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Abstract

Halide ions are found to enhance the inhibition performance of amines due to enhanced adsorption of amines by the adsorbed halide ions on the metal surface. In this work, the synergistic action of halide ions on the corrosion inhibition of iron in 0.5 M H₂SO₄ by diphenylamine has been found out by electrochemical impedance and polarization methods. Analysis of impedance data has been made with equivalent circuit with constant phase angle element for calculation of double layer capacitance values. Experiments have been carried out in the concentration range of 100–1000 ppm of diphenylamine in the presence of 0.5–1.0 × 10⁻³ M of halide ions. Diphenylamine is found to be a cathodic inhibitor and the inhibition efficiency of about 65% is obtained at 1000 ppm. The anodic and cathodic Tafel slopes in the presence of diphenylamine alone and with halide ions are 65 ± 5 and 105 ± 5 mV, respectively. Diphenylamine inhibits corrosion by adsorption and the surface coverage values are increased considerably in the presence of halide ions. In the presence of iodide ions, the inhibition efficiency of diphenylamine at 100 ppm is increased to more than 90%. In the case of other halide ions, the inhibition efficiency of diphenylamine is increased to 80% at 1000 ppm. The order of synergism of halide ions is I⁻ ≫ Br⁻ > Cl⁻. The highest synergistic effect of iodide ions is due to chemisorption with metal surface due to its larger size and ease of polarizability.

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1. Introduction

The study of corrosion inhibition is of high practical and technological interest. Acids find applications in industrial acid cleaning, acid pickling, acid descaling and oil well acidizing. Inhibitors are commonly employed in these environments to minimize the base metal corrosion by the acids. 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. 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.

Schmitt [1] in his review, discussed extensively about the types of inhibitors used in acid media. Mostly, organic compounds containing N, O or S groups or organic compounds having π bonds in their structures are found to be effective inhibitors in acid media [2–4]. Also presence of functional groups, such as =NH, –N=N–, –CHO, R–OH, C=C, 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 metal surface. Amines and their derivatives are well known corrosion inhibitors and can effectively protect metals from corrosion [7–11].

It is reported that the surface of iron is found to be positively charged in an inhibitor free sulphuric acid media [12] and the protonated inhibitor compound species would be less strongly adsorbed onto the metal surface resulting in less inhibition efficiencies. However, the addition of halide ions in acid media has been found to increase the adsorption of amines and hence inhibition [13,14]. This phenomenon can be thought of as an

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effective method of getting better performance or to decrease the amount of usage of the inhibitor.

Synergistic effects between inorganic halide anions and organic amines or ammonium salts [15–17], phosphonium salts [18–20] for the corrosion inhibition of iron in acid solutions have been studied. Addition of halide ions also found to enhance the inhibition efficiency of ethylenediamine for mild steel in H_2SO_4 , mono, di and triethylamine for the corrosion of iron in $HClO_4$ [21] and benzyl amine with halides on the corrosion of steel in dilute H_2SO_4 [22].

Individual halide ions have also been attempted for their synergistic effects along with amine and other inhibitors. The synergistic action of chloride ions with quinoline for carbon steel in 0.25 M H_2SO_4 [23] and with dodecylamine on the corrosion of iron in H_2SO_4 [24] and with *N,N*-dipropynoxymethylamine acetate on corrosion of pure iron in H_2SO_4 [25] is reported. The synergistic action of iodide with amines such as *n*-hexylamine, di-*n*-hexylamine on the corrosion of pure iron in deaerated 1N H_2SO_4 [26], mono, di and tributylamine [27] and dicyclohexylamine [28] for corrosion of iron in dilute H_2SO_4 has been studied. More recently, the synergistic influence of iodide ions on the inhibition of corrosion of carbon steel in sulphuric acid by some aliphatic amines [29] is reported. Besides the synergistic action of chloride with surfactant OP for cold-rolled steel in phosphoric acid [30] has been studied.

In this paper, the influence of halide ions on the adsorption and the corrosion inhibition property of diphenylamine on iron in 0.5 M H_2SO_4 is reported.

2. Experimental

Experiments were made using a conventional three electrode cell assembly. The working electrode was a pure iron (Johnson Matthey Ltd., UK) sample of 1 cm × 1 cm electrode with stem, exposing 1 cm² area and the rest being covered with araldite epoxy and a rectangular platinum foil of 6 cm² 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 diphenylamine in the concentration range of 100–1000 ppm in the presence of 0.5×10^{-3} M KI, 1×10^{-3} M KBr and 1×10^{-3} M KCl. The low concentration of KI (0.5×10^{-3} M) has been chosen since its inhibition efficiency is higher even at this concentration in comparison with other halide ions of concentration of 1×10^{-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 [31]. Solartron Electrochemical analyzer (Model 1280 B) interfaced with an IBM computer was used for measurements. The polarization studies were made at the end of 30 min of immersion at 28 ± 1 °C. The polarization was carried out using a Corrware 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 mV/s. The linear Tafel

segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (i_{corr}). The inhibition efficiency was evaluated from the measured i_{corr} values using the relationship

$$I.E.(%) = \left\{ \frac{i_{corr} - i'_{corr}}{i_{corr}} \right\} \times 100 \quad (1)$$

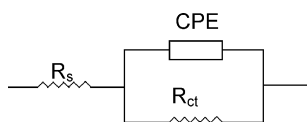
where i_{corr} and i'_{corr} are the corrosion current values without and with the addition of various concentrations of inhibitor.

For linear polarization measurements, a sweep from -0.02 to $+0.02$ V versus 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 η versus i curve in the vicinity of corrosion potential. From the measured polarization resistance values, the inhibition efficiency has been calculated using the relationship,

$$I.E.(%) = \left\{ \frac{R'_p - R_p}{R'_p} \right\} \times 100 \quad (2)$$

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 of impedance measurements. 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 impedance data were analysed using the equivalent circuit.



where R_s is the solution resistance, R_{ct} the charge transfer resistance and CPE is the constant phase element.

Assumption of a simple R_{ct} - C_{dl} is usually a poor approximation especially for systems showing depressed semicircle behaviour. For the description of a frequency independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) is used which is defined in impedance representation as:

$$Z(CPE) = Y_0^{-1} (j\omega)^{-n} \quad (3)$$

where Y_0 is the CPE constant, ω the angular frequency (in rad s^{-1}), $j^2 = -1$ the imaginary number and n is the CPE exponent. Depending on n , CPE can represent resistance ($Z(CPE) = R$, $n = 0$), capacitance ($Z(CPE) = C$, $n = 1$), inductance ($Z(CPE) = L$, $n = -1$) or Warburg impedance for ($n = 0.5$) [32]. The correct equation to convert Y_0 into C_{dl} is [33]:

$$C_{dl} = Y_0 (\omega_m'')^{n-1} \quad (4)$$

where C_{dl} is the double layer capacitance and ω_m'' the angular frequency at which Z'' is maximum. The surface coverage θ was estimated from the measured double layer capacitance C_{dl} values using the relationship:

$$\theta = \frac{C_{dl} - C'_{dl}}{C_{dl}} \quad (5)$$

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

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:

$$\text{I.E.}(\%) = \left\{ \frac{R'_{ct} - R_{ct}}{R'_{ct}} \right\} \times 100 \quad (6)$$

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

3. Results and discussion

3.1. Inhibition by diphenylamine (DPA)

The Nyquist representation of the impedance behaviour of iron in 0.5 M H_2SO_4 in the presence of various concentrations of diphenylamine is shown in Fig. 1. The existence of a single semicircle shows the presence of single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules. The slightly depressed nature of the semicircle which has the center below the x -axis is the characteristic for solid electrodes and such frequency dispersion has been attributed to roughness and other inhomogeneities of the solid electrode [34,35]. The charge transfer resistance (R_{ct}) and the interfacial double layer capacitance (C_{dl}) values derived from these curves are given in Table 1. R_{ct} is increased from the value of 33 to 105 $\Omega \text{ cm}^2$ and C_{dl} is decreased from 186 to 72 $\mu\text{F cm}^{-2}$ with the addition of diphenylamine inhibitor.

The polarization resistance (R_p) values obtained from the linear polarization studies showed an increase in values (Table 1) from 34 to 106 $\Omega \text{ cm}^2$ with the addition of maximum concentration of diphenylamine inhibitor. This corresponds to an inhibition efficiency of 67%.

The potentiodynamic polarization behaviour of iron in 0.5 M H_2SO_4 with the addition of various concentrations of diphenylamine is shown in Fig. 2. The corrosion kinetic parameters such as corrosion potential E_{corr} , corrosion current density i_{corr} , anodic and cathodic Tafel slopes b_a and b_c derived from these curves are given in Table 2. From the table, it is found that the addition of diphenylamine in the concentration range 100–1000 ppm decreases the dissolution rate of iron in 0.5 M H_2SO_4 . The corrosion current value is decreased from 410 $\mu\text{A cm}^{-2}$ for the inhibitor free solution to 144 $\mu\text{A cm}^{-2}$ at the highest concentration of diphenylamine studied.

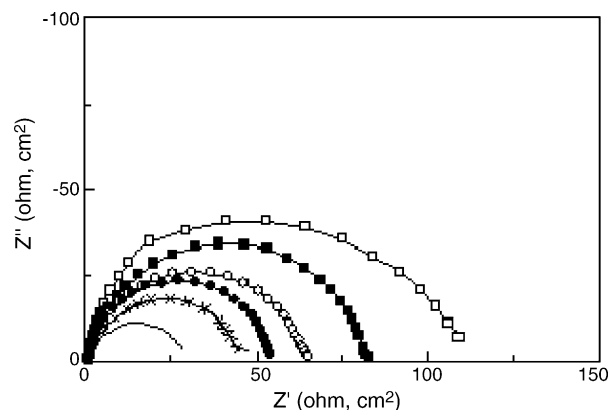


Fig. 1. Impedance plot of iron in 0.5 M H_2SO_4 in the presence of diphenylamine. (—) Blank; (x) 100 ppm; (●) 250 ppm; (○) 500 ppm; (■) 750 ppm; (□) 1000 ppm.

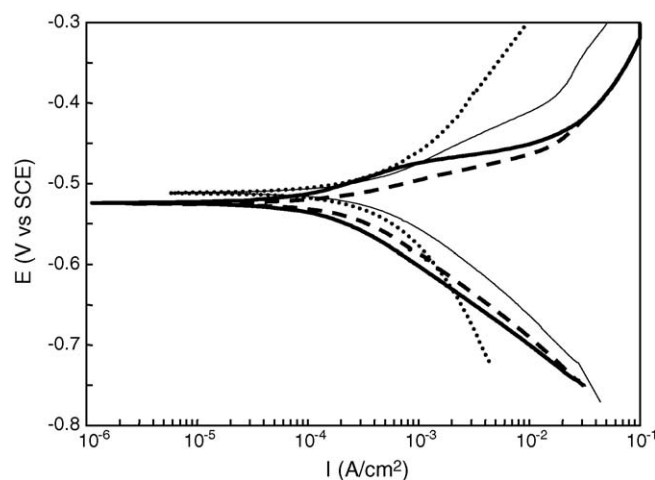


Fig. 2. Polarization curves of iron in 0.5 M H_2SO_4 in the presence of diphenylamine. (—) Blank; (···) 100 ppm; (---) 500 ppm; (—) 1000 ppm.

The steady state corrosion potentials are found to be shifted by 10–40 mV in cathodic direction in the presence of inhibitor. This shows that diphenylamine acts as cathodic inhibitor. However, the anodic and cathodic Tafel slopes are in the range of 65 ± 5 to 105 ± 5 mV, respectively. The absence of significant change in the Tafel slopes in the presence of inhibitor indicates that the corrosion mechanism of iron is not changed after adding DPA and the inhibitive effect is attributed to the simple adsorption of DPA.

Table 1
Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M H_2SO_4 with diphenylamine (DPA)

Concentration DPA (ppm)	Impedance method				I.E. (%)	Surface coverage θ	LPR method	
	R_{ct} ($\Omega \text{ cm}^2$)	Y_0 ($\mu\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$)	n	C_{dl} ($\mu\text{F cm}^{-2}$)			R_p ($\Omega \text{ cm}^2$)	Inhibition efficiency (%)
Blank	33	362	0.83	186	—	—	34	—
100	47	172	0.90	130	28	0.30	53	35
250	56	178	0.90	116	37	0.38	73	53
500	66	205	0.91	108	50	0.41	76	55
750	80	176	0.90	101	58	0.46	106	67
1000	105	125	0.91	72	67	0.61	106	67

Table 2
Corrosion kinetic parameters of pure iron in 0.5 M H₂SO₄ with diphenylamine

Concentration of diphenylamine (ppm)	E_{corr} (mV vs. SCE)	b_a (mV/dec)	b_c (mV/dec)	i_{corr} ($\mu\text{A cm}^{-2}$)	Inhibition efficiency (%)
Blank	-508	76	109	410	–
100	-521	63	110	315	23
250	-517	76	102	240	41
500	-555	70	107	210	49
750	-554	62	105	180	56
1000	-516	61	100	144	65

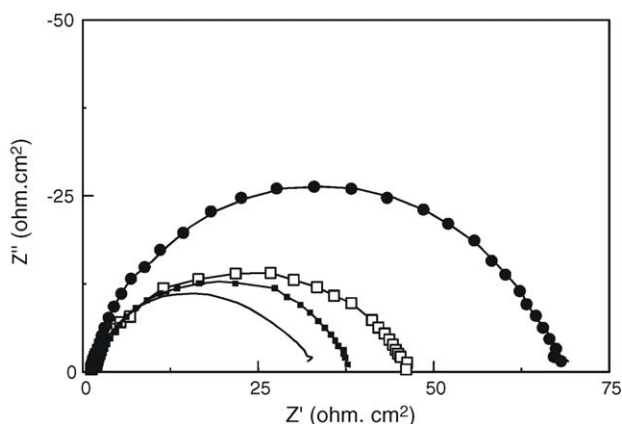


Fig. 3. Impedance plot of iron in 0.5 M H₂SO₄ in the presence of halide ions. (—) Blank; (■) 1×10^{-3} M Cl⁻; (□) 1×10^{-3} M Br⁻; (●) 0.5×10^{-3} M I⁻.

3.2. Inhibition by halide ions

The impedance and polarization behaviour of iron in 0.5 M H₂SO₄ containing 1.0×10^{-3} M Cl⁻, 1.0×10^{-3} M Br⁻ and 0.5×10^{-3} M I⁻ are shown in Figs. 3 and 4. The results obtained from these curves are summarized in Table 3. It can be seen that the inhibition efficiency of I⁻ is about 70% whereas the Br⁻ and Cl⁻ ions have given very low inhibition efficiency.

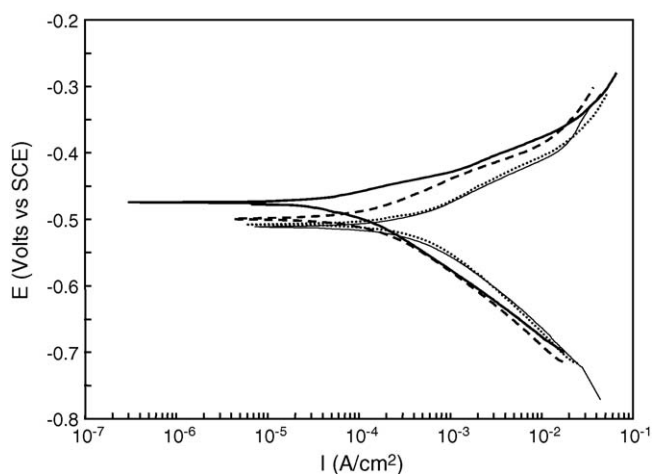


Fig. 4. Polarization curves of iron in 0.5 M H₂SO₄ in the presence of halide ions. (—) Blank; (···) 1.0×10^{-3} M Cl⁻; (---) 1.0×10^{-3} M Br⁻; (—) 0.5×10^{-3} M I⁻.

3.3. Synergism of halide ions with diphenylamine

3.3.1. Chloride ions

Fig. 5 shows the impedance behaviour of iron in 0.5 M H₂SO₄ containing 1.0×10^{-3} M Cl⁻ ions along with various concentrations of diphenylamine. The charge transfer resistance and the double layer capacitance with the constant phase element methodology deduced from these figures are presented in Table 4. The increase of charge transfer resistance value from 33 to $136 \Omega \text{ cm}^2$ resulting in 70% of inhibition efficiency has conveyed the synergistic action of 1.0×10^{-3} M chloride anions along with diphenylamine on iron in 0.5 M H₂SO₄. The double layer capacitance C_{dl} is decreased to $60.2 \mu\text{F cm}^{-2}$ and the surface coverage is increased to a maximum of 0.68. On comparing the θ values for different concentration, there is a slight decrease in θ values with concentration which is contrary to normal observation. However, the correlation between the surface coverage and inhibitor efficiency is good for concentrations 250–1000 ppm (I.E. = 70 ± 4 ; $\theta = 68 \pm 4$) except for 100 ppm where the inhibition efficiency is 50% even though the θ values is 0.76. The reason for this low value of inhibition efficiency is not clear.

From the linear polarization studies, it is observed that the polarization resistance R_p values increase from 34 to $135 \Omega \text{ cm}^2$ (Table 4) with increase in diphenylamine concentration in presence of chloride ions.

The polarization curves for iron in 0.5 M H₂SO₄ containing various concentrations of diphenylamine along with

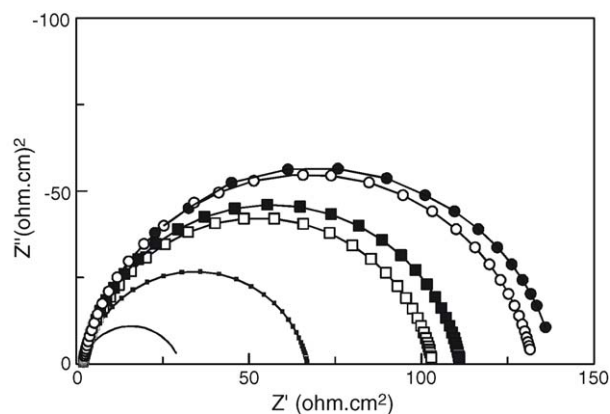


Fig. 5. Impedance plot of iron in 0.5 M H₂SO₄ in the presence of DPA and 1.0×10^{-3} M Cl⁻ ions. (—) Blank; (■) 100 ppm; (□) 250 ppm; (●) 500 ppm; (○) 750 ppm; (●) 1000 ppm.

Table 3
Corrosion inhibition property of halide ions for pure iron in 0.5 M H₂SO₄

Inhibitor	Tafel method		EIS method		LPR method	
	i_{corr} ($\mu\text{A cm}^{-2}$)	I.E. (%)	R_{ct} (Ωcm^2)	I.E. (%)	R_{p} (Ωcm^2)	I.E. (%)
Blank	410	–	33	–	34	–
1.0×10^{-3} M Cl [–]	347	15	38	13	42	19
1.0×10^{-3} M Br [–]	296	28	45	26	46	26
0.5×10^{-3} M I [–]	89	78	67	50	100	66

Table 4
Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M H₂SO₄ with diphenylamine and 1.0×10^{-3} M Cl[–] ions

Concentration DPA (ppm)	Impedance method					LPR method		
	R_{ct} (Ωcm^2)	Y_0 ($\mu\Omega^{-1} \text{s}^n \text{cm}^{-2}$)	n	C_{dl} ($\mu\text{F cm}^{-2}$)	I.E. (%)	Surface coverage θ	R_{p} (Ωcm^2)	Inhibition efficiency (%)
Nil	33	362	0.88	186	–	–	34	–
100	66	94.5	0.88	44.1	50	0.76	81	58
250	100	100.0	0.88	53.5	67	0.71	98	65
500	109	104.1	0.89	59.7	70	0.68	110	69
750	130	113	0.89	67.1	74	0.64	130	74
1000	136	105.2	0.90	60.2	70	0.68	135	75

1.0×10^{-3} M Cl[–] are shown in Fig. 6. The corrosion current density is decreased from 410 to 96 $\mu\text{A cm}^{-2}$ yielding 77% of inhibition efficiency (Table 5). This may be compared with the chloride free case where the corrosion current density is 144 $\mu\text{A cm}^{-2}$.

3.3.2. Bromide ions

Addition of bromide ions at a concentration of 1.0×10^{-3} M improves the inhibitive property of diphenylamine at all concentrations as is evinced from Fig. 7 showing the impedance behaviour of iron in 0.5 M H₂SO₄. The charge transfer resistance R_{ct} is increased from 33 to 117 Ωcm^2 for 1000 ppm of diphenylamine. This corresponds to the inhibition efficiency of 86% which can be compared with 67% for the bromide free diphenylamine containing acid. The double layer capacitance

C_{dl} is decreased from 186 to 52.1 $\mu\text{F cm}^{-2}$ as given in Table 6. The surface coverage is increased to 0.72. The polarization resistance R_{p} obtained from linear polarization resistance method is increased from 34 Ωcm^2 corresponding to blank to 123 Ωcm^2 for 1000 ppm concentration of diphenylamine.

Fig. 8 shows the polarization behaviour of iron in the presence of bromide ions along with diphenylamine. The i_{corr} value is decreased from 410 to 66 $\mu\text{A cm}^{-2}$ and the maximum inhibition efficiency of 83% is observed at 1000 ppm of diphenylamine (Table 7). The Tafel constants b_a and b_c are in the range of 65 ± 5 and 105 ± 5 mV/dec, respectively.

3.3.3. Iodide ions

Fig. 9 shows the impedance behaviour of iron in 0.5 M H₂SO₄ containing 0.5×10^{-3} M I[–] ions along with various concentrations of diphenylamine. The charge transfer resistance and the double layer capacitance values obtained from these figures

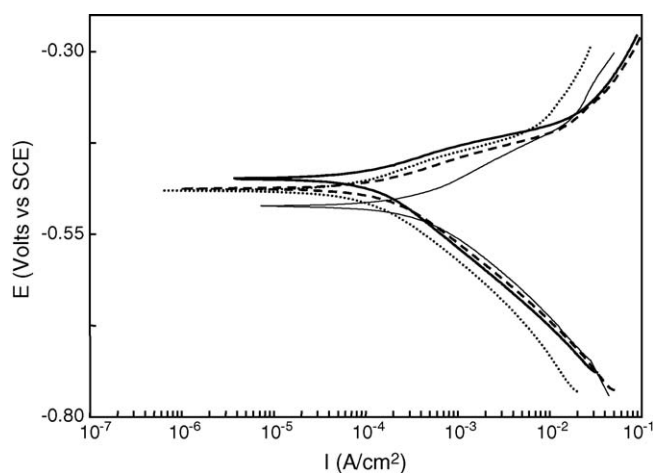


Fig. 6. Polarization curves for iron in 0.5 M H₂SO₄ in the presence of DPA and 1.0×10^{-3} M Cl[–] ions. (—) Blank; (···) 100 ppm; (---) 500 ppm; (—) 1000 ppm.

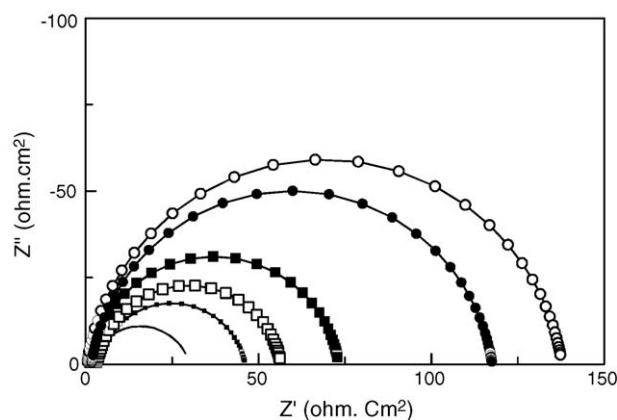


Fig. 7. Impedance plot of iron in 0.5 M H₂SO₄ in the presence of DPA and 1.0×10^{-3} M Br[–] ions. (—) Blank; (■) 100 ppm; (□) 250 ppm; (●) 500 ppm; (○) 750 ppm; (●) 1000 ppm.

Table 5

Polarization parameters for pure iron in 0.5 M H₂SO₄ with diphenylamine and 1.0 × 10⁻³ M Cl⁻ ions

Concentration of diphenylamine (ppm)	Corrosion potential E_{corr} (mV vs. SCE)	Corrosion current density i_{corr} ($\mu\text{A cm}^{-2}$)	b_a (mV/dec)	b_c (mV/dec)	Inhibition efficiency (%)	Synergism parameter S_I
Nil	-508	410	76	109	-	-
100	-514	169	72	105	59	4.60
250	-523	156	62	100	62	1.48
500	-500	126	68	100	69	1.68
750	-510	100	65	103	75	1.84
1000	-490	96	62	100	77	1.29

Table 6

Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M H₂SO₄ with diphenylamine and 1.0 × 10⁻³ M Br⁻ ions

Concentration DPA (ppm)	Impedance method						LPR method	
	R_{ct} ($\Omega \text{ cm}^2$)	Y_0 ($\mu\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$)	n	C_{dl} ($\mu\text{F cm}^{-2}$)	I.E. (%)	Surface coverage θ	R_p ($\Omega \text{ cm}^2$)	Inhibition efficiency (%)
Nil	33	362	0.88	186	-	-	34	-
100	43	153.0	0.88	76.7	79	0.59	53	36
250	53	120.2	0.90	68.3	81	0.63	57	40
500	72	115.2	0.91	67.8	81	0.63	84	56
750	137	77.7	0.91	47.1	87	0.75	140	76
1000	117	86.8	0.91	52.1	86	0.72	123	72

are presented in Table 8. The results show that the addition of 0.5 × 10⁻³ M I⁻ ions has increased the values of R_{ct} from the blank value of 33 to 347 $\Omega \text{ cm}^2$ corresponding to an inhibition efficiency of 91% at 1000 ppm of diphenylamine. This may be compared to the bare diphenylamine addition at a concentration of 1000 ppm yielding a R_{ct} value of 105 $\Omega \text{ cm}^2$ equivalent to 67% of inhibition efficiency. The double layer capacitance values also decreased to a low value of 37 $\mu\text{F cm}^{-2}$ as compared to that of blank (186 $\mu\text{F cm}^{-2}$). This resulted in an enhanced surface coverage θ of 0.91 compared to iodide free value of 0.61.

From the linear polarization studies, it is observed that the polarization resistance R_p value is increased from 34 to 273 $\Omega \text{ cm}^2$ in 1000 ppm diphenylamine concentration in presence of iodide ions.

The co-adsorption effect of iodide ions on the polarization behaviour in presence of various concentrations of diphenylamine for iron in 0.5 M H₂SO₄ is shown in Fig. 10. The corrosion kinetic parameters obtained from these curves are tabulated in Table 9. The i_{corr} values decrease from 410 to 29 $\mu\text{A cm}^{-2}$ and the inhibition efficiency (90%) is observed at 1000 ppm of

Table 7

Polarization parameters for pure iron in 0.5 M H₂SO₄ with diphenylamine and 1.0 × 10⁻³ M Br⁻ ions

Concentration of diphenylamine (ppm)	Corrosion potential E_{corr} (mV vs. SCE)	Corrosion current density i_{corr} ($\mu\text{A cm}^{-2}$)	b_a (mV/dec)	b_c (mV/dec)	Inhibition efficiency (%)	Synergism parameter S_I
Nil	-508	410	76	109	-	-
100	-529	182	66	112	48	1.07
250	-521	175	73	104	57	1.22
500	-515	120	60	109	70	1.46
750	-494	109	65	100	73	1.24
1000	-487	66	68	100	83	1.48

Table 8

Electrochemical impedance and linear polarization parameters for pure iron in 0.5 M H₂SO₄ with diphenylamine and 0.5 × 10⁻³ M I⁻ ions

Concentration DPA (ppm)	Impedance method						LPR method	
	R_{ct} ($\Omega \text{ cm}^2$)	Y_0 ($\mu\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$)	n	C_{dl} ($\mu\text{F cm}^{-2}$)	I.E. (%)	Surface coverage θ	R_p ($\Omega \text{ cm}^2$)	Inhibition efficiency (%)
Nil	33	362	0.88	186	-	-	34	-
100	349	94.5	0.86	51	91	0.73	445	92.0
250	433	70.5	0.87	42	92	0.77	489	93.0
500	507	44.2	0.86	23	94	0.88	550	94.0
750	405	72.5	0.89	44	92	0.76	371	91.0
1000	347	69.0	0.87	37	91	0.78	273	88.0

Table 9
Polarization parameters for pure iron in 0.5 M H₂SO₄ with diphenylamine and 0.5 × 10⁻³ M I⁻ ions

Concentration of diphenylamine (ppm)	Corrosion potential E_{corr} (mV vs. SCE)	Corrosion current density i_{corr} ($\mu\text{A cm}^{-2}$)	b_a (mV/dec)	b_c (mV/dec)	Inhibition efficiency (%)	Synergism parameter S_1
Nil	-508	410	70	109	—	—
100	-483	27	60	120	93	2.42
250	-497	17	60	115	96	3.63
500	-488	12	65	106	97	4.47
750	-473	15	60	100	96	2.97
1000	-473	29	70	100	90	1.77

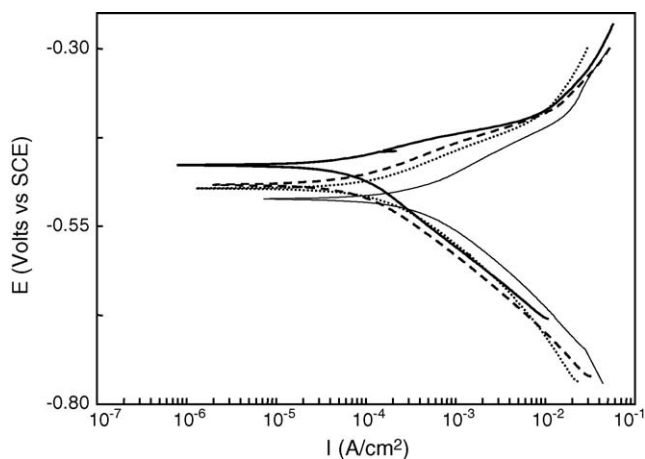


Fig. 8. Polarization curves for iron in 0.5 M H₂SO₄ in the presence of DPA and 1.0 × 10⁻³ M Br⁻ ions. (—) Blank; (···) 100 ppm; (---) 500 ppm; (—) 1000 ppm.

diphenylamine. The Tafel constants b_a and b_c are in the range of 65 ± 5 and 105 ± 5 mV/dec, respectively.

3.4. Synergism parameter

All the experimental results have shown that the addition of halide ions to the inhibitor containing solution increases the inhibition efficiency and the degree of surface coverage (θ). This behaviour is attributed to the synergistic effect between added halide ions and diphenylamine.

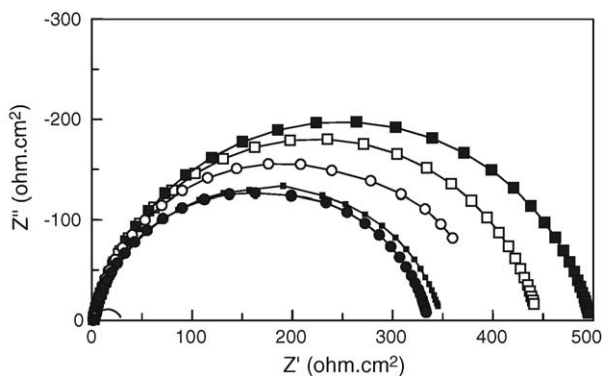


Fig. 9. Impedance plot of iron in 0.5 M H₂SO₄ in the presence of DPA and 0.5 × 10⁻³ M I⁻ ions. (—) Blank; (■) 100 ppm; (□) 250 ppm; (●) 500 ppm; (○) 750 ppm; (●) 1000 ppm.

The synergistic effect of halide ions with diphenylamine may be due to co-adsorption of halide ions and diphenylamine molecules which may be either competitive and co-operative [36]. In competitive adsorption the anion and cation are adsorbed at different 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 diphenylamine has been analysed by estimating the synergism parameter obtained from the inhibition efficiency (from Tafel polarization method) according to Aramaki and Hackerman [37] as:

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \quad (7)$$

where $I_{1+2} = (I_1 + I_2) - (I_1 I_2)$; I_1 is the inhibition efficiency in the presence of synergistic halide ions; I_2 the inhibition efficiency of diphenylamine; I'_{1+2} is the measured inhibition efficiency of synergistic ions in combination with diphenylamine.

Tables 5, 7 and 9 give the computed S_1 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 diphenylamine.

Amines in aqueous acidic solutions may exist as either neutral molecules or in the form of cations [38] depending upon the concentration of H⁺ ions in the solutions. The potential of zero charge (PZC) of iron in sulphuric acid solutions is about -650 mV versus SCE [39]. In this context, the aromatic amines can interact through the π -electrons of benzene ring with the pos-

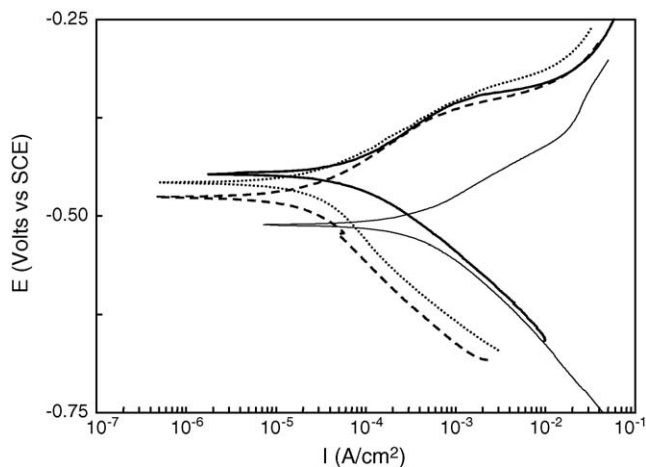


Fig. 10. Polarization curves for iron in 0.5 M H₂SO₄ in the presence of DPA and 0.5 × 10⁻³ M I⁻ ions. (—) Blank; (···) 100 ppm; (---) 500 ppm; (—) 1000 ppm.

itively charged metal surface [40] and offer marginal corrosion inhibition only. But the presence of halide ions, show very good synergism with diphenylamine. 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 [41]. 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 [42]. The corrosion inhibition of medium sized polymer – polymethyleneimine and its synergistic effect with iodide ions has been studied by Aramaki and Hackerman [37] and it is found that anions in acidic solutions play a significant role in influencing the inhibitive ability of the organic compound [43]. Fouda et al. [29] 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 chemisorption 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).

The increase in inhibition efficiency and synergism factor show that the mechanism of synergistic action is due to the co-adsorption of halides and diphenylamine. The strong chemisorption of halide ions on iron electrode surface is responsible for synergistic effect of halide ions in combination with cations of diphenylamine. Since iron is positively charged in H_2SO_4 solutions, the adsorption tendency of amines through the protonated nitrogen is less. Hence, in the case of halide free acidic solutions, diphenylamine, being an aromatic compound, exhibit parallel adsorption through their de-localised π -electrons [44] resulting in a moderate inhibition efficiency. This is very similar to the observation made by Blomgren and Bockris [45] for the adsorption of aromatic amines on the mercury surface. Very good agreement between observed and calculated surface concentrations for monolayer adsorption of aromatic amines in the planar configuration supported this view [46]. But in the presence of halide ions, the adsorbed halide ions make the iron surface into a negatively charged one and due to electrostatic interaction, strong adsorption of protonated nitrogen of amine with halide covered surface takes place. The stabilization of adsorbed halide ions by means of electrostatic interaction with amine cations leads to more surface coverage and hence greater inhibition. Similar hypothesis for the synergistic inhibition of benzotriazole or thiourea and iodide ion on the corrosion of Al-bronze in acidified 4% NaCl is also discussed [47]. A near infrared FT Raman (SERS) and electrochemical study of synergistic effect of 1-[(1',2-dicarboxy) ethyl]-benzotriazole (BTM) and KI on the dissolution of copper in aerated sulphuric acid by Schweinsberg et al. [48] confirmed the displacement of protonated BTM on copper surface by iodide ions which is followed by an over layer of protonated BTM molecules. Due to the change in the orientation of the adsorbed amine, higher surface coverage and higher inhibition efficiency is observed in the presence of halide ions. It can be inferred from this study that the order of synergism of halide ions with diphenylamine molecule is found to

be in the order $I^- > Cl^- > Br^-$. The reason for better synergism with iodide ions may be due to the large size and ease of polarizability of I^- ions which facilitates electron pair bonding [49] with iron surface.

4. Conclusions

Diphenylamine is found to inhibit the corrosion of iron in 0.5 M H_2SO_4 . The inhibition efficiency of diphenylamine is enhanced by the addition of small concentration of halide ions due to the increase in surface coverage values of diphenylamine in the presence of halide ions. The synergistic effect of halide ion is due to increased electrostatic interaction of amine cations by the specifically adsorbed halide ions. The extent of synergism is found to be $I^- > Cl^- > Br^-$.

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