The Effect of Gramine on Corrosion Behaviour of Brass in Phosphoric Acid

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Abstract

The corrosion behavior of brass in phosphoric acid was studied with Gramine as inhibitor at different temperatures and various time intervals by weight-loss measurements and potentiodynamic polarization. It is reported that the inhibition efficiency varied with concentrations of the inhibitor, immersion time, and temperatures. The adsorption of inhibitor on the brass surface obeyed Temkin adsorption isotherm. The activation energy was calculated. The polarization measurements showed that the inhibitor behaves as a mixed type inhibitor and the higher inhibition surface coverage on the brass was predicted. Surface analytical techniques were carried out to the inhibitive nature of the inhibitors.

Introduction

Phosphoric acid is a major chemical product which has many important uses especially in the production of fertilizers. Most of the acid is produced from phosphate rock by wet process. Generally Nickel-base alloys and stainless steel are frequently used in many parts of the wet process and a considerable quantity of data has been published about the resistance of these materials to corrosion by phosphoric acid solution (1-5). Most of the previous studies were focused on the inhibition of stainless steel or chromium-nickel steel in HCl or H_2SO_4 solutions using organic compounds containing nitrogen, sulfur and oxygen atoms as corrosion inhibitors (6-7). Hence, the study of corrosion inhibition of brass in aqueous aggressive media is very important. Different nitrogen containing organic compounds have been studied as corrosion inhibitors for brass (8-10). Organic inhibitors are widely used in various industries. Among them, heterocyclic compounds comprise a potential class of inhibitors. There is wide consideration in the literature regarding corrosion inhibition studies by nitrogen containing heterocyclics (11-18). Compounds containing nitrogen and sulphur atoms are of particular importance as they often provide excellent inhibition compared with compounds containing only nitrogen or sulphur (19-24). The corrosion inhibiting property of these compounds is attributed to their molecular structure. These compounds contain π electrons and heteroatoms, which induce greater adsorption of the inhibitor molecules onto the metal surface. The aim of the present investigation was to examine the inhibitive action of Gramine towards the corrosion of brass in 1N by mass loss and potentiostatic polarization methods at 302K-333K.

Experimental

Mass loss measurement

Brass specimens were cut to the size of 5cm x 1cm from the brass sheets. Mass loss measurements were performed as per ASTM method described previously (25-27). Mass loss measurements were carried out in 1N concentration of phosphoric acid with inhibitor (Gramine) in the concentration range of 0.02% to 0.1% at 302K to333K for an immersion period of 5 hours with and without inhibitors. At 302K, the immersion period of 24, 48, 72 and 96 hours were also studied. All the solutions were prepared using AR grade chemicals with double distilled water.

Potentiostatic polarization measurement

Polarization measurements were carried out in a conventional three-electrode cell assembly. Brass strips of same composition coated with lacquer with on exposed area of 1 cm^2 were used as working electrode.

The saturated calomel electrode and the platinum foil were used as reference and counter electrode respectively. The potentiostatic polarization was carried out using BAS-100A model instrument and the experiments were carried out at 302K to333K.

Results and Discussion

Mass loss studies

Table I shows the values of inhibition efficiency (IE%), surface coverage (θ) and corrosion rate obtained for different concentrations of these inhibitor in 1N phosphoric acid for immersion period of 5 hours at 302K-333K. From the mass loss value, the inhibition efficiency (IE%) and surface coverage (θ) were calculated using the following equation (28-29).

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

$$\theta = \frac{Wu - Wi}{Wu} \quad (2)$$

Where Wu and Wi are the corrosion rates for brass in the absence and presence of inhibitor respectively at the same temperature.

It clearly indicates that addition of inhibitor to the acid has reduced the corrosion rate. The inhibition efficiency increased with increase in concentration of inhibitor and decreased with rise in temperature from 302K to 333K in acid concentration 1N. The values of corrosion rate and inhibition efficiencies of the inhibitor were found to depend on the molecular structure of inhibitor. The maximum inhibition efficiency of Gramine was 98.57% in 1N phosphoric acid.

Thermodynamics / Kinetics consideration

Table II shows the calculated values of activation energy Ea (KJ/mole), free energy of adsorption ΔGads (KJ/mole), enthalpy of adsorption ΔH (KJ/mole), entropy of adsorption ΔS (KJ mole^{-1} K^{-1}), rate constant k (Sec^{-1}) and half-life $t_{1/2}$(Sec) for brass corrosion in 1N and 5N phosphoric acid with and without inhibitor. Energy of activation (Ea) has been calculated from the slopes of plots of log p versus 1/T in fig. 1 for Gramine and also with the help of Arrhenius equation (30-32).

$$\log \frac{p_2}{p_1} = \frac{Ea}{2.303 \times R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad (3)$$

Where p_1 and p_2 are the corrosion rate at temperatures T1 and T2 respectively. Ea values given in table II show that the Ea values for the corrosion of brass in 1N phosphoric acid are 28.86KJ/mole and 48.34 KJ/mole respectively.

In acid containing inhibitor, the Ea values are found to be higher than that of the uninhibited system.

The higher values of Ea indicate physical adsorption of the inhibitors on metal surface (33). The values of Ea calculated from the slopes of Arrhenius plot and by using equation-1 are approximately almost similar.

The free energy of adsorption (ΔGads) at different temperatures was calculated from the following equation (34).

ΔGads = -RT ln (55.5K) (4)

And K is given by

$$K = \frac{\theta}{C(1-\theta)} \quad (5)$$

Where θ is surface coverage on the metal surface, C is concentration of inhibitor in mole/l and K is equilibrium constant.

From table-II, the negative values of ΔGads obtained indicate the spontaneous adsorption of the inhibitor and are usually characteristics of strong interaction with the metal surface. It is found that the ΔGads values are less than (less – ve values) – 40KJ/mole indicating that inhibitors are physically adsorbed on the metal surface (35-36).

Free energy of adsorption ΔGads of Gramine can be calculated from the results of fig. 1 and equation 4 at 302K to 333K while the enthalpy of adsorption ΔH and entropy of adsorption ΔS can be calculated from the following equation.

ΔH = Ea - RT (6)

ΔG = ΔH - T Δ S (7)

ΔS can be easily calculated at 302K to 333K for the concentration of Gramine. Table II shows thermodynamic data obtained from the inhibitor used in this study. It is clear that the activation energy increases regularly with increasing the efficiency of the inhibitor.

Ideally, a corrosion inhibitor is a substance that greatly increases the activation energy of corrosion. The negative values of ΔGads indicate the spontaneous adsorption of inhibitor on the surface of brass. It is also observed that ΔS is increased with increasing the efficiency of the inhibitors. This is opposite to that we expect, since the adsorption is an exothermic process and is always accompanied by a decrease of entropy. Ateya *et al.,* (37) have described this situation as the adsorption of the organic compound, which is accompanied by desorption of water molecules off the surface. Thus, while the adsorption process is believed to the exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent. Therefore, this gain in entropy that accompanies the substitutional adsorption process is attributed to the increase in solvent entropy.

Fig.2 show the relation between the inhibition efficiency and temperature for 0.02% to 0.10% of Gramine on brass in 1N phosphoric acid. The order of the efficiency is decreased with increasing temperature. These results indicate that the protective film start to break down with increasing temperature.

The values of rate constant k were evaluated from the plots of log W_f versus time (days) in fig. 3 for Gramine. Linear plots were obtained which revealed first order kinetics. The values of half-life $t_{1/2}$ were calculated using the equation below (31).

$$t_{1/2} = \frac{0.693}{k} \quad (8)$$

The rate constant k decreases with increase in concentration of inhibitor whereas the half-life increases with concentration of inhibitor (28). The adsorption of the organic molecules can affect in several ways, the behaviour of the electrochemical reactions involved in the corrosion process. The action of organic inhibitors also depends on the type of interaction between the substance and the metallic surface. This interaction causes a change either in the electrochemical process mechanism or in the surface available to the process (38-40).

Adsorption Isotherms

The electrochemical process on the metal surface is likely to be closely related to the adsorption of the inhibitor (41) and the adsorption is known to depend on the chemical structure of the inhibitor (42-44).

The adsorption of the inhibitor molecules from aqueous solution can be regarded as quasisubstitution process (42) between the organic compound in the aqueous phase, org $_{(aq)}$ and water molecules at the electrode surface, $H_2O_{(s)}$.

$Org_{(aq)} + x\ H2O_{(s)} = Org_{(s)} + x\ (H_2O)_{(aq)}$ (9)
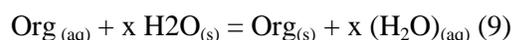
Where x the size ratio, is the number of water molecules displaced by one molecule of organic inhibitor.

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used isotherms are those of Langmuir, Frumkin, Parsons, Temkin, Flory-huggins and Bockris-Sinkles (45-48). All these isotherms are of the general form:

$f(\theta, x)\ exp\ (-a\ \theta) = KC$ (10)

Where f (θ, x) is the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm (49).

Table.1 Calculated corrosion rate, inhibition efficiency (IE%) and surface coverage (θ) values for Thiocarbamide from mass loss data in 1N and 5N H_3PO_4

Temp. (°K)	Conc. Of Thiocarbamide (%)	1N		
		Corrosion Rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE`%)
302	Blank	6.80	-	-
	0.02	1.55	0.7723	77.23
	0.04	1.20	0.8246	82.46
	0.06	0.67	0.9025	90.25
	0.08	0.21	0.9690	96.90
	0.10	0.10	0.9857	98.57
313	Blank	11.93	-	-
	0.02	3.08	0.7420	74.20
	0.04	2.39	0.7998	79.98
	0.06	1.42	0.8814	88.14
	0.08	0.70	0.9412	94.12
	0.10	0.49	0.9589	95.89
333	Blank	19.82	-	-
	0.02	6.99	0.6476	64.76
	0.04	5.55	0.7199	71.99
	0.06	3.95	0.8010	80.10
	0.08	2.45	0.8766	87.66
	0.10	2.05	0.8967	89.67

Table.2 Calculated values of activation energy Ea (KJ/mole), free energy of adsorption ΔGads (KJ/mole), enthalpy of adsorption ΔH (KJ/mole), entropy of adsorption ΔS (KJmole^{-1}K^{-1}), rate constant k (Time^{-1}) and half-life t $_{½}$ (time) for brass corrosion in 1N phosphoric acid with Gramine (TC)

Inhibitor	Conc. of Inhibitor (%)	Ea from Eqn.1 (KJ/mole)	Ea from Plot (KJ/mole)	ΔGads (KJ/mole)	ΔH (KJ/mole)	ΔS (KJmole^{-1}K^{-1})	Rate constant k x 10-6 (Sec^{-1})	Half-life t $_{½}$ (Sec)
	Blank	28.86	28.72	-	23.87	-	5.73	120934
TC	0.02	40.63	41.00	-27.71	35.64	0.1902	4.58	151165
+	0.04	41.31	42.10	-28.12	36.32	0.1915	4.19	165586
1N	0.06	47.52	48.12	-28.64	42.52	0.2137	3.81	181829
H_3PO_4	0.08	66.27	65.98	-29.62	61.28	0.2730	3.47	199981
	0.10	81.47	82.02	-30.20	76.47	0.3203	3.25	213080

Table.3 Electrochemical polarization parameters for the corrosion behaviour of brass in 1N Phosphoric acid in absence and presence of Gramine at 302K

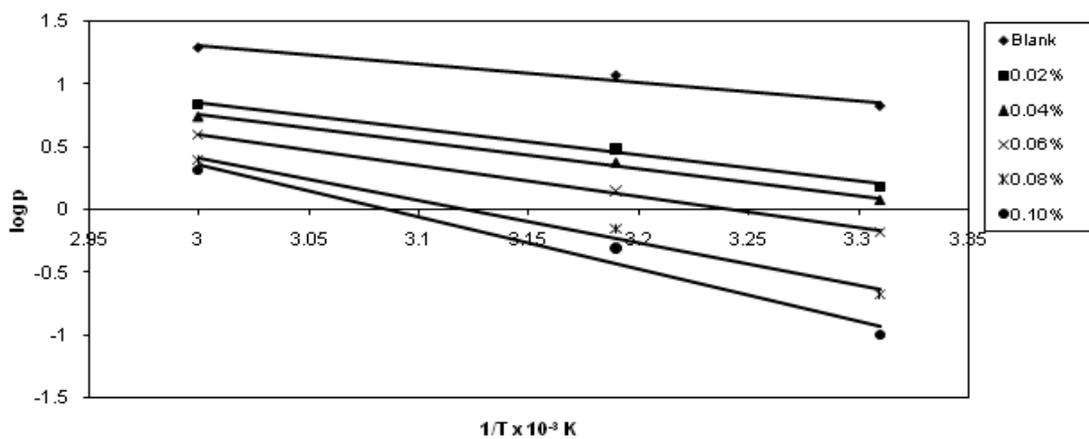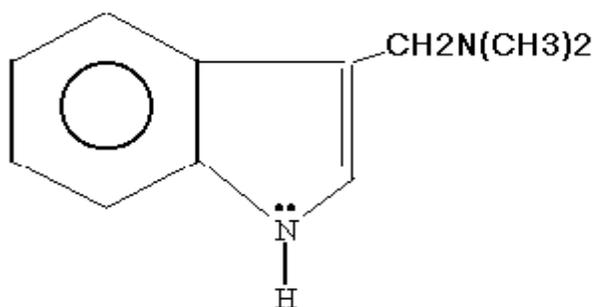| Conc. of inhibitor (%)	E_{corr} Vs SCE (mV)	I_{corr} µA/cm^2	Tafel slopes (mV / decade)		IE%	LPR Rp (ohm cm^2)
			ba	- bc		
302 K						
Blank H_2SO_4	-543	210	50	130	-	74.67
0.1	-573	98	50	129	53.33	159.66
0.2	-563	76	48	124	63.38	197.71
0.3	-553	64	46	120	69.52	225.61
0.4	-548	56	49	117	73.33	267.79
0.5	-539	22	45	120	89.52	645.94

Structure of Gramine (3-dimethylaminomethylindole)

Fig.1 Arrhenius plot for 1N H_3PO_4 with Gramine

Fig.2 Relation between the inhibition efficiency and temperature for 0.02% to 0.10% of Gramine on brass in 1N H_3PO_4
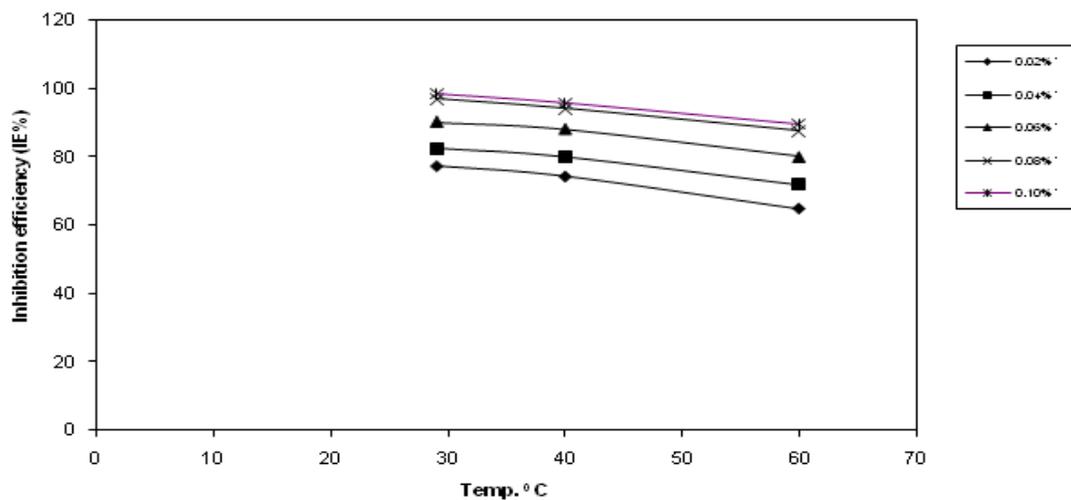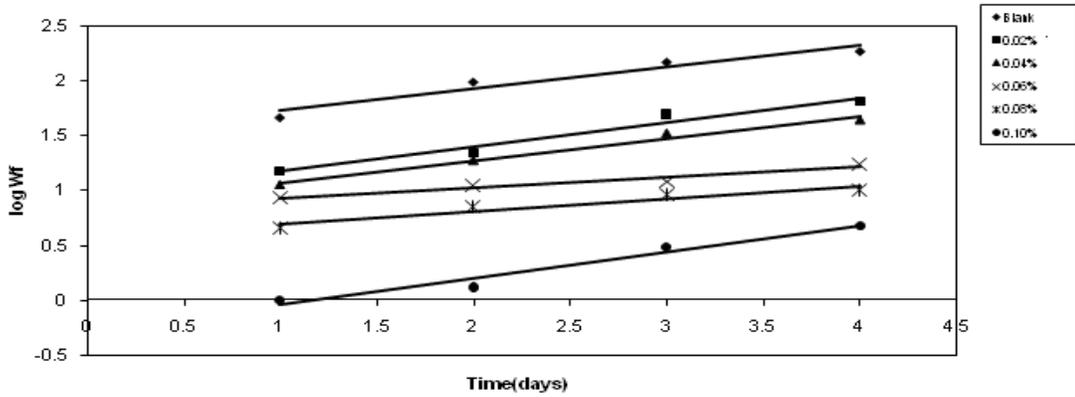

Fig.2

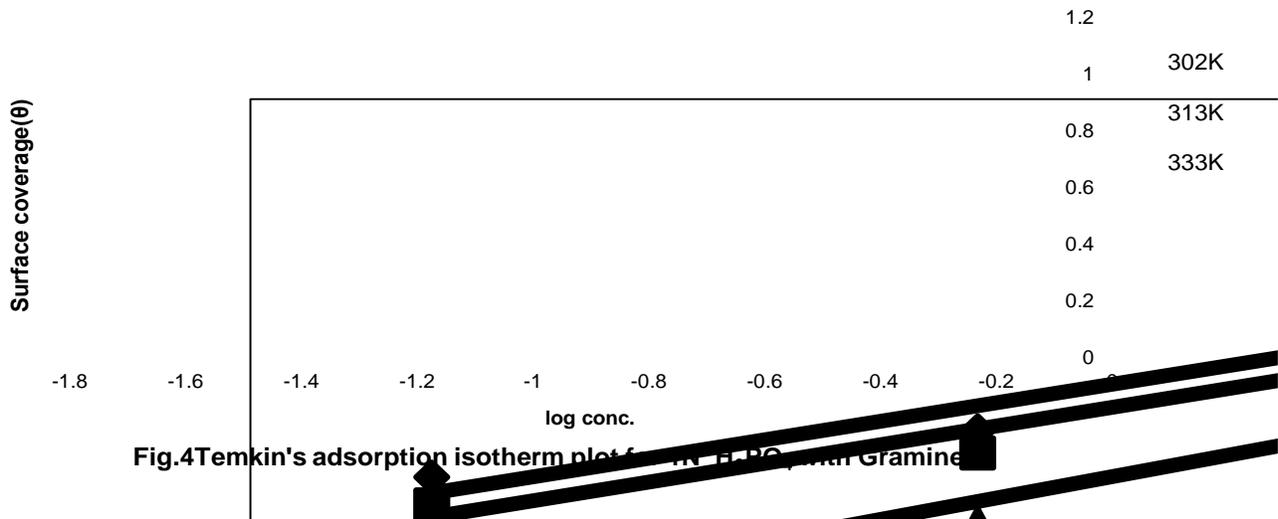Fig. 3 Plot of log Wf versus time(days) for 1N H₃PO₄ with Gramine

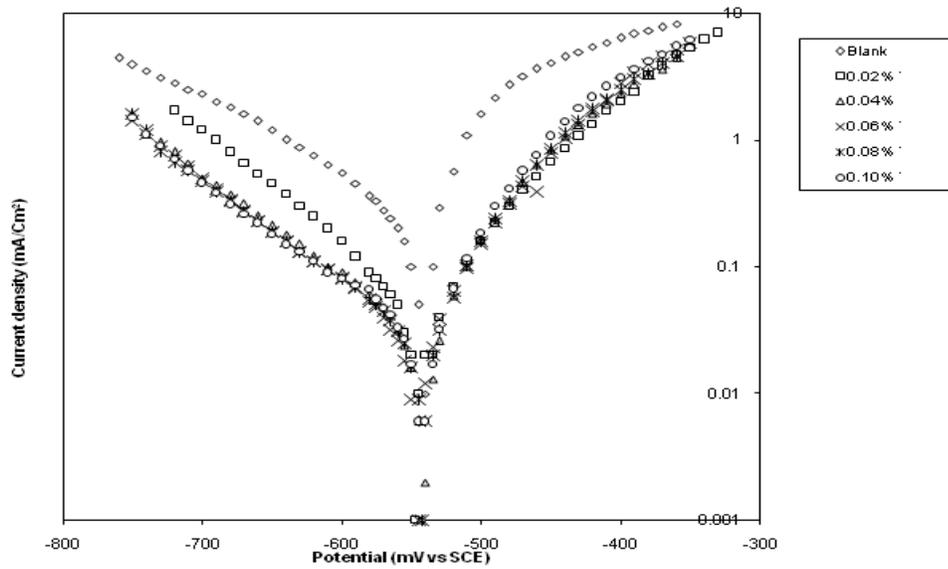Fig.4 Temkin's adsorption isotherm plot for 1N H₃PO₄ with Gramine

Fig. 6 Typical potentiostatic curves for mild steel in 1N H₃PO₄ with Gramine at 302K

The mechanism of inhibition of corrosion is generally believed to be due to the formation and maintenance of a protective film on the metal surface.

The plot of surface coverage (θ) obtained by mass loss method versus log C for different concentrations of the compound show a straight line indicating that the adsorption of the compounds from acids on brass surface follows Temkin's adsorption isotherm (34). This also pointed to corrosion inhibition by these compounds being a result of their adsorption on the metal surface. Fig 4 shows the Temkin's adsorption isotherm for Gramine.

Potentiostatic polarization studies

The polarization behaviour of brass functioning as cathode as well as anode in the test solutions is shown in fig. 5 for 1N H_3PO_4 at 302K for Gramine. Similar curves were also obtained for Gramine in 1N phosphoric acid at 302K and the electrochemical data obtained from the studies are shown in table-III. It is evident that amide bring about considerable polarization of the cathode as well as anode. It was, therefore, inferred that the inhibitive action is of mixed type. The cathodic and anodic Tafel slopes increased with increasing inhibitor concentrations and the increase was predominant in the case of the former indicating that the cathodic inhibition was dominating through the inhibitive active is of mixed nature. The non-constancy of Tafel slopes for different inhibitor concentration reveals that the inhibitor act through their interference in the mechanism of the corrosion processes at the cathode as well as the anode.

The corrosion parameters deduced from Tafel polarization such as corrosion current i_{corr}, corrosion potential E_{corr}, Tafel constant ba and –bc and inhibition efficiency are given in table-III. The i_{corr} values were decrease with the increasing concentration of inhibitors. The inhibition efficiencies were determined from the values of corrosion current and the inhibition efficiency values were found to show good agreement, with those obtained from mass loss measurements.

The conclusions reported in this paper are the following:

Gramine acted as efficient corrosion inhibitor in 1N phosphoric acid

The inhibition efficiencies 98.57% in 1N phosphoric acid have been obtained with small amount of Gramine (0.1%) by mass loss technique at 302K.

Inhibition of inhibitor decreased with increasing temperature.

The inhibition efficiency value obtained from mass loss studies and polarization measurements showed fairly good agreement. The corrosion inhibition appears to be of mixed type.

Gramine inhibited corrosion by adsorption mechanism and the adsorption of these compounds from acid solution followed Temkin's adsorption isotherms at all the concentrations.

Thermodynamic values obtained from this study, Ea, ΔH and ΔS indicate that the presence of the inhibitors increase activation energy, and the negative values of ΔGads indicate spontaneous adsorption of the inhibitor on the surface of the brass.

In the kinetic studies, linear plots were obtained which revealed first order kinetics.

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