DYES AS CORROSION INHIBITORS PART II TRIPHENYL METHANE DYES AS INHIBITORS FOR ALUMINIUM – COPPER ALLOY IN PHOSPHORIC ACID

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The inhibitive efficiency of triphenylmethane dyes for B26S aluminium in phospheric acid increases with inhibitor concentration but decrease with acid concentration. At 0.5% inhibitor concentration in 0.033M H_3PO_4,the efficiency increases in the order : Methyl vilet 6B (15%) < crystal violet < fuchsine acid < fuchsine base (36%) < malachite green (68%) < victoria blue (75%) < light green < fast green (88%). A rise in temperature decreases the efficiency, the energy of activation for the corrosion process being 14.7 Kcal/mole.

B26S aluminium in 0.033 M H_3PO_4 develops a corrosion protential of -755 mV vs SCE. The potentials are found to range from -740 (fuchsine acid) to -805 mV (crystal violet). In inhibited acid, galvanostatic polarisation curves show polaisation of both, cathodes as well as anodes. The inhibitors appear to function through general adsorption following Langmuir isotherm.

Solutions of phosphoric acid are frequently employed for cleaning aluminium <1,2>, in commercial preplating anodic oxidation <3> and in chemical polishing <4,5> or etching of Aluminium. For electroplating <5,6> phosphoric acid baths containing thiourea <2>, ethylene glycol, glucose<5>, gelatin etc are used. These additives function as corrosion inhibitors and also as surface brightners. Although dyes are used to give multi-coloured effects to anodised aluminium surfaces, data regarding their effect on the acid corrosion of aluminium is not much available. Talati and Gandhi have studied the effect of some dyes as corrosion inhibitors for B26S aluminium in hydrochloric acid <8>. The present work was undertaken to study the effect of some triphenylmethane dyes as corrosion inhibitors for B26S aluminium (Al-4% Cu alloy) in phosphoric acid.

EXPERIMENTAL

Rectangular specimens (50x40 mm) of B26S aluminium (supplied by Indian Aluminium Co Ltd., Bombay) were used for the determination of the corrosion rate. The alloy used and the experimental procedure followed was the same as that described by Talati and Gandhi<8>, with H_3PO_4as the corroding medium. The ranges of concentrations studied were 0.0033M to 1.3M for the acid and 0.01 – 0.5% for the inhibitors.

For galvanostatic polarisation studies circular metal coupon, dia. 28.4 mm with a handle 32.2 x 4.8 mm, were used. The area exposed to the test solutions was 6.33 cm^2 while the appllied c.d. was varied in the range 1.58×10^{-5} to 7.943×10^{-4} A/cm^2 .

RESULTS AND DISCUSSION

Observations

In inhibited acid, the specimens were covered with a loose film of the same colour as that of the dye and it could be easily removed by the cleaning solution. The surface of the corroded specimens on cleaning showed a dull metallic appearence.

Corrosion In Unihibited Phosphoric Acid

Effect of Acid Concentration and Immersion Period

To study the effect of acid concentration and immersion period on corosion, weight losses were determined in 0.033M to 0.667M plain phosphoric acid for immersion periods ranging from 1/2 to 3 days and are shown in Fig.1.

The decrease in corrosion rate at lower acid concentrations may be traced to a slight increase in the pH of the solution due to the depletion of the acid during

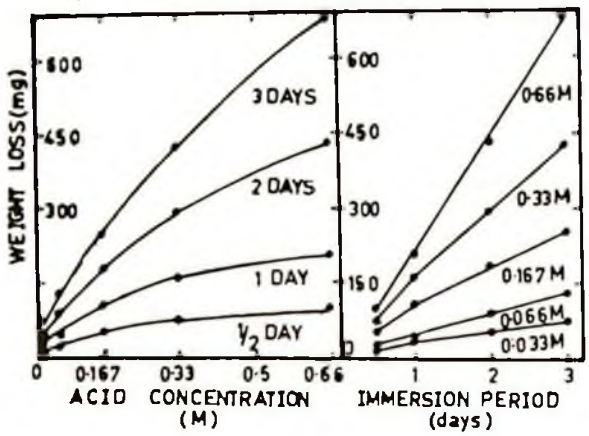


Fig. 1 Effect of acid concentration and exposure period on the corrosion of B26S aluminium in phophoric acid (30 C).

corrosion. This increase in pH may favour the formation of protective oxide film which is reported to be more stable in the pH range 3 - 10 <9,10>. Further as the solubilities of the various aluminium phosphates increase in the order :- $AlPO_4$ < $Al_2(HPO_4)_3$ < $Al(H_2PO_4)_3$. There will not be any formation of the film of aluminium phosphate on the metal surface and hence aluminium will dissolve in higher concentrations of the acid with the formation of $Al(H_2PO_4)_3$ leading to an increase in the corrosion rate.

Corrosion in Inhibited Acid

Effect of Inhibitor Concentration

To assess their effect as corrosion inhibitors, various triphenylmethane dyes were added in concentrations ranging from 0.01 -0.5% in 0.33 M phosphoric acid and the weight losses were determined in these solutions at 30 ± 0.5 C for 1 day immersion period. The results are given in Fig.2. From the results, it may be generalised that in almost all the cases, the inhibitive efficiency increases with inhibitor concentration. Thus at an inhibitor concentration of 0.01%, the efficiency of the various inhibitors is found to increase in the order: Methyl violet 6B (1.6%) < fuchsine base (6.17%) < crystal violet (6.5%) < malachite green (7.1%) < fuchsine acid (8.3%) < Victoria blue (13.6%) < fast green (17.5%) < light green (28.0%).

At 0.5% concentration the efficiency increases in the order : Methyl violet 6B (15.1%) < crystal violet (25.8%) < fuchsine acid (30.6%) < fuchsine base (36.4%) < malachite green (68.0%) < victoria blue (74.8%) < light green (75.5%) < fast green (88.0%).

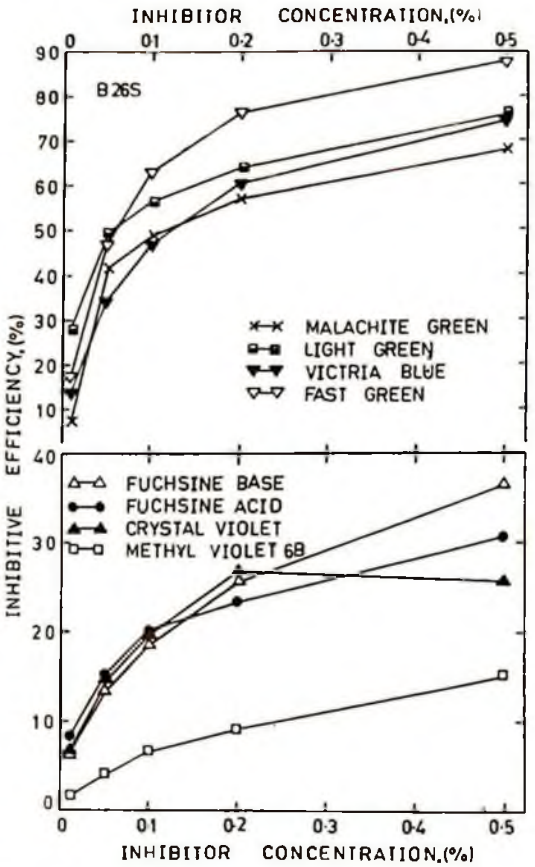


Fig. 2 Effect of inhibitor concentration on inhibitive efficiency of some dyes for B26S aluminium in 0.033 M phosphoric acid (30 C 1 day)

It is apparent from the results that of the eight compounds studied malachite green, victoria blue, fast green and light green show better efficiency (> 50%) at concentrations ranging from 0.1 - 0.5%.

Effect of Acid Concentration on Inhibitive Efficiency.

To determine the effect of acid concentration on inhibitive efficiency, weight losses were determined in different concentrations of acid (0.167M to 1.33M) containing a constant inhibitor concentration of 0.1%. From the results given in Fig.3, it may be generalised that the efficiency of almost all the inhibitors decreases with increase in acid concentration. Thus in 0.167 M acid, the efficiency

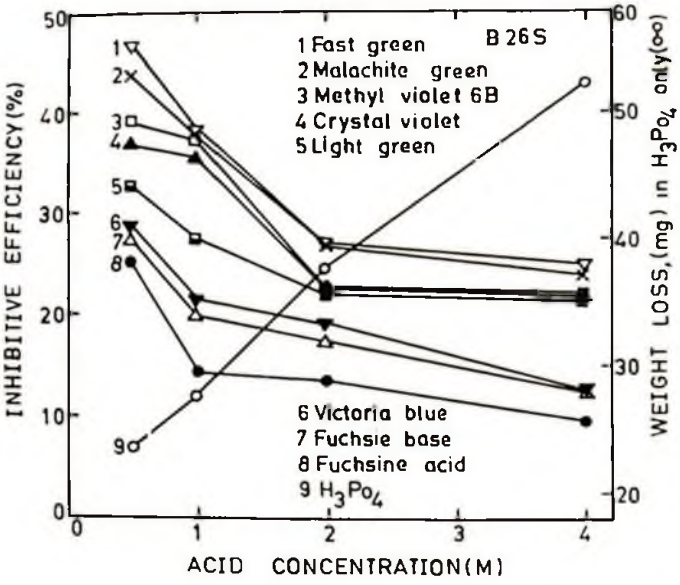


Fig. 3 Effect of concentration of H_3PO_4 on inhibitive efficiency of triphenylmethane dyes for B26S aluminium (30° C)

increases in the order : Fuchsine acid (25.2%) < fuchsine base (27.3%) < victoria blue (28.6%) < light green (32.5%) < crystal violet (36.7%) < methyl violet 6B (38.9%) < malachite green (43.6%) < fast green (44.6%). In 1.33 M acid, the various dyes studied conferred only 9.4% (fuchsine acid) to - 26.8% (fast green) protection. The behaviour of the inhibitors in phosphoric acid is thus quite different from that in hydrochloric acid <8,11>, wherein the efficiency was found to increase with acid concentration.

The presence of chloride ions was suspected to be the cause of this anomalous behaviour and therefore weight losses were determined in 0.033 M H_3PO_4 containing 0.1% inhibitor and 0.1 M sodium chloride (Table 1). It was found that the inhibitive efficiency of malachite green, fuchsine base, fuchsine acid, crystal violet and methyl violet 6B increased by 4 - 26% in the presence of chloride ions. Thus the chloride ions seems to augment the inhibitive behaviour of the dyes,, perhaps by the in situ formation of compounds like (inhibitor) Al_xCl_y H_2O on the metal surface <12,17>, which may account for an increase in efficiency with increase in acid concentration in the case

TABLE 1

Effect of chloride ion on inhibitive efficiency of triphenylmethane dyes for B26S aluminium in H_3PO_4.

(<H_3PO_4>, 0.033 M; inhibitor 0.1%
Temperature, 30° C; Exposure period, 1 day)

Inhibitor	0.033 M H_3PO_4		0.033 H_3PO_4 0.1 M NaCl	
	Loss,mg	%I.	Loss,mg	%I.
Nil	33.7	-	26.6	21.0
Victoria blue	16.5	51.0	22.8	32.5
Fast green	12.3	63.5	12.2	63.3
Light green	14.6	56.7	18.8	44.2
Malachite green	17.2	49.0	12.3	63.5
Fuchsine base	27.5	18.4	18.7	44.5
Fuchsine acid	26.9	20.2	25.4	24.6
Crystal violet	27.1	19.6	22.4	33.5
Methylviolet 6B	31.5	6.5	25.9	23.1

of hydrochlorochloric acid

Effect of Temperature

To study the effect of temperature on inhibitive efficiency, weight losses were determined in 0.167M H_3PO_4 containing 0.1% inhibitor at solution temperature of 30°, 40°, 50° and 60° C. The results are given in Table 2. From the results it is evident that in inhibited as well as in unihibited acid, the extent of corrosion increases and the inhibitive efficiency decreases with a rise in temperature. The decrease in efficiency is maximum with fast green and malachite green which happen to be better inhibitors at ordinary temperatures. At 60° C, the inhibitive efficiencies were quite lower and ranged from 6.0 (fuchsine acid) to 22.5% (fast green).

The values of the energy of activation. E, were caluclated from the slopes of the Arrhenious plots of log corrosion rate (mg/dm^2) vs 1/T, (Fig 4). The E values are given in Table 3. A comparison of the E values in the presence and absence of inhibitors indicates that the values for inhibited acid are almost the same (within ± 2 kcal/mole) as that in unihibited acid. According to Putilova et al, the behaviour of such inhibitors resembles that of stable poison in heterogeneous catalysis which do not effect the temperature coefficient of the reaction <18>.

The values of heat of adsorption, Q, were calculated from the equation:

TABLE 2

EFFECT OF TEMPERATURE ON INHIBITIVE EFFICIENCY OF TRIPHENYL METHANE DYES FOR B26S ALUMINIUM IN 0.167 M H_3PO_4.

(Inhibitor concentration, 0.1% ; exposure period, 5 hrs surface area of specimen, 40 cm^2).

Inhibitor	% Inhibition at temperature of			
	30°C	40°C	50°C	60°C
Nil	(23.4)*	(44.7)	(85.4)	(152.2)
Victoria blue	28.6	17.7	15.9	14.1
Fast green	46.6	31.3	27.0	22.5
Light green	32.5	21.3	17.3	14.8
Malachite green	43.6	36.7	33.8	19.7
Fuchsine base	27.3	17.0	10.8	8.0
Fuchsine acid	25.2	15.6	7.0	6.0
Crystal violet	36.7	30.6	25.8	15.5
Methyl violet 6B	38.9	33.5	25.5	16.3

* The value in the parentheses indicates the weight loss in plain 0.167 M H_3PO_4.

TABLE 3

ENERGY OF ACTIVATION, (E), HEAT OF ADSORPTION, (Q), AND FREE ENERGY OF ADSORPTION, (ΔG_A°), OF TRIPHENYLMETHANE DYES DURING CORROSION OF B26S ALUMINIUM IN 0.167 M H_3PO_4

(Inhibitor concentration, 0.1%, Exposure period, 5hrs, surface area of specimen, 40 cm^2)

Inhibitor	% I at 30°C	E* kcal/mole	Q, k cal/mole, for the range 30-40°C	40-50°C	50-60°C	ΔG_A° (kcal/mole)
Nil	-	14.7	-	-	-	-
Victoria blue	28.6	12.9	-11.3	- 2.5	- 3.0	-3.1
Fast green	46.6	14.3	-13.1	- 4.2	- 5.3	-3.5
Light green	32.5	13.8	-10.9	- 5.1	- 3.9	-3.1
Malachite green	43.6	15.2	- 5.4	- 2.5	-15.6	-3.5
Fuchsine base	27.3	13.5	-11.5	-10.6	- 6.9	-2.9
Fuchsine acid	25.2	15.4	-11.2	-18.1	- 3.7	-2.7
Crystal violet	36.7	14.1	-10.4	- 4.9	-13.6	-3.3
Methyl violet 6B	38.9	14.9	- 4.4	- 7.8	- 4.6	-3.2

* From Fig. 6.

$$Q = 2.303\ R\left\{\log \frac{\theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1}\ \frac{T_1 T_2}{T_2 - T_1}\right\} \quad \ldots(1)$$

where θ_1 and θ_2 are the fractions of the metal surface covered by the inhibitor at tempperatures T_1 and T_2 (°K) respectively. The θ values are given in Table 3. From the table, it is evident that in all the cases the θ values are negative and range from -2.4 to -18.1 kcal/mole. The negative θ values show that the adsorption and hence the inhibitive efficiency decreases with a rise in temperature.

The values of the free energy of adsorption, ΔG_A°, are calculated with the help of the equation

$$\log C = \log \frac{\theta}{1-\theta} - \log B \quad \ldots\ldots(ii)$$

$$\log B = -1.74 - (\Delta G_A^\circ / 2.303\ RT) \quad \ldots\ldots(iii)$$

where C is the inhibitor concentration. These are given in Table 3. A comparison of the values of inhibitive efficiency and the free energy of adsorption shows that

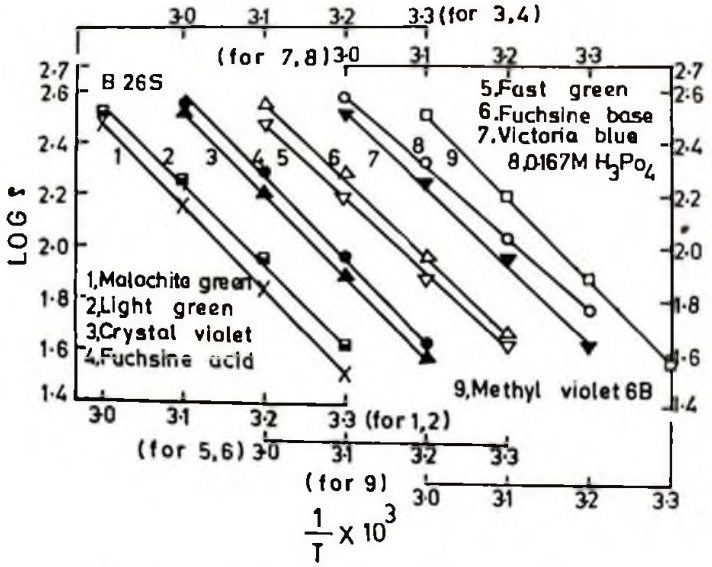


Fig. 4 Arrhenicus plots for corrosion of B26S aluminium in 0.167 M H_3PO_4 containing 0.1 inhibitor (5 h).

those compounds which show better efficiency give more negative free energy of adsorption.

Polarisation Behaviour

A specimen of B26S aluminium, when immersed in 0.0033 M H_3PO_4, developes a corrosion potential of -690 mV vs SCE. As the acid concentration is increased, the open circuit potential becomes more and more negative, it being -755 mV and -785 mV in 0.033 M and 0.33 M H_3PO_4 respectively. (Fig. 5).

In inhibited 0.033 M acid, the potentials are found to range from -740 (fuchsine acid) to -805 mV (crystal violet) (Table 4). The anodic and cathodic galvanostatic polarisation curves for B26S aluminium in 0.033M H_3PO_4 alone and containing 0.002 M concentration of the various inhibitors (i.e.,the same number of molecules of each inhibitor) are shown in Fig.6. The curves show polarisation of both, the cathodes as well as the anodes, the anode being polarised to a greater extent than the cathode. The predominant polarisation of local anodes under the influence of an anodic current suggests that the inhibitors may be useful when anodic protection of aluminium in phosphoric acid is desired.

Inhibitive efficiency calculated from corrosion currents obtained by extrapolation

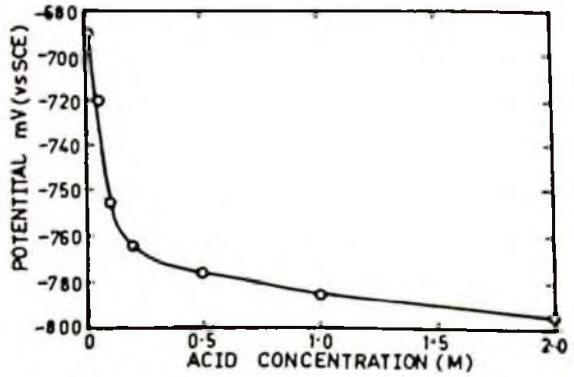
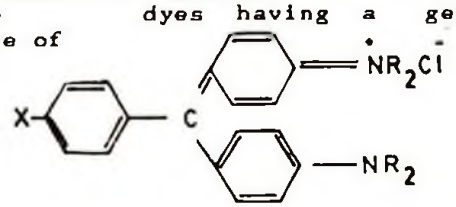


Fig. 5 Influence of acid conentration on the open circuit potential of B26S aluminium in H_3PO_4.

of the cathodic and anodic Tafel lines to the open circuit potentials are also given in Table 4. In almost all the cases, the Tafel plot efficiencies agree well (within ± 7%) with the values obtained from weight loss data.

Mechanism of Inhibition

All the inhibitors discussed are triphenylmethane dyes having a general structure of



Where X = -H, $-NHCH_3$, $-N(CH_3)_2$, $-N^+(CH_3)Cl^-$ and R = -H, $-CH_3$, $-C_2H_5$

In addition, fuchsine acid, fuchsine base and victoria blue contain some more subtituent groups.

The dyes investigated do not have much effect on the pH of the corroding solution as is evident from the pH values of the inhibited acid (Table 4). Further, both aluminium hydroxide and aluminium phosphate are insoluble in near neutral solutions and, therefore, in cases where, due to the corrosion process, the acid becomes depleted of a certain amount of hydrogen ions, there is every possibility that a film of oxide (or hydroxide) or phosphate may be deposited in situ. This would lead to a diminution of attack. On the other hand, if the inhibitor molecule contains one or more polar units having atoms of nitrogen, sulphur, oxygen etc., the inhi-

TABLE 4

TAFEL PARAMETERS AND INHIBITOR EFFICIENCIES OF THE DYES FOR B26S ALUMINIUM IN 0.033 M H_3PO_4 (Inhitior 0.002 M; Temperature, 30 ± 0.5°C ; Surface area of the secimen, 6.33 cm^2).

Inhibitor	pH of 0.033 M H_3PO_4 containing 0.1% inhibitor.	Open Circuit potential mV (vs SCE)	Tafel slope V/decade		Energy transfer coefficient (cathodic)	I Corr ($A/cm^2 \times 10^5$), from extraplotation of		Inhibitor efficiency % from Tafel Line		
			Cathodic	Anodic		Cathodic	Anodic	Cathodic	Anode	Weight loss data
Nil	1.8	-755	0.78	0.12	0.077	4.17	4.17	-	-	-
Victoria blue	1.80	-785	0.053	0.064	-	2.24	2.4	46.3	42.5	47.5
Fast green	1.80	-785	0.24	0.32	0.25	1.91	1.91	54.3	53.2	52.8
Light green	1.85	-775	0.064	0.19	0.94	2.0	2.1	52.1	48.7	55.8
Malachite green	1.85	-795	0.12	0.27	0.50	2.3	2.5	45.0	39.7	42.4
Fucshine base	1.85	-745	0.102	0.21	0.59	3.5	3.5	14.9	14.9	14.5
Fucshine acid	1.80	-740	0.13	0.26	0.46	3.4	3.4	18.7	18.7	21.4
Crystal violet	1.85	-805	0.096	0.11	0.55	3.4	3.4	18.7	18.7	18.1
Methyl violet 6B	1.80	-775	0.066	0.15	0.91	3.9	3.9	6.7	6.7	5.9

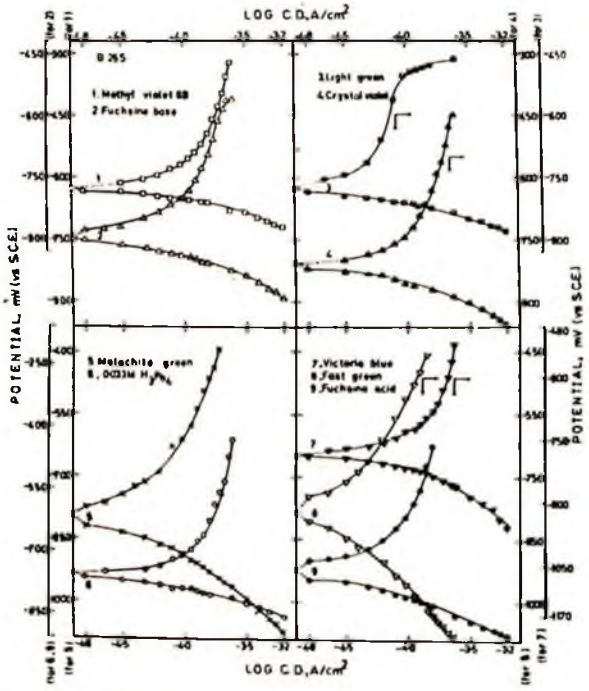


Fig. 6 Effect of current density on cathode and anode potentials of B26S aluminium in 0.033 M H_3PO_4 containing 0.002 M inhibitor.

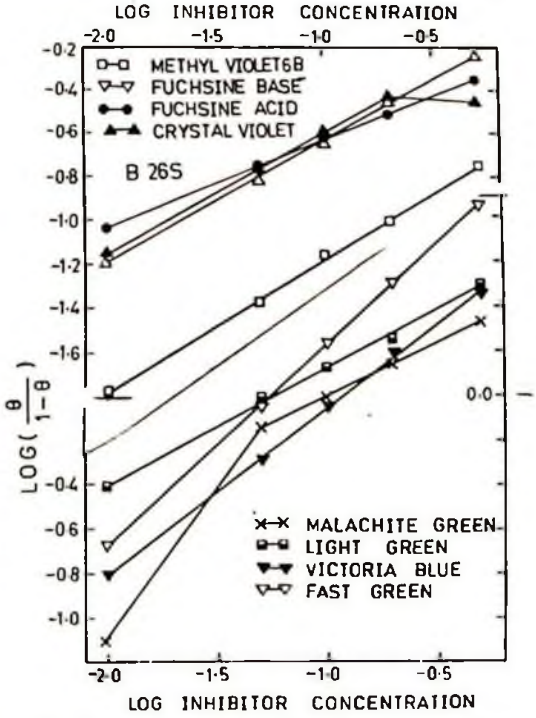


Fig. 7 Langmuir adsorption isotherms for corrosion of B26S aluminium in 0.033 M H_3PO_4 containing various inhibitors.

bitor would get adsorbed on the metal surface through the polar unit and thus decease the attack.

The steady state corrosion potentials in inhibited acid were found to be slightly more negative than that in unihibited acid in almost all the cases, except fuchsine acid and fuchsine base, suggesting that there is preferential polarisation of the local cathodes. However, with an applied current, the anode becomes more polarised than the cathode. When log $\theta/(1-\theta)$ is plotted against log inhibitor concentration, straight lines are obtained in the case of methyl violet 6B, fuchsine base, fuchsine acid, fast green, victoria blue and light green (Fig. 7). In such cases straight lines are obtained for limited ranges of concentrations. This suggests that the inhibitor covers both the anodic and cathodic regions following Langmuir isotherm.

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