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Inhibitory effect of some dyes on 60/40 brass in nitric acid

M. B. Mahida*, H. G. Chaudhari and M. H. Metawala

Sir P. T. Sarvajanik College of Science, Surat, Gujarat, India

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ABSTRACT

The inhibition effect of some dyes like methyl red, eriochrome black-T, congo red and alizarin red-S on the corrosion of 60/40 brass in nitric acid solution has been studied by using weight-loss and galvanostatic polarization technique. The corrosion rate was calculated in the presence and absence of the various dyes. The efficiency of the inhibitors was increases with increase in the inhibitor concentration and decreases with increase of temperature. The activation energy was obtained through weight-loss experiment at different temperature. For all the inhibitors the heat of adsorption (Q_{ads}) and the free energy of adsorption (ΔG_{ads}) obtained were negative. The plot of $\log(\theta/1-\theta)$ versus log C results in a straight line, which suggest that the inhibitors function through Langmuir adsorption isotherm. The polarization results show that the inhibitors are of mixed type inhibitor.

Key words: Corrosion, Brass, Nitric acid, Dyes.

INTRODUCTION

Copper and copper based alloys like varieties of brasses are of paramount interest in the industrial applications due to their characteristic properties and especially due to their higher electrical and heat conductivity. Though, the cost of brasses are higher than steel, brasses find excellent applications for heat transfer in reaction vessels, cooling towers, condensers and heaters unfortunately brass are more susceptible to corrosion due to the selective dissolution behaviour of 60/40 brass in acid environment. Due to various industrial applications and economic importance of brass, its protection against corrosion attracted much attention. One of the most important methods in corrosion protections is to use inhibitors. Due to restrictive inhibitor lows, inorganic corrosion inhibitors such as chromate and nitrates are replaced by organic compounds [1-3]. Generally both aliphatic and aromatic organic molecules containing oxygen, nitrogen, sulphur atoms are used as corrosion inhibitors [4-7]. In the present investigation an attempt has been made to study the influence of varying concentration of various dyes on the corrosion rate of 60/40 brass in different concentration of nitric acid.

MATERIALS AND METHODS

To study the effect of some dyes on corrosion of brass in nitric acid, methods such as weight-loss and polarization have been used.

The test specimens of the size 5.5 cm $\times$2.5 cm $\times$ 0.2 cm having a small hole of about 3 mm diameter just near the one end of the specimen, were completely immersed in 200 ml of the corrosive electrolyte for the complete immersion test. Only one specimen was suspended in a pyrex beaker of 250 ml capacity. The test specimens were polished by buffing, clean with distilled water several times degreased by acetone and dried by air drier. Then each specimen was suspended to the same depth using pyrex glass hook. The concentrations of nitric acid studied were 0.1, 1.0, 1.5 and 2.0 N, and the concentrations of the different inhibitors are 0.1, 0.5, 1.0, 1.5 and 2.0 mM. The weight-loss experiment were carried out at temperature 302 $\pm$ 1 k for 24 hours. To study the effect of temperature the test specimens were immersed in 1.0 N nitric acid at temperature 303, 313 and 323 k for 3 hours, with and without the various dyes as inhibitor. The corrosive solution was prepared in double distilled water. All the chemicals used were of A. R. grade. At the end of the immersion period specimens were removed carefully, cleaned and after drying weighted. From the weight-loss measurement data, corrosion rate in mdd, inhibition efficiency (IE%), activation energy (E_a), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG_{ads}) were calculated.

Using galvanostatic polarization technique anodic and cathodic polarization was carried out. Test specimens having an area of 1 cm^2 were immersed in 200 ml 0.1 N nitric acid solution in presence and absence of 2.0 mM of various dyes. The brass test specimens act as the working electrode and platinum as auxiliary electrode. Equal increments of constant current were applied by regulated DC power supply. The steady values were used in anodic and cathodic polarization curves to obtained Tafel slopes. The intersect point of anodic and cathodic Tafel lines gives the corrosion current (I_{corr}) and the corrosion potential (E_{corr})[8]. From the polarization data, inhibition efficiency and Tafel slopes β_c and β_a were calculated.

RESULTS AND DISCUSSION

To study the influence of varying concentration of various dyes on the corrosion rate of 60/40 brass in different concentration of nitric acid, weight-loss were determined in 1.0, 1.5 and 2.0 N nitric acid with and without the various concentration of inhibitor at temperature 302 ± 1 k for exposure period of 24 hours.

Inhibition efficiency (IE%) in percentage has been calculated as follow.

$$IE\% = \frac{Wu - Wi}{Wu} \times 100 \qquad (1)$$

Where, W_u is the weight loss of the metal in uninhibited and, W_i is the weight loss of metal in inhibited acid.

The corrosion rate of brass has been increased from 32.98×10^2 mdd to 74.42×10^2 mdd in 1.0 N to 2.0 N plain nitric acid solutions respectively. The value of corrosion rate (mdd) and inhibition efficiency (IE%) for the dyes were calculated and reported in table-1. The results saw that for all the concentration of the acid, the concentration of the inhibitor is increases the weight loss due to corrosion decreases. The order of efficiency of the various dyes at 2.0 mM concentration is as follow:

(a) In 1.0 N HNO_3 :
Congo red (97.11%) > Eriochrom black-T (80.86%) > Alizarin red-S (78.35%) > Methyl red (73.53%)
(b) In 1.5 N HNO_3 :
Alizarin red-S (61.37%) > Eriochrome black-T (58.32%) > Methyl red (57.51%) > Congo red (57.49%)
(c) In 2.0 N HNO_3 :

Alizarin red-S (55.04%) > Eriochrome black-T (53.25%) > Congo red (51.39%) > Methyl red (49.57%)
The value of surface coverage 'θ' ($\theta = W_u - W_i / W_i$) were calculated directly from the percentage inhibition efficiency of the compounds by weight-loss method. The plot of log θ/1–θ versus log C have been illustrated in figure-1 have shown linearity in case of all the dyes studied, which indicates the Langmuir adsorption isotherm [9].

To study the effect of temperature on the corrosion rate, the specimens were immersed in 200 ml of 1.0 N nitric acid solution with and without different concentration of various dyes at temperature 303, 313 and 323 k for a period of 3 hours.

Energy of activation (E_a) has been calculated from the slop of log ρ versus 1/T (ρ = corrosion rate, T= absolute temperature) and also with the help of Arrhenious equation [9].

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (2)$$

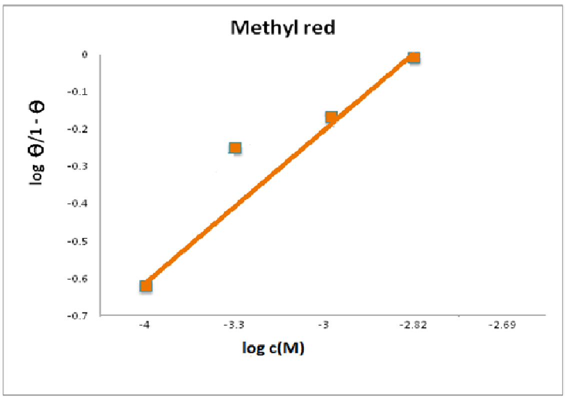
Where, ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively.

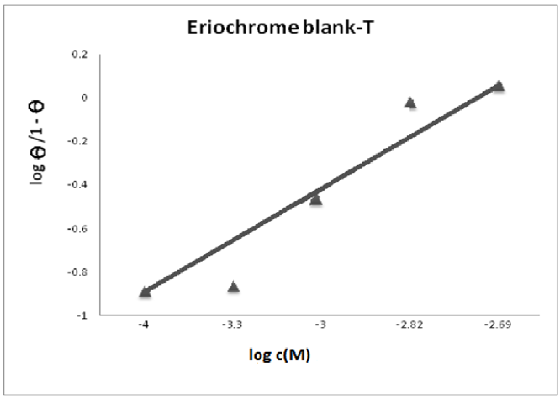
Table 1 : Weight Loss Data for Corrosion of60/40 Brass in Nitric Acid Solution : Effect of Various Dyes.

Surface area of specimen : 30.70 cm^2 Temperature : 302 ± 1 k

immersion period : 24 hrs

Acid concentration :		1.0 N		1.5 N		2.0 N	
Inhibitor and its concentration in mM		**Corrosion rate (mdd) (1×10^2)**	**Inhibition Efficiency (IE%)**	**Corrosion rate (mdd) (1×10^2)**	**Inhibition Efficiency (IE%)**	**Corrosion rate (mdd) (1×10^2)**	**Inhibition Efficiency (IE%)**
Blank		32.98	-	44.55	-	74.42	-
Methyl red	**0.1**	26.03	21.06	41.23	7.45	70.10	5.80
	0.5	20.43	38.05	40.38	9.35	60.04	19.32
	1.0	15.98	51.52	31.41	29.48	47.62	36.01
	1.5	11.02	66.57	23.15	48.03	43.58	41.44
	2.0	87.28	73.53	18.93	57.51	37.52	49.57
Eriochrome black-T	**0.1**	23.45	28.86	36.66	17.71	65.91	11.44
	0.5	18.20	44.79	28.93	35.06	65.42	12.09
	1.0	7.70	76.63	23.75	46.68	58.63	21.21
	1.5	7.26	77.98	20.43	54.14	37.99	48.94
	2.0	6.30	80.86	18.56	58.32	34.79	53.25
Congo red	**0.1**	23.08	30.00	40.85	8.29	66.33	10.86
	0.5	18.39	44.21	22.46	49.57	58.74	21.07
	1.0	7.14	61.28	21.46	51.83	53.99	27.45
	1.5	2.34	92.89	19.50	56.21	47.43	36.27
	2.0	0.95	97.11	18.94	57.49	36.17	51.39
Alizarin red-s	**0.1**	21.00	36.31	30.01	32.62	71.96	3.30
	0.5	15.16	54.01	29.13	34.62	67.32	9.54
	1.0	11.41	65.39	24.22	45.63	50.44	32.23
	1.5	7.50	77.25	18.94	57.48	40.36	45.76
	2.0	7.13	78.35	17.21	61.37	33.46	55.04





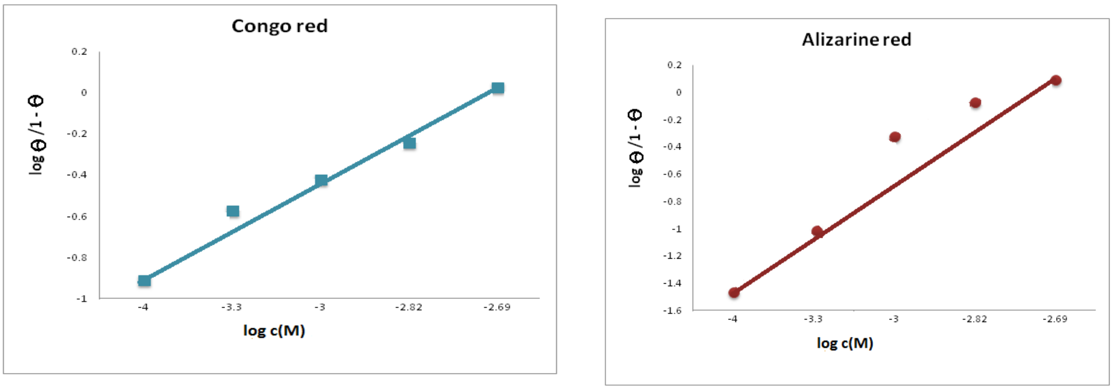


Fig 1 : Langmuir Adsorption Isotherm for Corrosion of 60/40 Brass in 2.0 N HNO_3 Solution Containing Various Dyes.

The values given in table-2, shows that, for all the inhibitors at temperature 303-313 k the value of activation energy were higher in inhibited acid solution compared to uninhibited acid solution, which indicates that the inhibitor induces energy barrier for the corrosion reaction, which leads to the decreasing the rate of corrosion of brass in presence of inhibitors. At the higher temperature 313-323 k the value of activation energy were lower which indicates that as the temperature rises the effectiveness of inhibitor is decreases.

Table 2 : **Effect of Temperature on Corrosion Rate (mdd), Inhibition Efficiency (IE%), Energy of Activation (Ea), Heat of Adsorption (Q_{ads}), and Free Energy of Adsorption (ΔG_a) for 60/40 Brass in 1.0 N Nitric Acid containing Various Dyes as Inhibitor.**

surface area of specimen : 30.70 cm^2 Immersion period : 3 hours

inhibitor and its concentration in mM		Temperature (K)						Energy of Activation (Ea) K Cal. mole^{-1}				Head of Adsorption Q_{ads} K.cal.mole^{-1}		Free Energy Of Adsorption ?G_a K.cal.mole^{-1}
		303K		313K		323K								
		CR (1×10^2)	IE	CR (1×10^2)	IE	CR (1×10^2)	IE	303-313 K	313-323 K	Mean E from eq.	E from Arhenius Plot	303-313 K	313-323 K	Mean
Blank		18.88	---	53.56	---	142.71	---	19.65	19.69	19.67	19.14			
Methyl red	**0.1**	15.32	18.05	49.84	6.94	103.20	27.68	22.23	14.62	18.43	18.05	-20.41	32.86	-7.17
	1.0	12.57	32.74	40.70	24.01	80.78	43.39	22.14	13.77	17.96	17.60	-8.15	17.81	-6.35
Eriochrome black-T	**0.1**	10.86	41.00	46.06	14.00	88.60	37.91	27.23	13.14	20.19	19.86	-28.05	26.56	-7.67
	1.0	8.58	55.53	27.10	49.39	64.63	54.71	21.68	17.46	19.57	19.10	-4.65	4.29	-6.87
Congo red	**0.1**	13.86	25.84	49.14	8.26	70.42	50.65	23.86	7.23	15.54	15.37	-25.51	48.89	-7.52
	1.0	11.93	36.19	33.83	36.84	52.38	63.29	19.65	8.78	14.21	14.00	0.53	21.77	-6.68
Alizarin red-s	**0.1**	14.70	21.34	42.20	21.21	91.60	35.81	19.88	15.57	17.72	16.65	-0.15	14.64	-7.56
	1.0	5.60	69.58	37.52	29.95	65.21	54.30	35.85	11.11	23.48	23.08	-31.61	20.54	-6.82

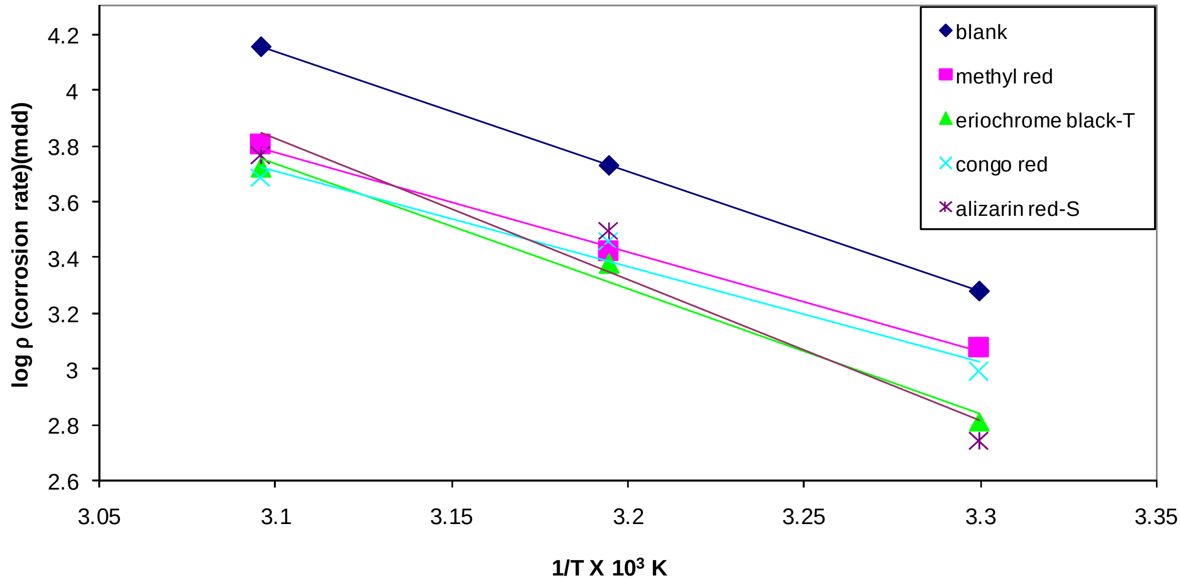


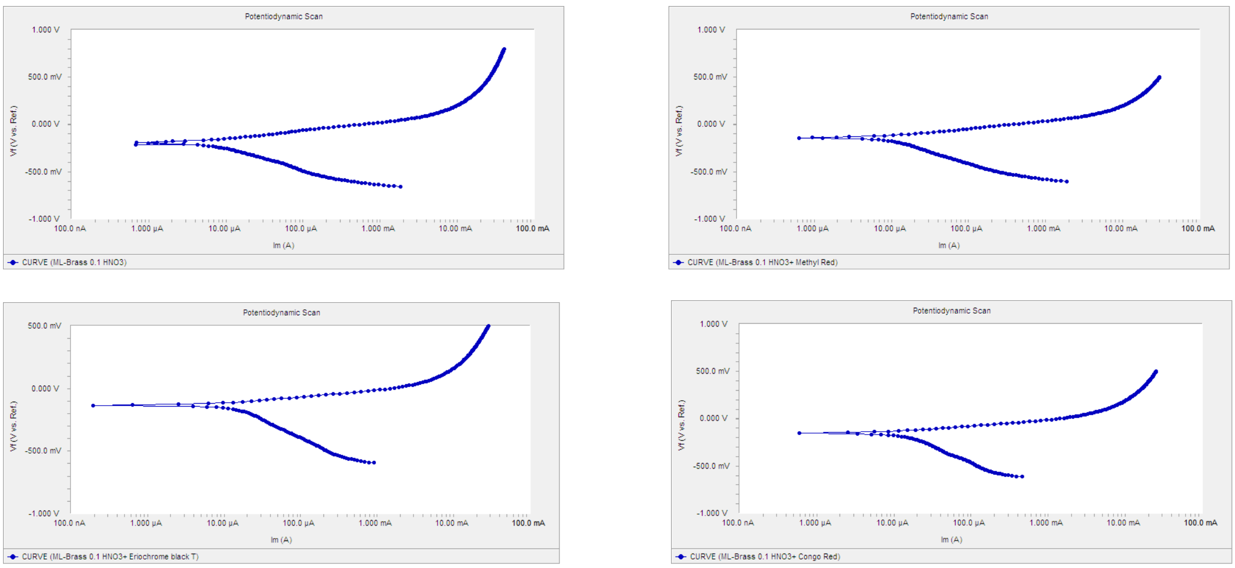
Figure 2: Arrhenius Plot for Corrosion of 60/40 Brass in 1.0 N HNO_3 in Presence and Absence of 2.0 mM of Various Dyes.

Table 3 : Tafel Parameters and Inhibition Efficiency (IE%) for 60/40 Brass in 0.1 N Nitric acid solution containing Various Dyes.

Surface area of specimen : 1 cm^2 Temperature : 23°C

Inhibitor Concentration : 2.0 mM

Inhibitor	Open circuit potential (mV)	Corrosion current density I_{corr} (mA/cm^2)	Tafel slope (V/decade)		Inhibition effeciency (IE%) Calculated from	
			Cathodic β_c	Anodic β_a	Polarization method	Weight loss method
Blank	-159.50	5.45	216.30	102.30		
Methyl red	-102.90	2.88	76.60	53.50	47.18	46.19
Eriochrome black-T	-97.28	1.75	24.40	35.50	67.83	64.92
Congo red	-114.00	3.75	44.90	46.90	31.22	32.69
Alizarine red-S	-85.60	49.60 nA	40.40	53.80	90.90	85.87



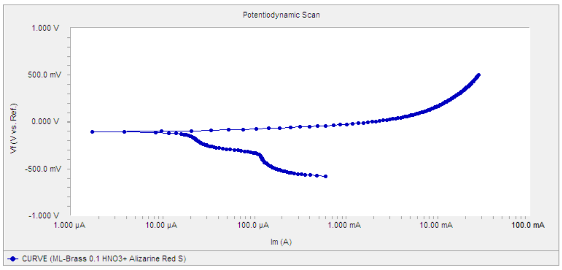


Figure 3: Polarization Curve for Corrosion of 60/40 Brass in 0.1 N HNO_3 solution Containing 2.0 mM Inhibitor Concentration.

The value of heat of adsorption (Q_{ads}) was calculated by the following equation[10]

$$Q_{ads} = 2.303R\left[log\left(\frac{\theta_2}{1-\theta_2}\right)\left(\frac{\theta_1}{1-\theta_1}\right)\right]\left[\left(\frac{T_1T_2}{T_2-T_1}\right)\right] \_\_\_\_\_\_\_\_\_\_\_\_\_(3)$$

Where, θ_1 qnd θ_2 (θ=W_u – W_i / W_i) are the fraction of metal surface covered by the inhibitor at temperature T_1 and T_2 respectively.

The value of the free energy of adsorption ($\Delta G°_{ads}$) was calculated with the help of following equation.[11]

$$\log C = log\left(\frac{\theta}{1-\theta}\right) - log\beta \_\_\_\_\_\_\_\_\_\_\_\_\_(4)$$

Where, $log\beta = -1.74 - \left(\frac{\Delta G°ads}{2.303RT}\right)$ and C is the inhibitor concentration.

The values of $\Delta G°_{ads}$ and Q_{ads} are given in table-2. The values of heat of adsorption and free energy of adsorption are relatively small and negative, which indicates the spontaneity of the adsorption process. The value of $\Delta G°_{ads}$ ranging from –6.35 to –7.17 k cal./mole. The value of free energy of adsorption more negative than –9.5598 k cal. /mole (–40 k Joule /mole) involves charge transfer from the inhibitor molecule to the metal surface to form bonds of coordinate type which indicates chemisorptions[12]. The value of free energy of adsorption is nearer to this, which indicates that the inhibitor does not chemisorbed on metal surface, but strong interaction occurs between inhibitor and metal surface.

Galvanostatic polarization measurements were carried out in 0.1 N nitric acid solution in the presence and absence of 2.0 mM of various dyes. The values of corrosion potential (E_{corr}), corrosion current (I_{corr}) and the Tafel parameters β_c and β_a are presented in table-3 and figure-3.

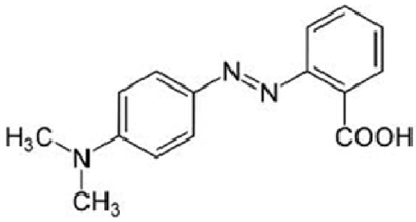
The cathodic Tafel lines are shifted to more negative potential relative to the blank, and the inhibitror adsorption shifted the corrosion potential in the negative direction with respect to blank, which means that suppression of the cathodic reaction is the main effect of the inhibitors. But this shift is not more than 85 mV. According to Riggs and others the classification of a compound as an anodic or cathodic inhibitor is feasible when the potential displacement is at least 85 mV in compared to that measured for the blank. So it can be said that the inhibitors are of mixed type inhibitor.

MECHANISM OF ACTION:

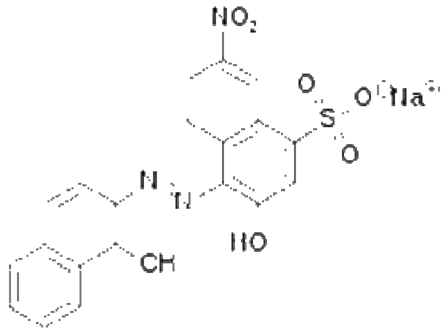
Increase in corrosion rate with rise in temperature may be due to increase in formation of NO_2. Nitric acid can undergo an autoprotolysis reaction as below [13].

$$2HNO_3 \leftrightarrow NO_2^+ + NO_3^+ + H_2O$$

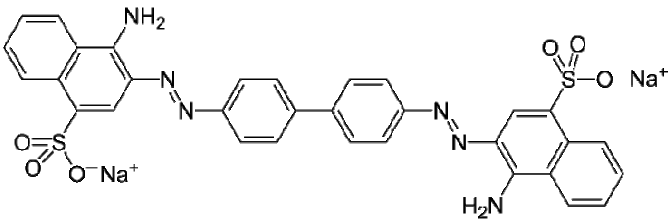
Higher inhibition in presence of dyes may be attributed to the prevention of the formation of nitrous acid. Increase in inhibitive effect with increase in dyes concentration may be due to surface coverage by protective nature of the compound.



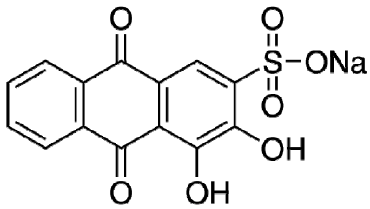
Methyl red



Eriochrome black-T



Congo red



Alizarin red-S

It is also clear from the results that very low corrosion rate in presence of the dyes can be attributed to the molecules containing polar unit and in such case the inhibitor might have been absorbed on the metal surface.

In congo red six nitrogen atoms with the higher electron density acted as the reaction centres. It is interesting to note that the four fold symmetry in congored metal complexes in which readjustment of the bond angle do not take place, which may be responsible for the higher inhibitive action of the compound.

Methyl red also gives good inhibition, which can be due to the presence of azo group in contact with metal surface. Eriochrome black-T also reduced the corrosion rate. The presence of N and S along with –C=C– bond contributes to a large extent to the inhibition.

Alizarin red –s and eriochrome black-T has better inhibition efficiency, which may be due to –OH group, which is an electron donating group. Compound containing electron donating group are more efficient than compound containing electron withdrawing groups. The electron donating group enhance adsorption and increase the surface area covered by the compound and consequently increase the inhibition efficiency [14]. The efficiency of methyl red as an inhibitor is lesser than other dyes studied in this study, which can be explain by the presence of electron withdrawing group –COOH.

CONCLUSION

from the above discussion following conclusion can be drown:

1. The corrosion rate of 60/40 brass increase with increase in nitric acid concentration.
2. The extend of inhibition increase with the increase in concentration of inhibitor.
3. The higher values of activation energy indicate that electrostatic interaction between charged inhibitor molecule and the metal surface occurs.
4. The values of free energy of adsorption were almost constant. This indicates that there was no change in corrosion mechanism.
5. All the dyes molecules under the investigation, influence cathodic reaction to greater extent than anodic reaction and thereby inhibitive action is observed. The inhibitors are mixed type inhibitor.

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