INHIBITIVE ACTION OF PIPERIDINE ON HSLA STEEL CORROSION AND HYDROGEN EVOLUTION REACTION IN H_2SO_4 MEDIA

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A study of the corrosion behaviour of HSLA steel in 1N-H_2SO_4 solution suggest that piperidine acts as a good inhibitor for corrosion and hydrogen evolution reaction (h.e.r.). The rate of h.e.r. on HSLA steel was found to be of first order with respect to $[H^+]$. The corrosion current decreases with increasing concentration of piperidine. The adsorption of piperidine on the surface of the steel follows Langmuir adsorption isotherm.

Hydrogen induced failure of pipe lines and fittings exposed to petroleum and natural gas containing H_2S has been one of the most severe problems in the petroleum industry for the past few decades [1]. Commendable efforts are on in search of appropriate inhibitors to minimise this type of failure [2,3]. In recent years, electrochemical polarization measurements have been used to investigate the inhibitive action of N-containing compounds (Benzotriazole, tolyltriazole, pyridine, piprazine, Quinoline, β-naphthquinoline, aniline) on the corrosion of iron and steel [4-13]. In addition to the inhibitive action of such nitrogen-containing compounds, several workers have observed appreciable reduction in the rate of h.e.r. in the presence of benzotriazole [14,15] and tolyltriazole [16]. The inhibitive action of piperidine (one of the nitrogen-containing compounds) on steel in H_2SO_4 media has not been investigated in detail.

HSLA steels are widely used in pipe lines and fittings. Therefore, the study of h.e.r. and hydrogen embrittlement susceptibility of these steels in the presence of inhibitors is of considerable importance.

In the present paper the role of piperidine as inhibitor for corrosion and h.e.r. for a HSLA steel and the h.e.r. mechanism on this steel in sulfuric acid solution have been investigated.

EXPERIMENTAL

HSLA steel supplied by the Research and Development Centre, Steel Authority of India Ltd was used in this study. This steel obtained as 4 mm thick,hot rolled strip had the chemical composition given in Table 1.

The steel was cut into rectangular pieces (5 x 3 cm) and cold rolled to 1 mm thickness with an intermediate annealing at 650° C. Samples of 2 cm^2 area were cut from this cold rolled sheet, polished with emery papers upto 4/0 grade and cleaned with water, acetone and dried. Cathodic polarization was carried out in 1 N H_2SO_4 solution (prepared from AR acid and triple distilled water) using a Wenking Potentioscan (Model No. POS73). A saturated calomel electrode was used as reference electrode. Various concentrations of piperidine ranging from 0.2 mM to 15 mM were added to the sulfuric acid and the cathodic polarization behaviour of the steel was determined. Measurements were made in solutions of pH ranging from 0.3 to 2.25 prepared by the addition of required amounts of KOH. Before starting the cathodic polarization, the working electrode was stabilised in the electrolyte for about one hr. All the experiments were conducted at ambient temperature of 34 $\pm$ 1° C.

RESULTS AND DISCUSSION

Corrosion Inhibition

Fig.1 gives the cathodic polarization curves for the HSLA steel in H_2SO_4 of different pH in the range 0.3 to 2.25. The polarization curves are seen to be shifted towards lower current densities and corrosion potential shifted towards more active potentials as the pH increases. The Tafel slopes calculated from these curves are given in Table 2 and are

TABLE 1

CHEMICAL COMPOSITION OF HSLA STEEL

Element	C	Mn	Si	S	P	Al	Nb	Fe
Wt. %	0.14	1.38	0.14	0.018	0.019	0.05	0.022	Balance

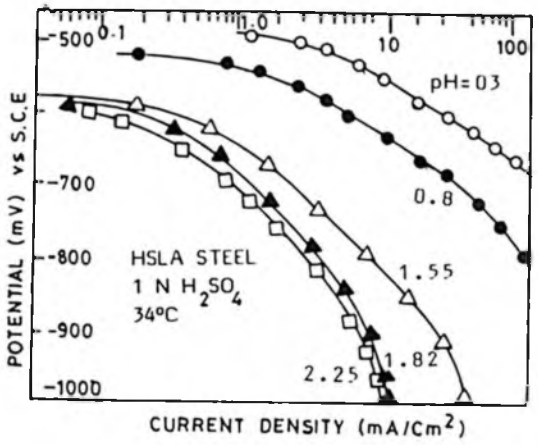


Fig.1 Effect of pH on the polarization curves of HSLA steel in 1 N-H_2SO_4.

nearly identical in magnitude at all pH levels. which is in agreement with previous observations [15,16] on iron in H_2SO_4. The cathodic Tafel slope for the steel in 1 N-H_2SO_4 is found to be 115±5 mV/decade.

The cathodic polarization curves of the HSLA steel in 1 N-H_2SO_4 (0.3 pH) containing different concentrations of piperidine are shown in Fig.2. The corresponding Tafel slopes are given in Table 2 and are also found to be 115 ± 5 mV/decade. As seen from Fig.2, the hydrogen evolution current decreases with the increase of inhibitor concentration. Similar inhibition behaviour was observed at the other pH values also and the data are given in Table 2. These results indicate that the h.e.r mechanism is unaffected by the presence of piperidine in H_2SO_4 of different pH values.

Table 2 gives the various corrosion and inhibition parameters calculated from the polarization curves. The corrosion current density corresponds to the current at the point of intersection of cathodic Tafel line with the corrosion potential.

The corosion potential of the HSLA steel is

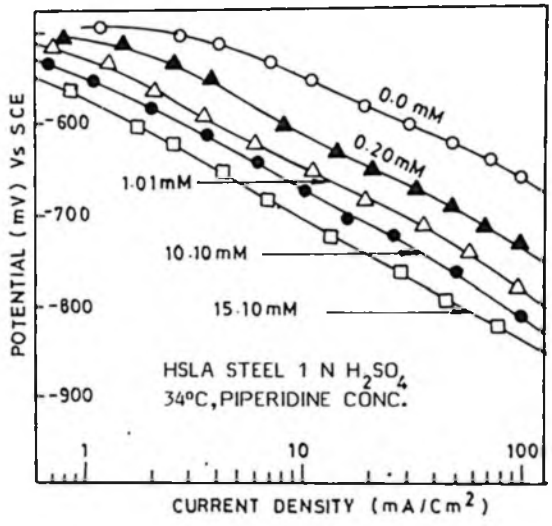


Fig. 2 Effect of piperidine concentration on the polarization curves of HSLA steel in 0.3 pH- 1 N H_2SO_4.

seen to be almost unaltered by the presence of piperidine. This situation is possible if both the anodic and cathodic polarization curves are shifted to lower current densities by the inhibitor in a proportional manner so that their intersections occur at the same potential but at reduced current densities. This is the behaviour of a mixed inhibitor. The present data suggests that piperidine is a mixed inhibitor for the HSLA steel in H_2SO_4 solutions.

It is seen from the Table 2 that the corrosion current density decreases with increase in inhibitor concentrations at all pH levels. On the basis of this corrosion current density, the inhibition efficiency of piperidine was calculated and was found to increase with inhibitor concentration as given in Table 2. It is evident from the table that piperidine is an effective inhibitor for HSLA steel at higher concentrations.

TABLE 2

CORROSION PARAMETERS OBTAINED FROM POTENTIOSTATIC POLARIZATION CURVES
Inhibitor Piperidine

pH	Inhibitor concentration (mM)	Corrosion potential vs SCE (mV)	Corrosion current density (mA/cm^2)	Inhibition efficiency* (η) %	Cathodic Tafel slope mV/decade	Surface coverage θ
0.3	Uninhibited	-485	3.15		113	
	0.20	-491	1.13	64	112	0.699
	1.01	-491	0.538	83	110	0.904
	10.1	-500	0.394	87	110	0.954
	15.1	-502	0.253	92	110	1.00
0.8	Uninhibited	-519	1.25		111	
	0.20	-519	0.94	25	112	0.295
	1.01	-515	0.65	48	113	0.571
	5.06	-517	0.40	68	118	0.810
	15.1	-520	0.191	85	117	1.00
1.55	Uninhibited	-578	0.3		120	
	1.01	-570	0.22	27	120	0.285
	5.06	-567	0.178	41	121	0.434
	10.1	-585	0.028	90	120	0.966
	15.1	-587	0.019	94	121	1.00
1.82	Uninhibited	-585	0.188		113	
	0.20	-587	0.098	48	112	
	1.01	-584	0.078	58	113	
	5.06	-603	0.027	85	114	
	10.1	-625	0.004	98	110	Sufficient data was not obtained to determine θ
2.25	Uninhibited	-589	0.115		113	
	0.20	-590	0.092	20	113	
	1.01	-593	0.074	36	113	
	5.06	-610	0.031	73	117	
	10.1	-592	0.011	90	119	

$$* \eta\ \% = \frac{I_u - I_i}{I_u} \times 100$$

where I_u = Corrosion current density in uninhibited corrodent
I_i = Corrosion current density in inhibited corrodent.

In order to understand the inhibition mechanism, a plot between corrosion current and inhibitor concentration (Fig. 3) was drawn. According to this plot, corrosion current decreases with increasing inhibitor concentration and seen to reach a saturation at higher inhibitor concentration.

If it is assumed that the inhibition by piperidine occurs due to simple, adsorption, the apparent corrosion rate of inhibited steel is proportional to the surface area which is not covered by inhibitor. The surface coverage of the inhibitor (θ) is related to corrosion current [15] by the relation

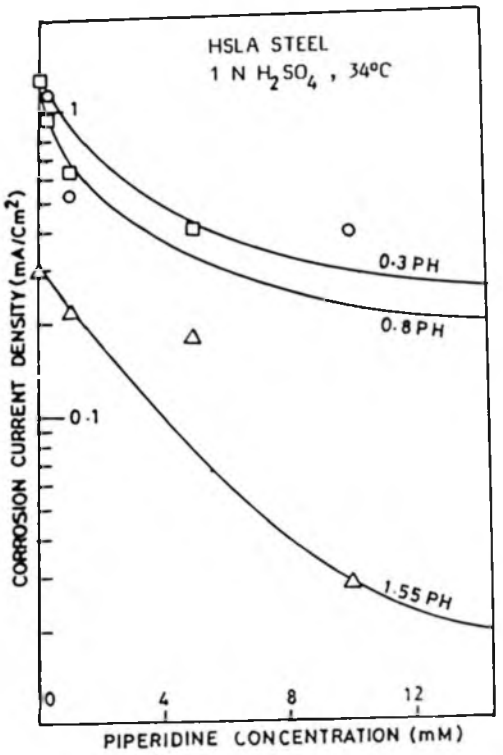


Fig. 3 Variation in corrosion current density with piperidine concentration in 1 N-H_2SO_4 of various pH values.

$$\theta = \frac{I_u - I_i}{I_u - I_{i,min.}} \qquad .....(1)$$

where I_u, I_i and $I_{i\ min}$ are corrosion current densities for uninhibited, inhibited and the minimum in inhibited solution respectively. Data from Fig.3 were used to calculate θ values for the HSLA steel exposed to H_2SO_4 by using equation (1). These values are also indicated in Table-2.

To examine the adsorption behaviour of the inhibitor, the data has been fitted to the Langmuir adsorption isotherm given by

$$\frac{c}{\theta} = \frac{1}{k} + c \qquad .....(2)$$

where k is the equilibrium constant for the adsorption process and c is the concentration of the inhibitor A plot of c/θ vs c for 0.3 pH H_2SO_4 is shown in Fig. 4. The data fit a straight line with a slope of unity. The

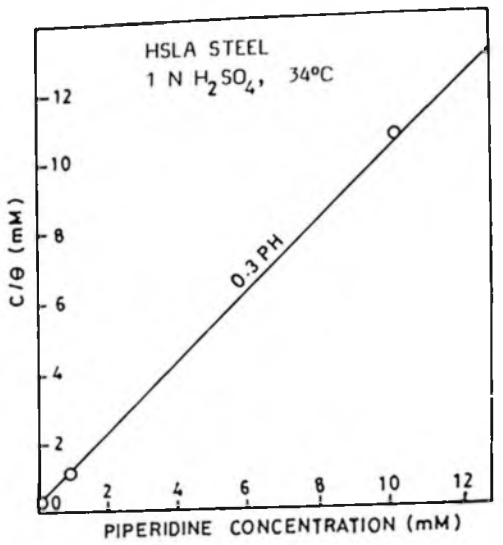


Fig. 4 Plot of Langmuir adsorption (Isotherm equation (2).

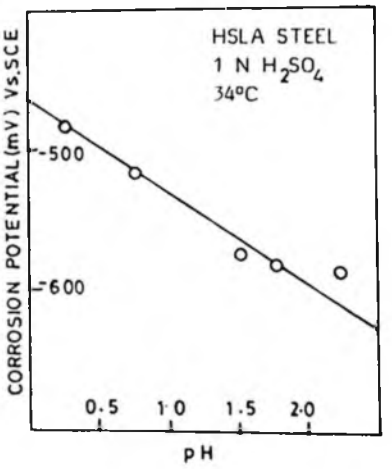


Fig. 5 Variation of corrosion potential with pH for HSLA steel in 1 N-H_2SO_4.

intercept of this plot on the ordinate determines the adsorption constant which was found to be 10 mM^{-1} This plot conforms the adsorption concept of inhibition by piperidine.

H.E.R. on HSLA Steel

Table 2 shows that the corrosion potential as well as the corrosion current density of the HSLA steel decrease with increasing pH of the H_2SO_4 solution. These variations are shown in Fig. 5 and 6 respectively. Both the corrosion potential and corrosion current decreases directly in proportion to the pH of the solution and the straight line relationships seen in Fig. 5 and 6 may be expressed as

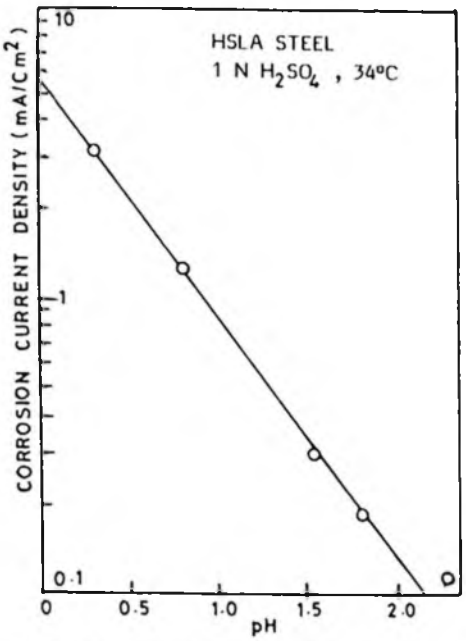


Fig. 6 Variation of corrosion current density with pH for HSLA steel in 1 N-H_2SO_4.

E_{corr} (mv) = -465-67 pH .... (3) --- Fig. 5

log i_{corr} (mA/cm^2) = 0.740-0.812 pH (4) Fig.6

This kind of polarization behaviour may be explained on the assumption that the reduced hydrogen ion concentration in the higher pH electrolyte retards the h.e.r. on the HSLA steel, the anodic polarization behaviour of which remains unaltered. In such a situation, the corrosion potential will shift towards more active potential and the corrosion current density will decrease as the pH increases

The reaction order, n for the h.e.r. with respect to the hydrogen ions may be calculated from the expression [16].

$$-\frac{d \log i_{corr}}{d\ pH} = n + \frac{\beta F}{2.303\ RT}\ \frac{dE_{corr}}{d\ pH} \quad ...(5)$$

where, i_{corr} = corrosion current
pH = Negative logarithm of the concentration of hydrogen ions
n = Reaction order
β = Symmetry factor (=0.5)
F = Faraday constant
R = Gas constant
T = Absolute temp.
E_{corr} = Corrosion potential

The values of dE_{corr} /d PH and d log i_{corr}/d PH, (slopes of the curves, obtained from Fig. 5&6) as -0.067 volt and 0.812 respectively and were substituted in equation (5) to obtain the value of n. It was found to be 1.36.

Fig 7 shows a plot of log i vs pH in the Tafel region (-600 mv) for both uninhibited and inhibited systems. The slope of this plot determines the reaction order parameter for h.e.r. with respect to hydrogen ions. Fig. 7 gave a slope of 1.44. This result is found to be in close agreement with the theoretically calculated value of 1.36.

These results show that in the presence of piperidine the rate of h.e.r. is decreased. The mechanism for the h.e.r. is the same in

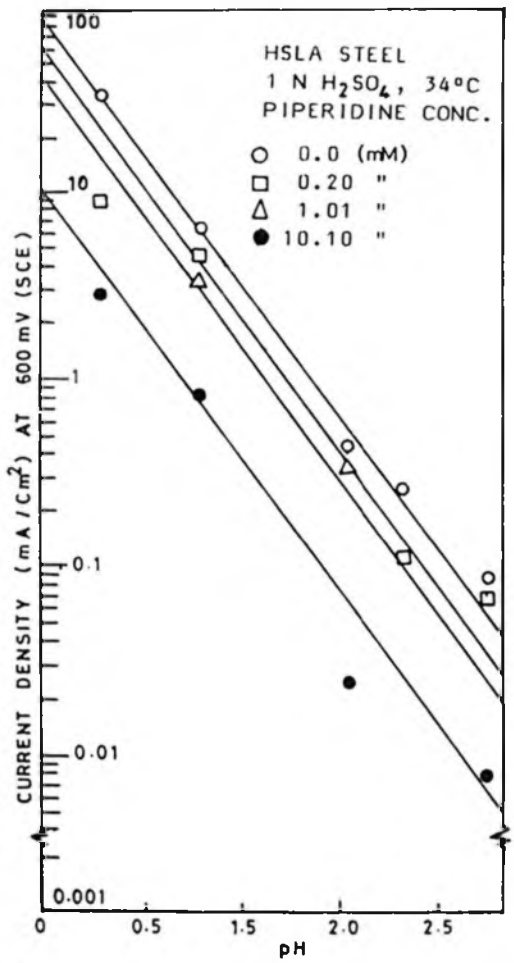


Fig. 7 Variation of current density at -600 mV (Tafel region) with pH for HSLA steel in 1 N-H_2SO_4 containing various concentration of piperidine.

both uninhibited and inhibited H_2SO_4 since the cathodic Tafel slopes and the reaction order with respect to the hydrogen ions remain unchanged.

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