

Galvanostatic Polarisation & Temperature Kinetic Studies of Acid Corrosion of Low Carbon Steel in Sulphuric Acid in Presence of Biguanide

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The inhibitive effect of biguanide on acid corrosion of steel in 1N sulphuric acid at different temperatures has been investigated. Corrosion potentials, corrosion current, cathodic and anodic Tafel's slopes as well as heat of adsorption and effective activation energies have been calculated in the presence and absence of biguanide. The nature of adsorption of biguanide on the metal surface has been studied and a correlation between surface coverage and corrosion potentials has been shown.

THE inhibition characteristics of dicyandiamide, guanlylurea and guanlylthiourea during acid corrosion of iron¹⁻³ and of guanlylurea and dicyandiamide during acid corrosion of low carbon steel^{4,5} have been reported. As an extension of these studies, the results of title investigation are presented in this paper. Biguanide like guanlylurea and dicyandiamide, is a conjugated molecule having all the atoms covered by extensively delocalised π -electrons, forms strong chelate complexes with transition metal ions and loses its π -electron delocalisation and complexing abilities completely in acid medium⁶. These peculiarities prompted us to study the effect of biguanide on the cathodically and anodically polarised metal surfaces and thereby to study the influence of biguanide on the hydrogen evolution as well as metal dissolution reactions.

Materials and Methods

Hot rolled low carbon steel (2 mm thickness) containing carbon (0.58%), sulphur (0.03%), phosphorus (0.05%) and manganese (1.06%) was used and the test specimens ($3 \times 1.5 \text{ cm}^2$) were cut, edges smoothed, abraded into uniform surfaces and finally polished with 150, 300, 400 and 600 grades emery papers. The working electrode soldered with insulated copper wire and after proper surface preparation were coated thoroughly with epoxy resin keeping 1.0 cm^2 surface area exposed for corrosion. Platinum wire gauze was used as an auxiliary electrode and dip-type calomel electrode was used as reference electrode. Cathodic and anodic polarisations were studied at 25°, 35°, 45° and $55^\circ \pm 1.0^\circ \text{C}$ in different acid solutions having different amounts of inhibitor and several runs were taken for each set of experiment^{4,5}.

Results and Discussion

Polarisation studies — Polarisation data in sulphuric acid (1N) containing various concentrations of

biguanide are given in Table 1. The effect of varying temperature as well as concentration of biguanide on the anodic and cathodic polarisation data are quite apparent from Table 1.

Temperature kinetic studies — The inhibition efficiencies ($I, \%$) at different temperatures and con-

Table 1—CORROSION PARAMETERS OF LOW CARBON STEEL IN 1N SULPHURIC ACID IN PRESENCE OF BIGUANIDE

[Biguanide] <i>M</i>	Corr. pot. mV (-E vs SCE)	Corr. curr. mA/cm ²	b_c mV/dec	b_a mV/dec	Inhibition efficiencies ($I, \%$)
TEMP., 25°C					
0	443	5.6	120	62	—
10^{-7}	446	3.4	124	74	39.30
10^{-5}	447	3.0	123	70	46.00
10^{-3}	446	2.7	120	72	51.78
10^{-1}	494	2.5	116	128	55.30
TEMP., 35°C					
0	452	6.0	106	48	—
10^{-7}	460	4.8	100	84	20.00
10^{-5}	460	4.4	124	88	27.30
10^{-3}	460	4.2	116	88	30.5
10^{-1}	486	3.9	112	108	35.50
TEMP., 45°C					
0	458	6.4	87	49	—
10^{-7}	464	5.7	104	104	10.93
10^{-5}	466	5.4	96	80	15.60
10^{-3}	466	5.2	102	96	19.00
10^{-1}	488	4.8	80	96	25.50
TEMP., 55°C					
0	461	6.9	58	26	—
10^{-7}	468	15.0	88	98	—
10^{-5}	468	10.0	82	106	—
10^{-3}	468	6.15	96	108	10.87
10^{-1}	502	5.85	70	114	15.20

centrations of biguanide were calculated from expression (1),

$$I\% = [(i_o - i_e)/i_o] \times 100 \quad \dots (1)$$

where i_o and i_e are corrosion currents at open circuit potentials in uninhibited and inhibited solutions respectively. It is seen that biguanide inhibits the corrosion at lower temperature and the inhibition diminishes sharply with rise in temperature and at higher temperature the compound acts as a catalyst in the acid dissolution of metal. At 55° biguanide inhibits corrosion at higher concentrations but acts in a catalytic manner at lower concentrations.

Within certain range of inhibitor concentration and temperature if it is assumed that the inhibitor gives a monolayer adsorption over the metal surface, Langmuir's adsorption isotherm⁷ as expressed by Eq. (2).

$$\theta/1 - \theta = Ace^{-Q/RT} \quad \dots (2)$$

may well interpret the adsorption kinetics of biguanide over the metal surface during acid corrosion process. Plots of $\log \theta/1 - \theta$ against $\log C$ at constant temperature and $\log \theta/1 - \theta$ against $1/T$ at constant inhibitor concentration should be linear. The plots are indeed linear over a certain range of concentration (Figs 1 and 2) indicating that simple Langmuir's adsorption isotherm is inadequate at all temperatures and concentrations. The slopes of the linear portion of the

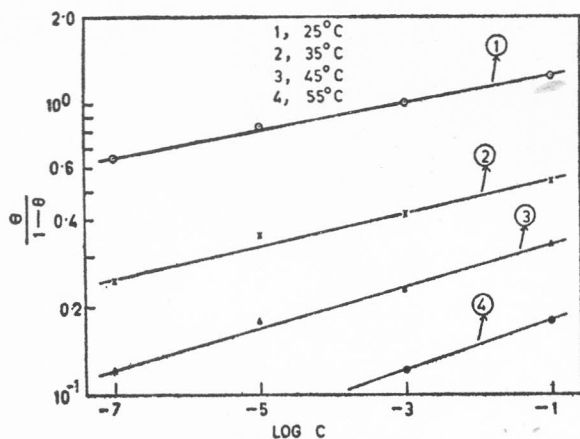


Fig. 1 — Dependence of surface coverage (θ) on inhibitor concentration at various temperature.

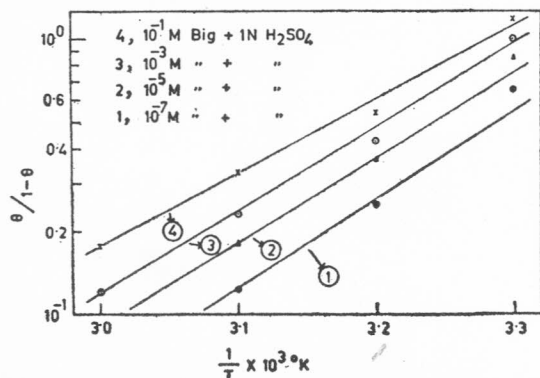


Fig. 2 — Dependence of surface coverage (θ) on the reciprocal of absolute temperature at various biguanide concentrations.

plots in Fig. 2 are equal to $-Q/2.303R$ from which the average heat of adsorption can be calculated. In the present case it is found to be 57.73 kJ/mol. This value of Q may favour weak chemisorption of biguanide over steel surface.

The reaction rate at unit concentration of reactants is related to temperature by the Arrhenius equation⁸.

$$\ln K = B - \frac{U}{RT} \quad \dots (3)$$

where U = activation energy; and B = a temperature invariant constant depending on the reaction type. The temperature coefficient of the rate constant is represented as

$$\frac{d \ln K}{dT} = \frac{U}{RT^2} \quad \dots (4)$$

For a metal dissolution the corrosion current is directly related to the above rate constant (K) and the replacement of K by i_{corr} yields Eq. (5)

$$\frac{d \ln i_{corr}}{dT} = \frac{U}{RT^2} \quad \dots (5)$$

A plot of $\log i_{corr}$ against $1/T$ should be linear from which the effective activation energy, U can be calculated for various inhibitor concentrations. This is found to be true in the present case (Fig. 3) and the effective activation energies, thus calculated for different biguanide concentrations show that it is higher in the presence of inhibitor than in the absence of it. In 1N sulphuric acid the results are as follows: $U_{steel} = 4.81$ kJ/mol without inhibitor; and $U_{steel} + biguanide = 19.25$ kJ/mol at $10^{-1}M$ biguanide solution.

This type of inhibitor, according to Putilova⁹ retards corrosion at lower temperature but inhibition is considerably reduced at elevated temperatures while unlike dicyandiamide and guanylurea at higher temperatures it acts as catalyst and thus accelerates corrosion of metal.

From galvanostatic data it is obvious that biguanide reacts with the surface active groups on the metal surface at higher temperatures and thereby influences the cathodic and anodic Tafel slope values.

At higher temperatures the protonated biguanide molecules diffuse towards the metal surface and dis-

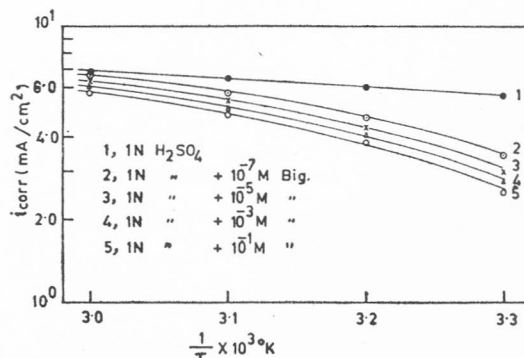


Fig. 3 — Dependence of corrosion current on the reciprocal of absolute temperature at various biguanide concentrations.

charge their proton for depolarisation, at the negatively polarised electrode, and thereby the inhibitor gets detached from the metal surface. Thus the protective action of the inhibitor is reduced and the metal surface becomes prone to corrosive attack. At the anodically polarised electrode surface, the inhibitor is adsorbed through its extensively delocalised π -electrons, but at higher temperatures, this adsorption of biguanide over the metal surface becomes less effective and thus the inhibitor loses its protective action. So in both ways perhaps due to decrease in the extent of adsorption at elevated temperature the metal surface gets less protected from the corrosive media and corrosion increases. This catalytic action is reduced to some extent in the presence of highly concentrated inhibitor solution at higher temperatures because there exists both catalytic action and inhibitive action which compete each other and nullify their respective effects.

Thus it may be concluded that biguanide, though acts as an inhibitor at ordinary temperature on the

acid corrosion of low carbon steel, cannot be used in solutions at elevated temperatures where the inhibitor acts as a catalyst in the acid dissolution of metal.

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