Carmine and Fast Green as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution

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The inhibition action of carmine and fast green dyes on corrosion of mild steel in 0.5 M HCl was investigated using mass loss, polarization and electrochemical impedance (EIS) methods at 300 K. The inhibition efficiency was found to increase with increasing concentration of the inhibitors. The inhibition efficiency of fast green (%η - 98) is higher than that of carmine (%η - 92) and found to be maximum in 1×10^{-3} M solution. The inhibitors act as mixed type with predominant cathodic effect. The inhibitors were adsorbed on the mild steel surface according to the Temkin adsorption isotherm. The surface morphology of the mild steel specimens was evaluated using SEM images.

INTRODUCTION

Mild steel is one of the most important widely used engineering materials particularly for the structural and automobile applications. However, it undergoes rusting easily in the humid atmosphere and its rate of corrosion is quite high in acidic environment. Thus, protection of mild steel from corrosion is an important problem. Out of several methods, use of chemical inhibitors is one of the most practical methods for the prevention of corrosion particularly in acidic media. Acid solutions are widely used in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid de-scaling and oil wet cleansing *etc*. [1,2].

Corrosion inhibitors are generally used to reduce the

corrosion rates. Most of the well known acid inhibitors are organic compounds containing electron donor atoms particularly nitrogen, sulfur, oxygen in their functional groups with aromatic and heterocyclic rings. These compounds have been reported by several workers [1,3-5]. Although nitrogen-containing compounds function more effectively in HCl, oxygen-containing compounds are also found to be equally suitable. Most of the corrosion inhibitors act by adsorption of their molecules on the metal surface. Their action depends on the nature and surface charge of the metal, nature of the medium and the chemical structure of the inhibitor [6].

The use of dyes as inhibitors for mild steel has been reported [7-11] but their use as effective inhibitors for mild steel in acidic media has been rarely cited. Some examples of the applications of these inhibitors are as follows. Inhibition of the corrosion of aluminium alloys by organic dyes: three azo

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compounds-methyl yellow, methyl red and methyl orange [12], corrosion inhibition and adsorption behavior of bismark brown dye on aluminium in sodium hydroxide solution [13], corrosion inhibition of mild steel in acidic media by some organic dyes:safranine-o, thymol blue and fluorescein-Na [14], corrosion inhibition of mild steel in hydrochloric acid solution by methylene blue dye [15-17], inhibition of mild steel corrosion in sulfuric acid using indigo dye and synergistic halide additives [18], triphenylmethane dyes as corrosion inhibitors for Al-Cu alloy in HCl [19].

The aim of this study was to investigate the corrosion inhibition action of carmine and fast green dyes on mild steel in 0.5 M HCl. at 300 K. The comparative inhibition efficiencies of these compounds were determined using mass loss, polarization and impedance (EIS) methods. Further, the work dealt with the study of mechanism of inhibition. The surface morphology study was undertaken to establish good corrosion protection of the compounds.

Carmine is a natural organic dye stuff made from the dried bodies of the female insect coccus cacti which lives on various cactus plants. A red lake pigment is obtained by extracting cochineal with boiling water. Equivalent to alizarin carmine is prepared from 1,2-dihydroxy anthraquinone. Chemically, it is an aluminium and calcium salt of carminic acid, which is soluble in water, and used for dyeing, painting, cosmetics, drinks *etc*. [20].

Fast creen is a biological stain and is an organic dye having the molecular formula $C_{37}H_{34}N_2O_{10}S_3Na_2$. It is soluble in water and used for dyeing, painting and staining [21]. Carmine and fast green are good brilliant dyes and electroactive compounds. The fast green molecules possess electroactive nitrogen, oxygen atoms and aromatic rings whereas carmine molecules possess electroactive oxygen atoms and electron rich *para* quinanoid aromatic rings. The structures of the molecules are shown in Fig. 1 [22].

EXPERIMENTAL

Mass Loss Measurements

Mild steel samples of the composition C = 0.04%, Mn = 0.35%, P = 0.022%, S = 0.036% and Fe = 99.552% were used for the measurement of the corrosion rates. Rectangular specimens of working surface area 5×2 cm^2 were used for the mass loss method and 1×1 cm^2 with a 5 cm long stem (isolated with Teflon tape) for the electrochemical methods. These specimens were polished mechanically using emery papers of grade no. 220, 400, 600, 800 and 1200 and washed thoroughly with triple distilled water, degreased with acetone and dried using air flow at room temperature. These specimens were dipped in 0.5 M HCl and inhibitor solutions separately for 4 h at 300 K and mass loss was determined. The volume of test solutions used was 150 ml. Duplicate experiments were performed in each case and the average values of mass loss were recorded. Mass loss was expressed in mg and corrosion rate in mg cm^{-2} h^{-1}.

The aggressive solution of 0.5 M HCl was prepared by dilution of A.R. grade HCl (35.4%, density 1.18). Research grade pure carmine and fast green are obtained from s.d.fiNE-CHEM LTD. They are water soluble dyes and test solutions were prepared in 0.5 M HCl solution.

Polarization Measurements

Polarization measurements were performed using a computer-controlled instrument Autolab PGSTAT 30 (Eco Chemie BV, Netherlands). A cell containing three compartments for electrodes was used. The working polished mild steel electrode with exposed area 1 cm^2 was dipped in the test solution. A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and the counter electrodes, respectively. All potentials were measured *vs*. SCE.

Impedance Measurements (EIS)

The impedance measurements were carried out in the frequency range of 10 kHz to 10 mHz, at the rest potential, by applying a 5 mV sine wave ac voltage. The same cell and instrument as in the polarization method were used. The double layer capacitance (C_{dl}) and resistance polarisation (R_p) were calculated from Nyquist plots as described elsewhere [23].

RESULTS AND DISCUSSION

Mass Loss Measurements

The corrosion of mild steel in 0.5 M HCl was studied by mass loss measurements at 300 K. The corrosion experiments
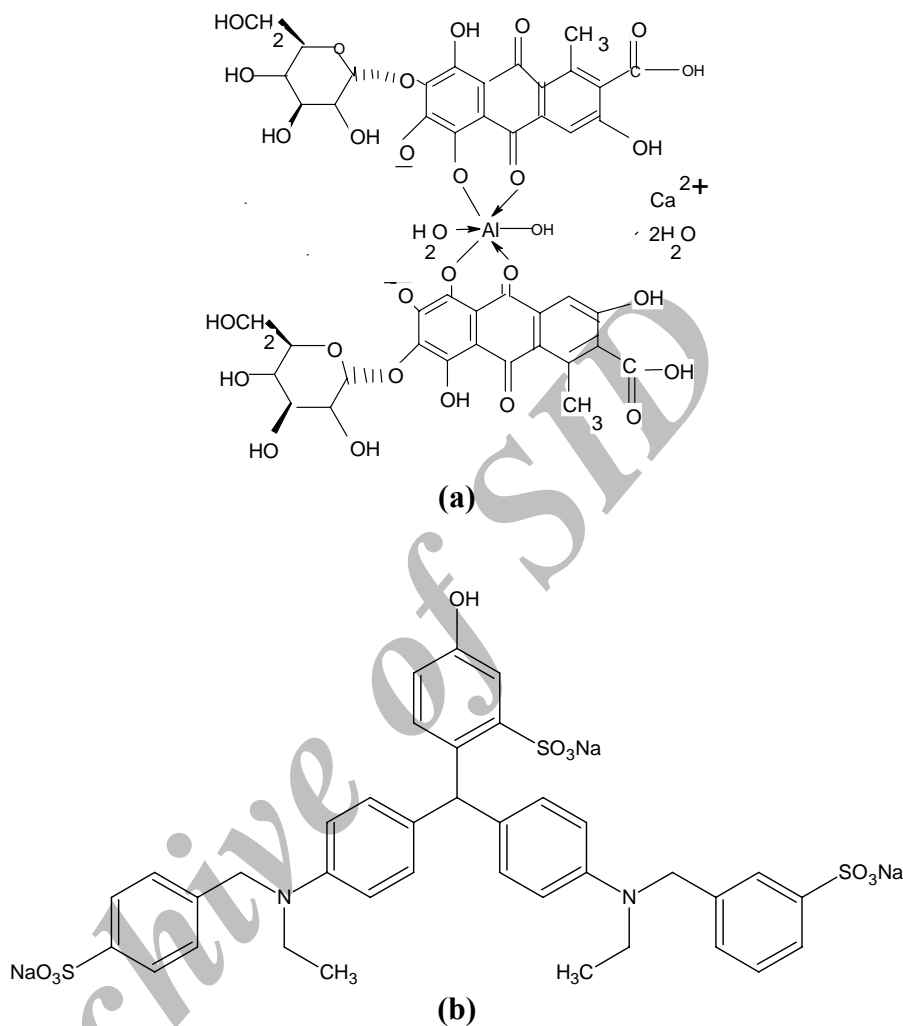
Fig. 1. Structures of carmine (a) and fast green (b).

were repeated at different concentrations of the inhibitors and, in each inhibitor concentration, the mass loss of mild steel was measured. The corrosion rate, W, of mild steel was determined using:

$$W = \Delta m / Sxt$$

where, Δm = mass loss, S = surface area, t = immersion period in h. The percentage inhibition efficiency, %η, was calculated using the relation:

$$\%\eta = [(W - W_I)/W] \times 100$$

Similarly, the parameter θ, which represents the surface coverage of the metal by the inhibitor molecules, was calculated using:

$$\theta = (W - W_I)/W$$

In above equations, W and W_I are the corrosion rates of mild steel in the absence and presence of the inhibitor. The values of corrosion rates and inhibition efficiencies of carmine and fast green in 0.5 M HCl are shown in the Table 1.

The data in the Table 1 revealed that the amount of mass loss decreased with increasing additive concentration, *i.e.*, the

Table 1. Corrosion Parameters and Inhibition Efficiency Obtained from the Mass Loss Measurements for Mild Steel in 0.5 M HCl Containing Various Concentrations of the Dyes at 300 K

Inhibitor	Concentration $\times 10^{-5}$ (M)	Loss in mass (mg)	Corrosion rate (mg cm^{-2} h^{-1})	Inhibition efficiency (%η)
Blank	-	113.2	1.244	-
Carmine	2	37	0.386	67
	5	30	0.330	73
	10	25	0.274	78
	20	20	0.224	82
	50	13.6	0.150	88
	100	9	0.100	92
Fast green	2	32	0.350	72
	5	23	0.250	80
	10	18	0.200	84
	20	14	0.150	88
	50	6.8	0.075	94
	100	1.2	0.013	99

increased inhibition efficiency with the inhibitors concentration. The maximum inhibition efficiency (99%) was obtained for fast green at 1×10^{-3} M. The inhibition efficiencies did not improve after 1×10^{-3} M concentration (optimum concentration) of the inhibitors.

Polarization Measurements

Polarization curves for mild steel in 0.5 M HCl in the absence and presence of carmine and fast green of various concentrations at 300 K are shown in Figs. 2 and 3. From the polarization curves it was evident that cathodic curves are affected more than anodic curves. The inhibitors act as mixed type with predominant cathodic effect. Electrochemical corrosion parameters, such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_a and b_c), corrosion current (I_{corr}) and inhibition efficiency (%η), obtained by extrapolation of the Tafel lines, are shown in Table 2. Inhibition efficiency, %η, was calculated using the formula:

$$\%\eta = [(I_{corr} - I'_{corr}/I_{corr})] \times 100$$

where I_{corr} and I'_{corr} are the corrosion current in the absence and presence of the inhibitors.

The data inferred that the percentage inhibition efficiency increased with increasing concentration of the inhibitors. Further, the concentration of the inhibitors employed for the study was in mM range and indicated the great deal of activeness of these compounds to steel surface.

The inhibition efficiency data showed that fast green inhibited the corrosion of mild steel to a greater extent than carmine. This might be due to the presence of active donor N atoms of fast green molecule. The maximum inhibition efficiency (98%) was obtained in fast green at a concentration of 1×10^{-3} M.

Electrochemical Impedance Spectroscopy (EIS)

Nyquist plots for mild steel in 0.5 M HCl in the absence and presence of dyes at various concentrations were shown in Figs. 4 and 5. The Nyquist plots show that, the diameter of the capacitive loop and consequently the value of the charge transfer resistance, R_p increased with the concentration of inhibitors, which is an indication of the inhibitive action.

In all cases, the semicircle corresponds to a capacitive loop. The semicircle radii depend on the inhibitor concentration. The diameter of the capacitive loop increased with increasing inhibitor concentration, the increase is more
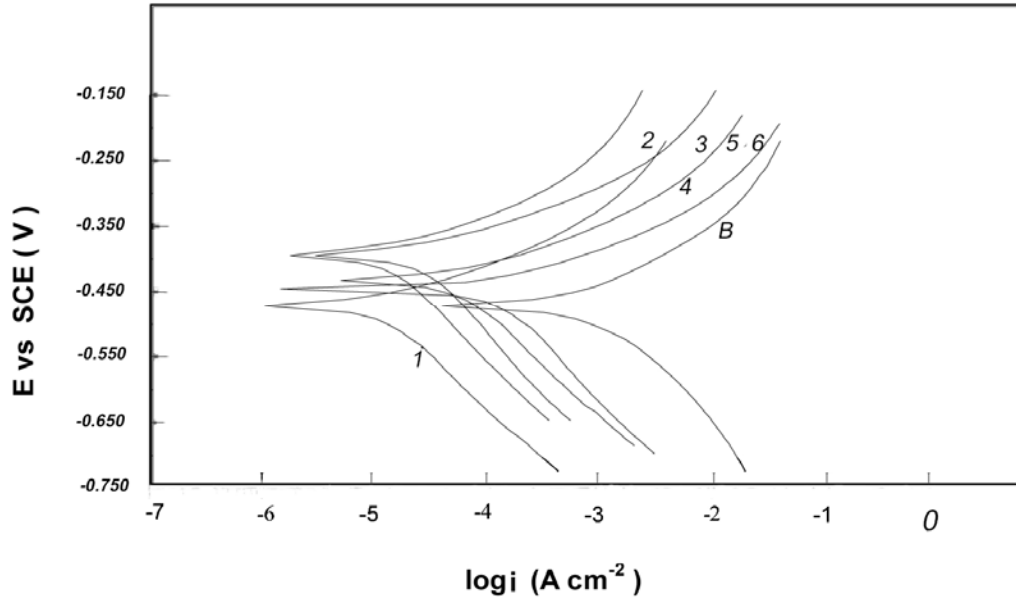
Fig. 2. Polarization curves for mild steel in 0.5 M HCl in the presence of carmine at different concentrations at 300 K: (B) Blank, (1) 1×10^{-3} M, (2) 5×10^{-4} M, (3) 2×10^{-4} M, (4) 1×10^{-4} M and (5) 5×10^{-5} M.
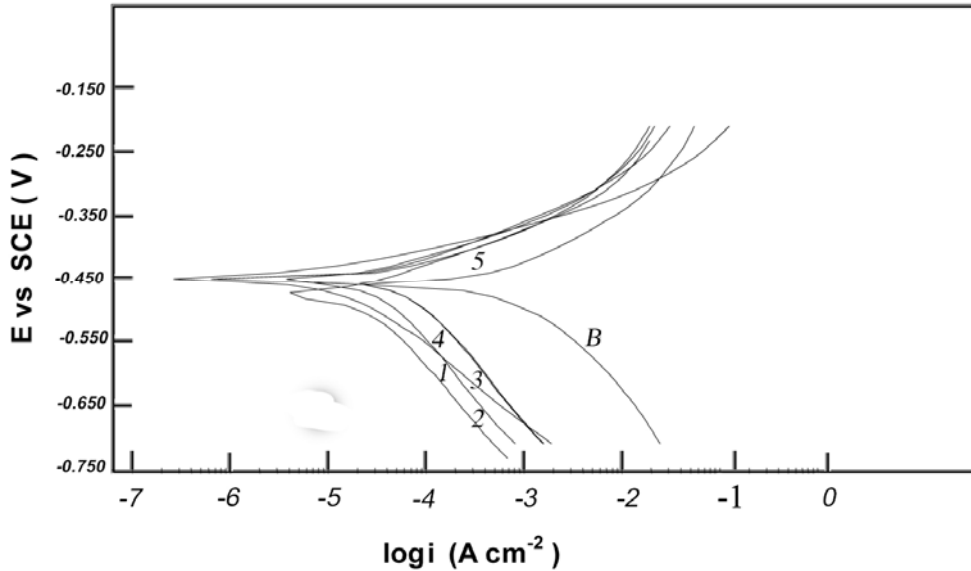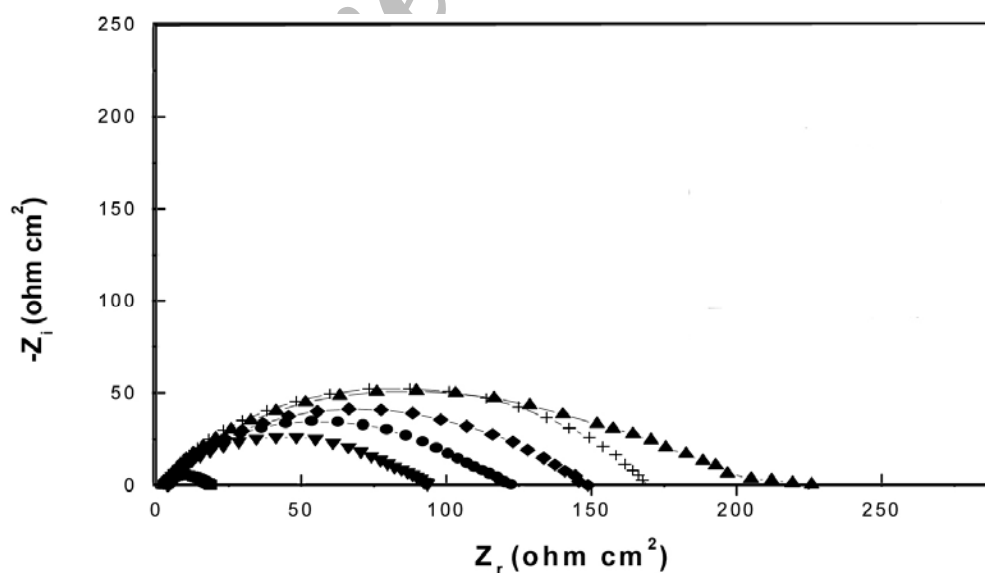

Fig. 3. Polarization curves for mild steel in 0.5 M HCl in the presence of Fast green at different concentrations at 300 K: (B) Blank, (1) 1×10^{-3} M, (2) 5×10^{-4} M, (3) 2×10^{-4} M, (4) 1×10^{-4} M and (5) 5×10^{-5} M.

significant in fast green. The results show that R_P values increased with an increase in inhibitor concentration. As R_P is inversely proportioned to the corrosion current, it was used to determine the inhibitor efficiency, %η, from the relationship:

$$\%\eta = [(R_p - R_P{}')/R_p] \times 100$$

Table 2. Polarization Parameters for the Mild Steel in 0.5 M HCl Containing Different Concentrations of the Dyes at 300 K

Inhibitor	Concentration (10^{-5} M)	$-E_{corr}$ (mV)	I_{corr} (mA cm^{-2})	b_a (mV dce^{-1})	$-b_c$ (mV dce^{-1})	%η
Blank	-	467	1.582	116	204	-
Carmine	2	448	0.540	66	153	66
	5	450	0.440	110	165	72
	10	441	0.370	74	179	77
	20	445	0.270	115	166	83
	50	451	0.200	107	163	87
	100	442	0.133	71	200	92
Fast green	2	463	0.430	112	169	73
	5	450	0.290	86	141	81
	10	466	0.250	103	156	84
	20	451	0.183	87	157	88
	50	442	0.080	79	162	95
	100	480	0.034	62	172	98

Fig. 4. Nyquist plots for mild steel in 0.5 M HCl in the presence of carmine at different concentrations at 300 K: (■) Blank, (▲) 1×10^{-3} M, (+) 5×10^{-4} M, (◆) 2×10^{-4} M, (●) 1×10^{-4} M and (▼) 2×10^{-5} M.

where R_P and R_P' are the polarization resistances in the presence and absence of inhibitors, respectively.

The electrochemical impedance parameters derived from the Nyquist plots and the inhibitors efficiencies (%η) are shown in Table 3. From the results obtained, it was clear that these two compounds inhibit the corrosion of mild steel in HCl
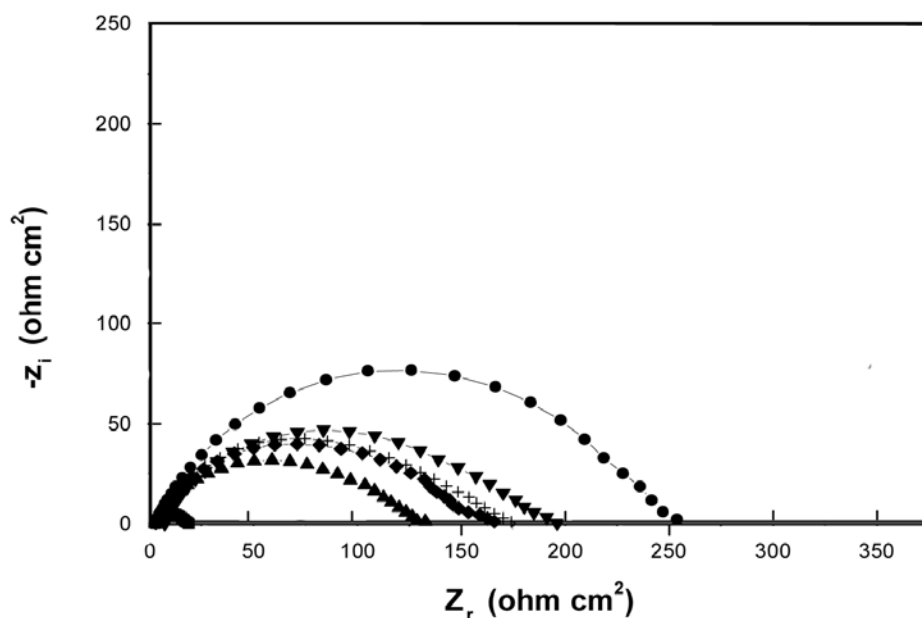
Fig. 5. Nyquist plots for mild steel in 0.5 M HCl in the presence of fast green at different concentrations at 300 K: (■) Blank, (●) 1×10^{-3} M, (▼) 5×10^{-4} M, (+) 2×10^{-4} M, (◆) 1×10^{-4} M and (▲) 2×10^{-5} M.

Table 3. Impedance Parameters and Inhibition Efficiency for Mild Steel in 0.5 M HCl Containing Different Concentrations of the Dyes at 300 K

Inhibitor	Concentration (10^{-5} M)	R_p (Ω cm^2)	Capacitance, C_{dl} (μF cm^{-2})	%η
Blank	-	8.16	540	-
Carmine	2	24.3	183	66
	5	28.7	156	71
	10	32.1	135	75
	20	40.2	108	80
	50	64.3	70	87
	100	90.5	48	91
Fast green	2	26.2	173	68
	5	42.6	103	81
	10	48.2	92	83
	20	60.0	75	86
	50	132.8	52.5	94
	100	224.5	21	96

solution to a different extent and the inhibition efficiency increased with increase of concentration of the inhibitors. Table 4 revealed that the results of all the three methods are in good agreement within the experimental error.

Scanning Electron Microscopic (SEM) Studies

Figures 6 shows the SEM images of mild steel surface after immersed in 0.5 M HCl in the absence and presence of fast green and carmine 4 h. Close examination of the SEM images revealed that the specimens immersed in the inhibitor solutions are in better conditions with smooth surfaces compared with those of corroded rough and coarse uneven surfaces of mild steel immersed in 0.5 M HCl alone. This observation indicated that corrosion rate is reduced to a very low value in the presence of the inhibitors. This might be due to the adsorption of inhibitor molecules on the metal surface as a protective layer.

Adsorption Isotherm

A plot of θ against logC gave almost a straight line (Fig. 7) which indicated that the inhibition action obeyed Temkin adsorption isotherm given by the equation:

$$\theta = k \ln C$$

where, θ is the surface coverage, C is the concentration of the inhibitor solution and k is an adsorption coefficient.

From Fig. 7 it was found that the extent of adsorption of the inhibitors is increased with their concentration. It was also revealed from Table 1 that inhibition efficiency increased with an increase in the concentration of inhibitors. This behavior could be attributed to the increasing surface coverage (θ) with to the adsorption of the inhibitor molecules at higher concentrations.

The adsorption coefficient, k, can be obtained from the slope of the linear plot of θ *vs*. logC (Fig. 7). The value of k for fast green (0.161) was found to be greater than that of carmine (0.141), indicating greater inhibition power of fast green.

Mechanism of Inhibition

This isotherm depicted in Fig. 7 characterizes the chemisorption of dye molecules on heterogeneous surfaces [24]. Thus, the mechanism of corrosion inhibition of mild steel in acidic solution by the dye molecules can be explained on the basis of adsorption on the metal surface. The adsorption of the inhibitor molecules on the mild steel surface is due to the donor acceptor interaction between π electrons of donor atoms N, O and aromatic rings of inhibitors and the vacant d orbitals of iron surface atoms [21-23].

The fast green molecules possess electroactive nitrogen, oxygen atoms and aromatic rings which favor the adsorption on metal surface. Similarly the carmine molecules possess electroactive oxygen atoms and electron rich *para* quinanoid

Table 4. Comparison of Inhibition Efficiencies (%η) Obtained from Different Methods

Inhibitor	Concentration (10^{-5} M)	Mass loss	Polarization	Impedance
Carmine	2	67	66	66
	5	73	72	71
	10	78	77	75
	20	82	83	80
	50	88	87	87
	100	92	92	91
Fast green	2	72	73	68
	5	80	81	81
	10	84	84	83
	20	88	88	86
	50	94	95	94
	100	99	98	96
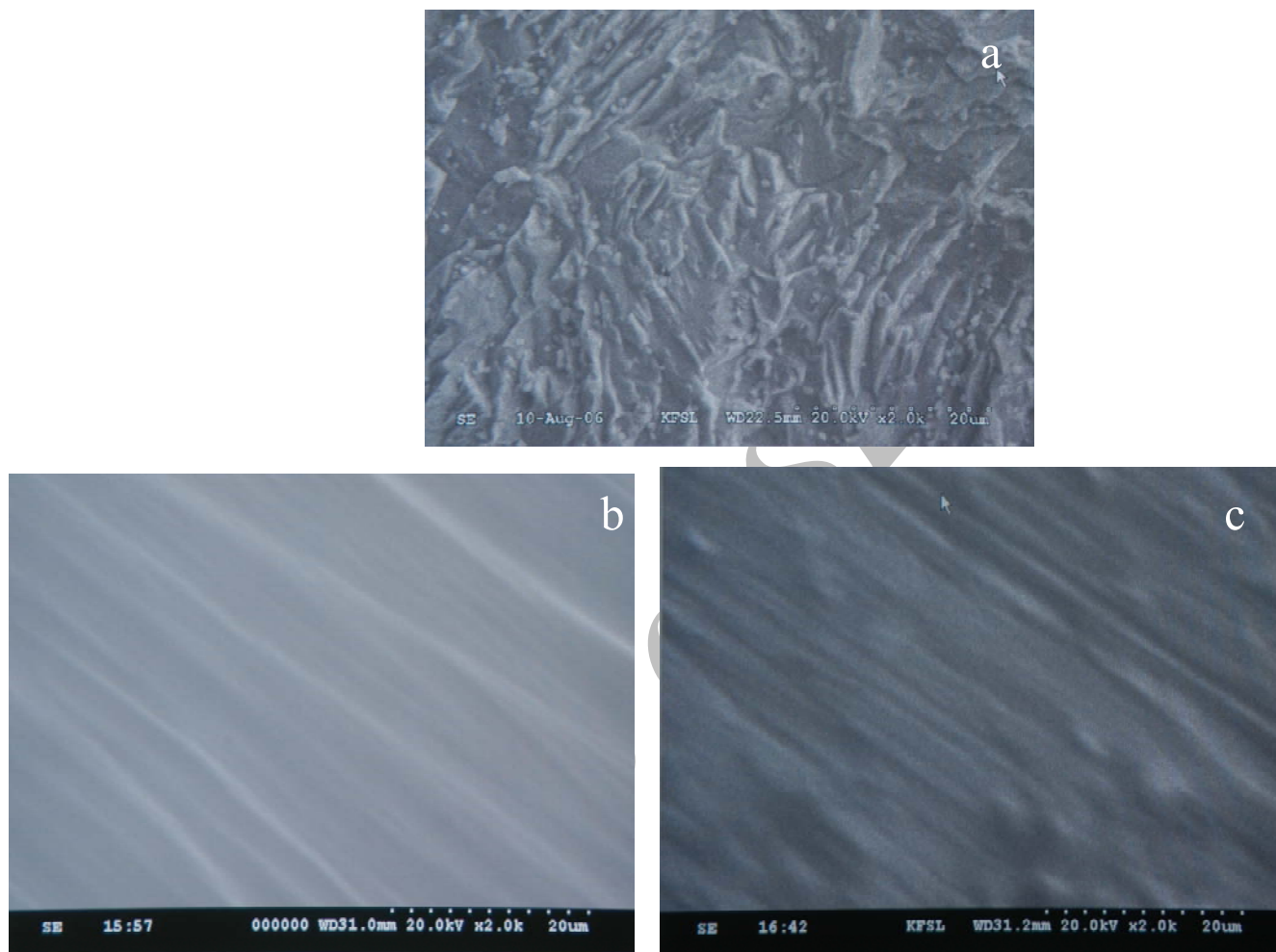
Fig. 6. Scanning electron micrographs of the mild steel surface after 4h immersion at 300 K in (a) 0.5 M HCl, (b) 0.5 M HCl + 0.001 M carmine, (c) 0.5 M HCl + 0.001 M fast green.

aromatic rings. Furthermore, both the molecules are large and flat enough to block more surface areas of the mild steel. The carmine molecule can also coordinately bond with the metal through aluminium. The inhibitor molecules can also be adsorbed on the metal surface in the form of negatively charged species which can interact electrostatically with positively charged metal surface.

CONCLUSIONS

Fast green and carmine are found to be good inhibitors for mild steel in HCl. Inhibition efficiencies vary linearly with concentration. The optimum concentration of the inhibitors

found to be 1×10^{-3} M at 300 K. The inhibitors act as mixed type with predominant cathodic effect. The results obtained from the mass loss, polarization and EMS methods match one another. The inhibitors obey Temkin adsorption isotherm in HCl medium. The presence of inhibitors simultaneously avoids the evolution of hydrogen and dissolution of metal.
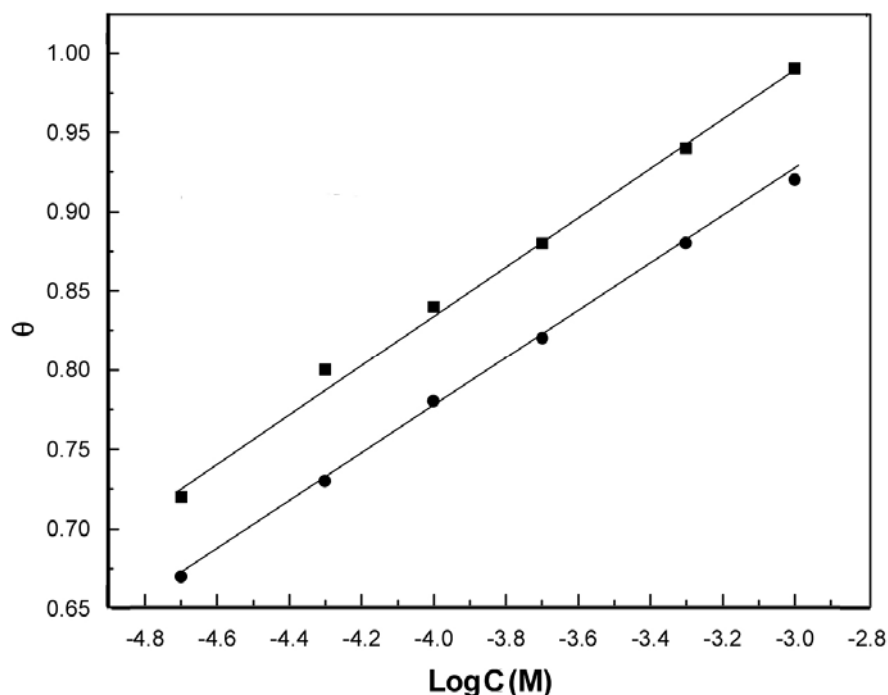
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Fig. 7. Temkin isotherm for the adsorption of the dyes on the mild steel surface: (●) carmine and (■) fast green.

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