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Corrosion of Low Carbon Steel in Sulphuric Acid Solution in Presence of Furane-Halides Mixture

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The corrosion behaviour of low carbon steel in stagnant aerated sulphuric acid solution and in presence of furane-halide mixture was studied. Furane inhibits the cathodic reaction, but halides inhibit the anodic reaction. These results form the polarisation technique. Weight-loss technique illustrates that the temperature increases the corrosion rate in the range (30°–85°C) in presence and in absence of inhibitors. The apparent activation energy is 12.4 kcal/mole.

INTRODUCTION

The corrosion behaviour of steel has been extensively studied in mineral acids. It has been stated that in O_2-free acid medium, the metal is under mixed control, and the corrosion rate is determined by both the anodic polarisation characteristics and the hydrogen overvoltage behaviour of the metal[1]. On addition of halide salt to sulphuric acid solution containing any organic compounds, co-operative effect results which inhibits iron dissolution[2–4]. Furane is one of a group of compounds found to be effective as inhibitors in sulphuric acid[5, 6]. Complete polarisation curves are useful in detecting inhibitor properties.[7–9].The inhibition characteristics of organic compound during acid corrosion of low carbon steel have been reported earlier at this laboratory.[10, 11]

The aim of this paper is to elucidate the mechanism of the corrosion of steel in halide-furane-H_2SO_4;the inhibitor efficiency has been measured by weight loss measurements, anodic and cathodic polarisation techniques at various temperatures.

EXPERIMENTAL

Rolled mild low carbon steel (0.05% C), 2 mm thick, was used. For weight-loss measurements, the test specimens were cut into pieces 3 cm × 1.5 cm with the help of a shearing machine and the edges smoothed. They were abraded into uniform surface with the help of a grinding machine and finally ground with 150, 300, 400 and 600 grade emery papers. The working electrode, soldered with insulated copper wire and after proper surface preparation, was coated thoroughly with epoxy resin keeping 0.2 cm^2 surface area exposed for corrosion. Platinum wire was used as an auxiliary electrode and a dip type calomel electrode was used as reference electrode (SCE). Polarisation was by a power supply with a potentiometer connected in circuit. The current was calculated by using a variable resistance and an ammeter. Potentials were measured by a Bay potentiometer against SCE. Weight-loss measurement and polarisation test were made under thermostatic conditions at 30. 50 and 85°C. The six 2 N sulphuric acid solutions (Table 1) were prepared freshly as required.

The cell used for polarisation measurements was composed of two compartments separated by a fritted glass disc to prevent mixing of anolyte and catholyte. The polarisation curves were obtained using a simple galvanostatic technique in absence (blank), in presence of furane and in furane-halide mixture,

The electrolyte used was 2 N sulphuric acid which was preferred to nitric acid or HCl since nitrite and chloride ions have a stronger tendency to adsorb than does sulphate[12]. The measurements were repeated several times and are highly reproducible.

RESULTS AND DISCUSSION

Weight-loss technique

The weight-losses for the low carbon steel (0.05% C), determined for different mixtures as shown in Table 1 as a function of time and at different temperatures in 2N sulphuric acid solutions containing no inhibitor and containing 0.2 M furane at 30, 50 and 85°C, are presented in Fig. 1. Similar plots for low-carbon steel immersed for various times in 2N sulphuric acid solutions containing 0.015 M KCl and 0.015 M KBr plus 0.2 M furane at the same temperature are presented in Figure 2. Similar plots for low-carbon steel immersed for various times in 2N sulphuric acid solution containing 0.015 M KBr plus 0.2 M furane at 30, 50 and

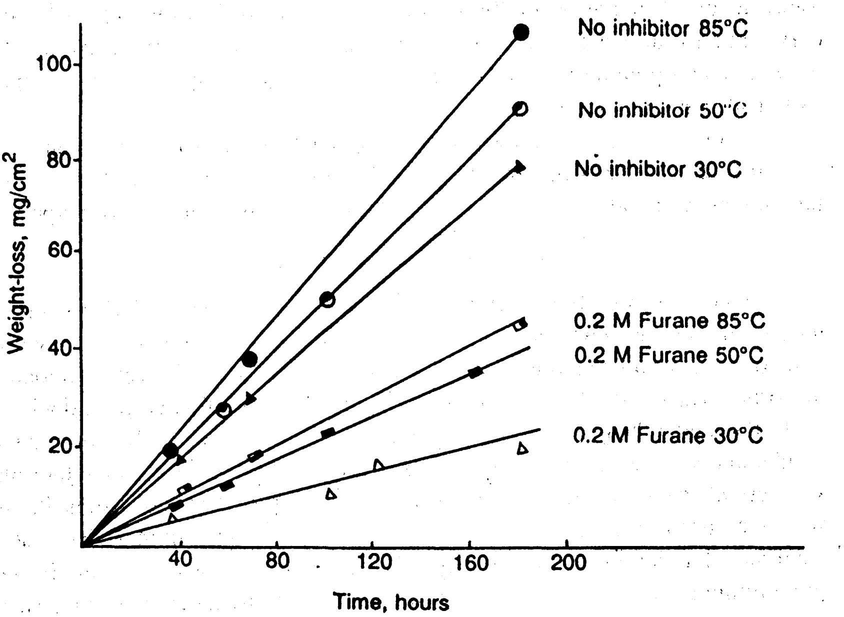

Fig. 1 Corrosion of low-carbon steel in halide-free 2 N H_2SO_4 solutions: effect of furane additions

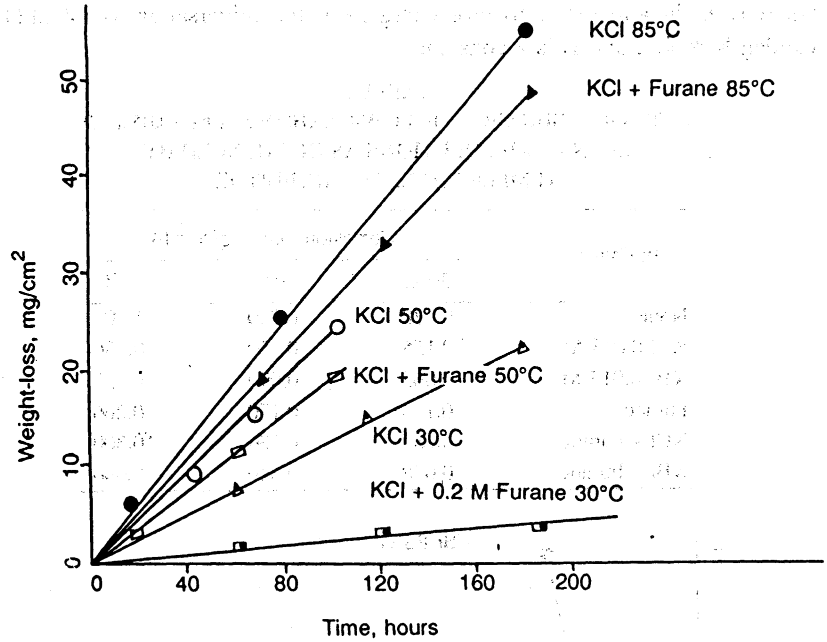

Fig. 2 Corrosion of low-carbon steel in 2 N H_2SO_4 solutions containing 0.015 M KCl: effect of furane additions

85°C are presented in Fig. 3. The result was obtained that a linear relationship holds between the loss in weight and time. The slopes of these relationships, which represent the corrosion rates, are collected in Table 2.

TABLE 1
2 N SULPHURIC ACID TEST SOLUTIONS

Furane concentration [M]	Concentration of halide [M]
0.0	0.0
0.2	0.0
0.0	0.015 KCl
0.0	0.015 KBr
0.2	0.015 KCl
0.2	0.015 KBr

The corrosion rate of low carbon steel (W) in 2N H_2SO_4 solutions increases with rise in temperature, both in presence and in absence of inhibitors (Table 2). Putilova *et al.*[13] pointed out that, for steel in acids, logarithm of rate of corrosion (W) can be represented as a straight-line function of 1/T (Arrhenius equation), where T is the absolute temperature.

$$\ln (W) = -E_a/RT + B \tag{1}$$

where E_a is the apparent activation energy, R is the universal gas constant (1.987 cal/deg K-mole), and B is a constant.

TABLE 2
RATE OF CORROSION OF LOW-CARBON STEEL (0.05% C) IN 2N H_2SO_4 SOLUTIONS AS INFLUENCED BY TEMPERATURE AND INHIBITOR

Inhibitor	Corrosion rate (mg/cm^2/h)		
	30°C	50°C	85°C
None	0.470	0.700	1.100
KCl 0.015 M	0.155	0.230	0.336
KBr 0.015 M	0.065	0.090	0.130
Furane	0.110	0.170	0.266
KCl + Furane	0.130	0.180	0.300
KBr + Furane	0.028	0.040	0.046

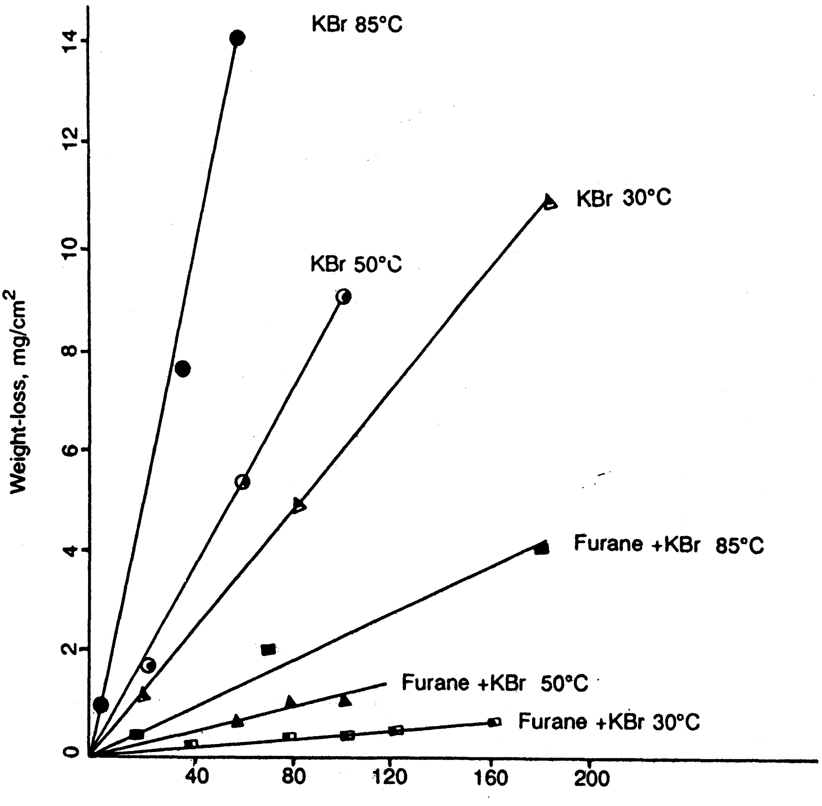

Fig. 3 Corrosion of low-carbon steel in 2 N H_2SO_4 solutions containing 0.015 M KBr: effect of furane additions

Fig. 4 shows the relation between the corrosion rates and 1/T. From that plots for the six 2N H_2SO_4 solutions investigated can be represented reasonably well by a group of parallel lines. This gives a transfer coefficient of the hydrogen evolution reaction (h.e.r.), B = 0.49. The fact that B has different values in presence and in absence of inhibitors (Fig. 4) has an influence on the mechanism of h.e.r. The calculated activation energy is 12.4 kcal/mole which agrees with 13.0 kcal/mole reported by Balezin *et al.*[14] for low-carbon steel in 2N H_2SO_4.

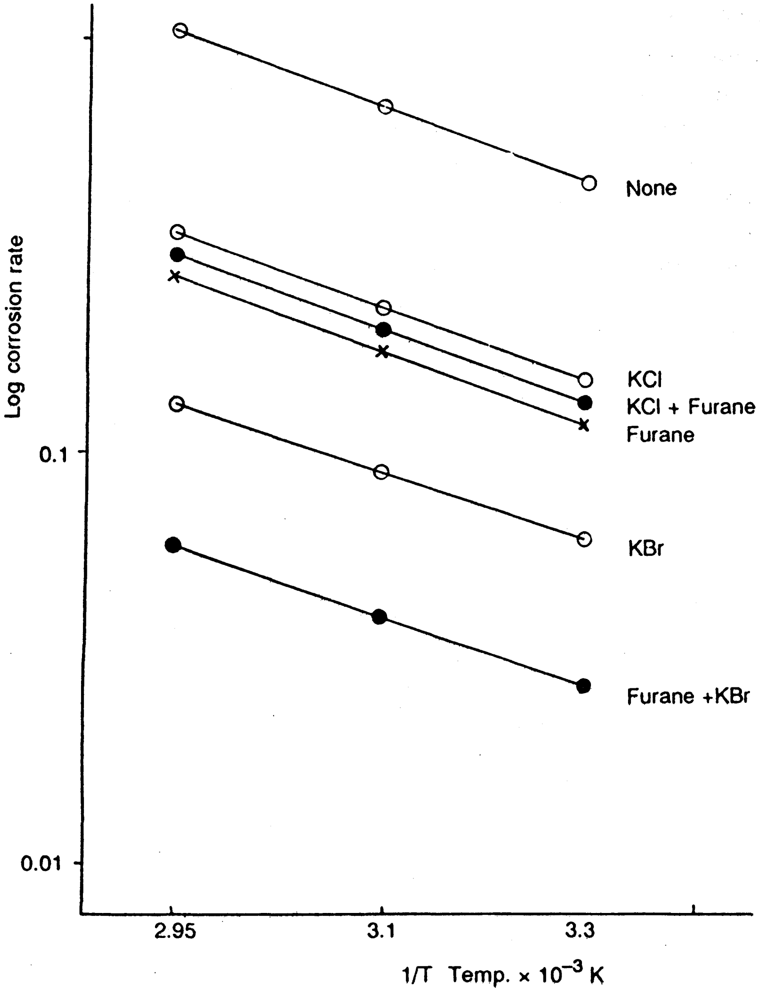

Fig. 4 Effect of temperature on corrosion rate of low-carbon steel in inhibited solutions of 2 N H_2SO_4

Polarisation measurement results

Sulphuric acid (2N) containing furane-halides mixture was used for polarisation studies. The cathodic and anodic polarisation curves for these solutions at various temperatures were drawn in Figure 5.

Corrosion currents

Corrosion current can be determined from weight-loss measurements. The following equation can be used:

$$I_{corr} = 0.96 \times (W) \qquad (2)$$

where i_{corr} is the corrosion current in mA/cm^2 and W is the corrosion rate in mg/cm^2/hr based on weight-loss over a period of hrs.[15]

Table 3 shows the effect of halide and furane at different temperatures on anodic and cathodic Tafel slopes (Figure 5) of low-carbon steel in 2N H_2SO_4. In acid without halides. anodic Tafel slope (B_a) averaged about 78% of the cathodic Tafel slope (B_c) and in the acid with furane and without halide, B_a averaged about

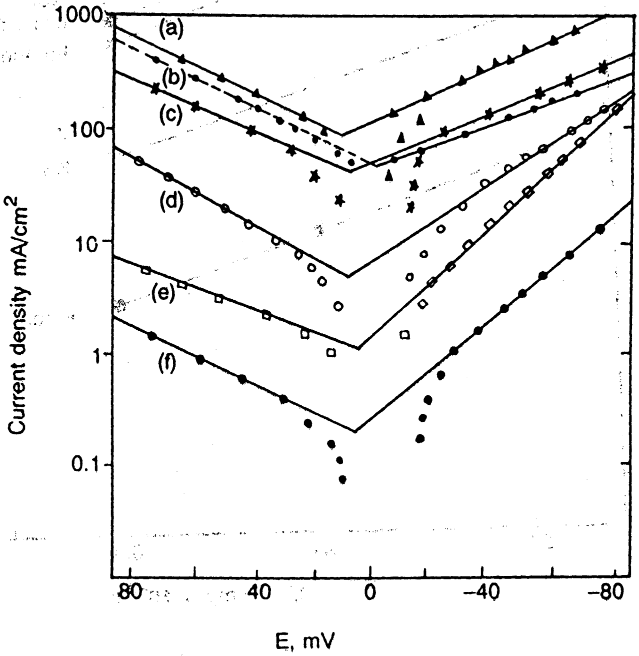

Fig. 5 Anodic and cathodic Tafel line for low-carbon steel in different media at 85°C

		Anodic B a	Cathodic B c
(a)	Blank	138 mV	165 mV
(b)	Sulphuric acid + furane	130 mV	186 mV
(c)	KCl + sulphuric acid	160 mV	170 mV
(d)	KCl + furane + sulphuric acid	114 mV	109 mV
(e)	KBr + sulphuric acid	150 mV	75 mV
(f)	KBr + furane + sulphuric acid	170 mV	85 mV

55% of B_c. This indicates that the process for these cases is cathodically controlled. Addition of KCl to the acid resulted in an increase in B_a and slight decrease in B_c producing a B_a/B_c ratio of about one. This indicates that the process is under mixed control. The addition of KBr to sulphuric acid leads to a greater increase in B_a and decrease in B_c producing a B_a/B_c ratio of about two. This indicates that the corrosion reaction is under anodic control. Similar effects of KCl and KBr on B_a/B_c ratio were obtained for different temperatures and for a given system with or without furane.

TABLE 3
EFFECT OF TEMPERATURE ON TAFEL SLOPES OF LOW CARBON STEEL IN INHIBITED SULPHURIC ACID SOLUTIONS

Addition to (2N) H_2SO_4		Tafel Slope (mV)		B_a/B_c
Halide (0.015 M)	Furane (0.2 M)	B_a	B_c	
		30° C		
None	None	77	98	0.78
None	0.2	58	105	0.55
KCl	None	89	94	0.94
KCl	0.2	70	80	0.87
KBr	None	124	65	1.90
KBr	0.2	183	91	2.01
		50° C		
None	None	82	100	0.82
None	0.2	80	136	0.59
KCl	None	101	102	0.99
KCl	0.2	90	83	1.08
KBr	None	148	75	1.97
KBr	0.2	187	85	2.20
		85° C		
None	None	138	165	0.83
None	0.2	130	186	0.70
KCl	None	160	170	0.94
KCl	0.2	114	109	1.04
KBr	None	150	75	2.00
KBr	0.2	170	85	2.00

CONCLUSION

1. Weight-loss measurements indicate that the corrosion rate increases with temperature over the range 30°–85°C in presence and in absence of inhibitors.
2. For unihibited acid and acid containing only furane, the corrosion reaction is mostly controlled by the cathodic reaction.

3. Addition of halides to uninhibited acid or acid containing furane change the mechanism to one in which corrosion is under anodic control.

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