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Inhibition of Zinc Corrosion in H_2SO_4 by Hexamethylenetetramine

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The inhibition of corrosion of zinc in H_2SO_4 by hexamethylenetetramine, thiourea and propargyl alcohol has been studied by potentiodynamic polarization method. The study shows that the inhibitor efficiency increases with temperature for hexamethylenetetramine but it is a less effective corrosion inhibitor. The amount of inhibitor of zinc dissolution is found to be dependent on the concentration of the inhibitor. The corrosion current increases with increase in thiourea and propargyl alcohol concentrations indicating that they accelerate the zinc dissolution reaction in H_2SO_4.

INTRODUCTION

The studies on the behaviour of zinc electrode in acidic solutions are important since zinc is used as anode material in zinc-chlorine secondary batteries.[1] The effect of H^+ ion concentration on the dissolution of zinc in acidic chloride solution[2] and the corrosion behaviour of zinc in H_2SO_4 at different H^+ and SO_4^{2-} concentrations[3] have been studied.

Substances such as decylamine[4], triphenylphosphonium bromide[5] and benzotriazole[6] have been studied as inhibitors for zinc in HCl. Compound oxidizers like VO_3^-, $Cr_2O_7^{2-}$, MnO_4^{2-}, WO_4^{2-}, MnO_4^- and TeO_4^{2-} have been reported as effective inhibitors for zinc in 0.01 N sulphate solution.[7] The effect of benzenethiol and its methyl, amino and carbonylic ring substituted derivatives, benzylthiol and thioglycollic acid on the electrochemical and corrosion behaviour of zinc in H_2SO_4 and HCl solutions were studied.[8]

In this investigation, hexamethylenetetramine, thiourea and propargyl alcohol have been tested as corrosion inhibitors for zinc in H_2SO_4. The performance of these inhibitors with inhibitor and acid concentrations and temperature has been studied.

EXPERIMENTAL

Zinc rod (99.99% purity) of diameter 0.8 cm was fixed tightly in Teflon so as to expose an area of 0.283 cm^2. The electrode was polished with 1/0 and 4/0 emery papers and degreased with trichloroethylene. Inhibitor concentrations ranging from $1.0–5.0 \times 10^{-3}$ M in 0.1 N H_2SO_4 at different temperatures were used. All the solutions were prepared using AnalaR chemicals with double distilled water.

Experiments were carried out in the polarization cell at different temperatures using a thermostat. The potential of the working electrode was measured with

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respect to saturated calomel electrode (SCE). The steady-state potentials were attained within 15–30 minutes.

The polarization measurements of zinc in H_2SO_4 were carried out by potentiodynamic polarization method at a sweep rate of 1 mV s^{-1} using potentiostat (PAR model 173), universal programmer (PAR model 175) and X-Y recorder (PAR model 0074). The corrosion current values were obatained by Tafel extrapolation method[9].

RESULTS AND DISCUSSION

The measurement of corrosion currents by polarization method for zinc in 0.1 N H_2SO_4 containing 1.0–5.0 × 10^{-3} hexamethylenetetramine have been made at diffenent temperatures from 303 K to 333 K (Fig. 1–4). The corrosion potential is shifted in the negative direction with the increase of hexamethylenetetramine concentration and with the increase of temperature (Table-1). The corrosion current is measured by the linear polarization method using the equation

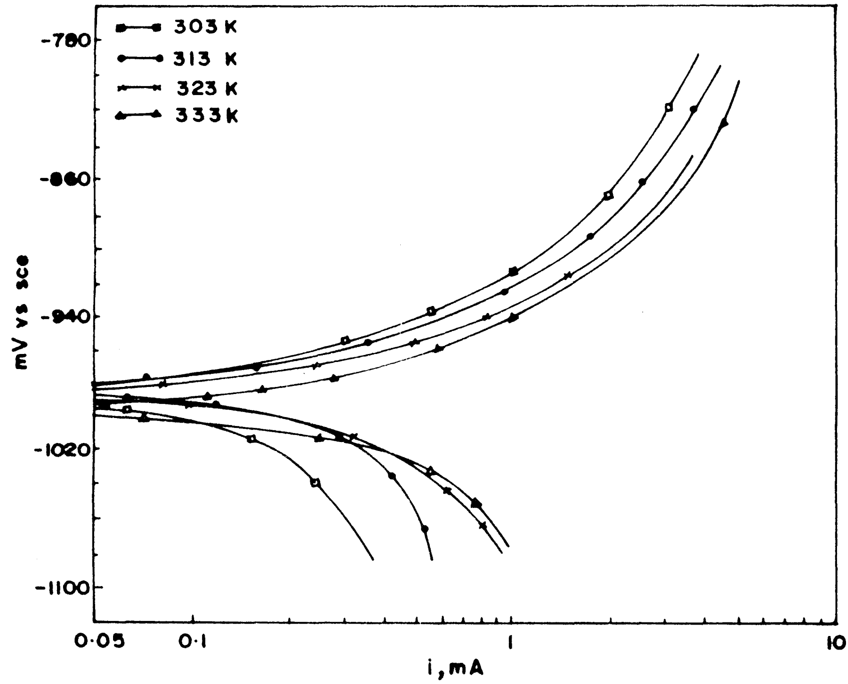

Fig. 1 Polarization curves of zinc in 0.1 N H_2SO_4 acid at different temperatures

$$i_{corr} = \frac{ba \times bc}{2.303(ba + bc)} \times \frac{1}{R_p}$$

where b_a and b_c are the anodic and cathodic Tafel slopes respectively and R_p is the polarization resistance. It is seen that at one and the same temperature, the

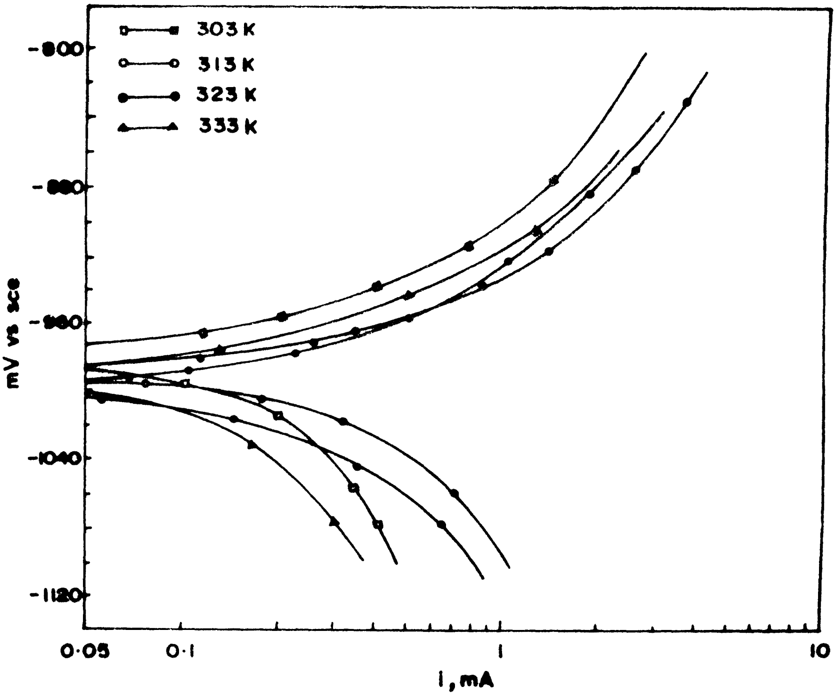

Fig. 2 Polarization curves for zinc in 0.1 N H_2SO_4 containing 1×10^{-3} M hexamethylenetetramine at different temperatures

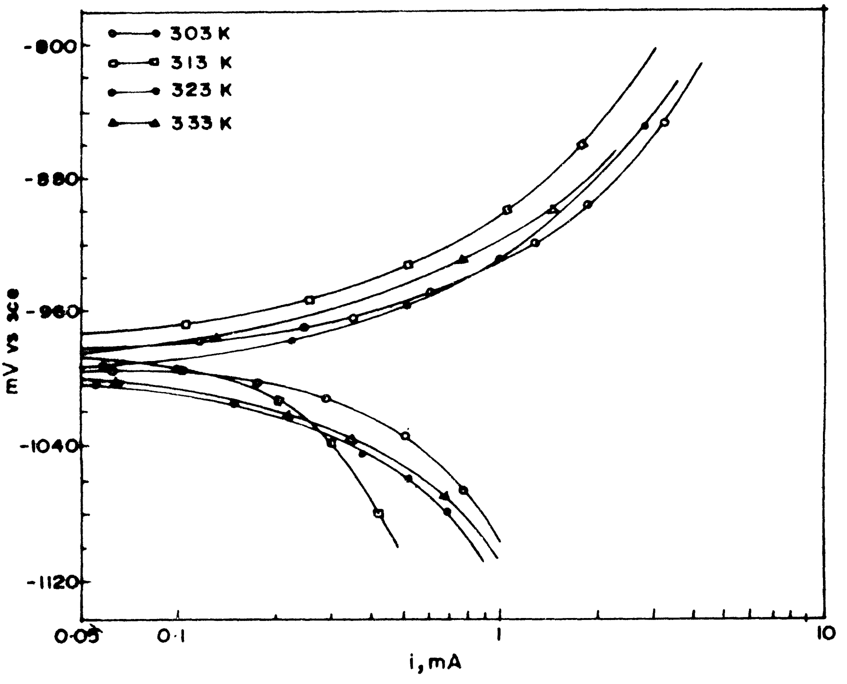

Fig. 3 Polarization curves for zinc in 0.1 N H_2SO_4 containing 3×10^{-3} M Hexamethylenetetramine at different temperatures

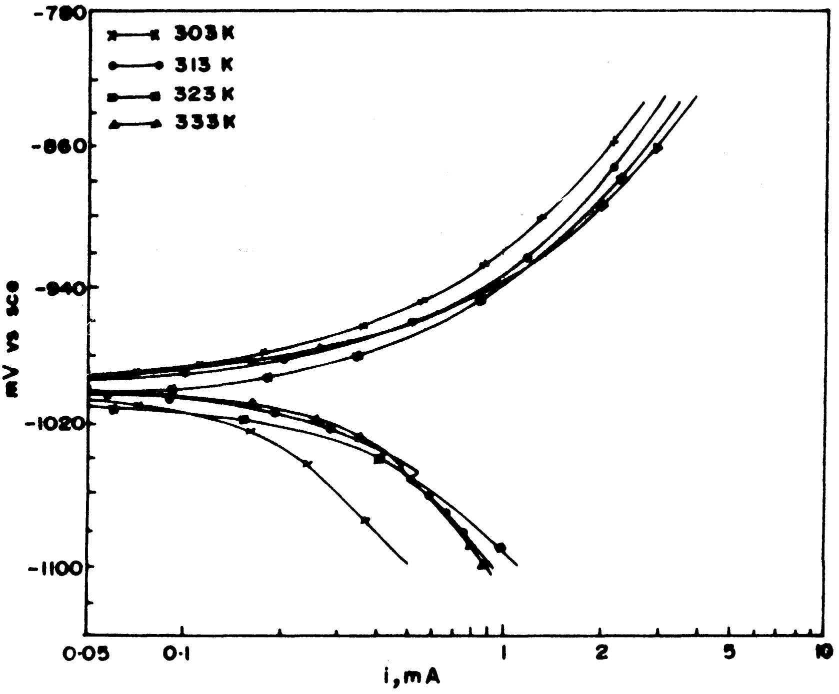

Fig. 4 Polarization curves for zinc in 0.1 N H_2SO_4 with 5×10^{-3} M hexamethylenetetramine at different temperatures

gradients of the linear portion do not change significantly with the hexamethylenetetramine concentration. For the same solution the Tafel slope b_c increases with temperature. The anodic Tafel slopes are found to be in the range of 55–70 mV and cathodic Tafel slopes are in the range of 110–140 mV.

At the lowest concentration of hexamethylenetetramine, the potential shifts towards the anodic direction due to the adsorption of the additive on the anodic sites. Since the additive concentration is insufficient to block all the anodic sites, there is corrosion acceleration. Upon increase of the additive concentration, first the anodic and then the cathodic sites are blocked. Hence the linear portion of the cathodic polarization curve is shifted towards the cathodic direction and it acts as an inhibitor. The variation of inhibitor efficiency with the hexamethylenetetramine concentration is given in Table-2. The inhibitor efficiency is calculated from the relation

$$\text{inhibitor efficiency} = \frac{i_{corr} - i_{corr(i)}}{i_{corr}} \times 100$$

where i_{corr} and $i_{corr(i)}$ are the corrosion currents in the absence and presence of additive. The inhibitory action of the additive increases with its concentration and temperature in 0.1 N H_2SO_4 solution (Fig. 5).

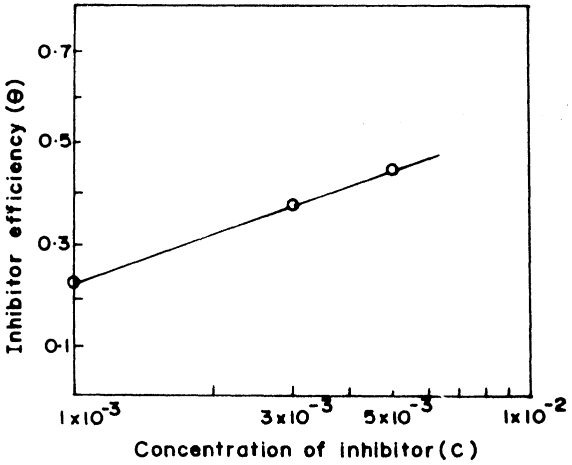

Fig. 5 Temkin adsorption isotherm plots of hexamethylenetetramine

TABLE-1
CORROSION PARAMETERS FOR ZINC IN 0.1 N H_2SO_4 CONTAINING VARIOUS CONCENTRATIONS OF HEXAMETHYLENETETRAMINE AT DIFFERENT TEMPERATURES

Temperature K	Conc. of hexamethylene-tetramine mole	$-E_{corr}$ mV *vs.* SCE	b_a mV	b_c mV	i_{corr} mA/cm^2	θ
303	Zero	972	60	120	0.46	–
	1.0×10^{-3}	982	56	110	0.35	0.12
	3.0×10^{-3}	984	54	120	0.28	0.25
	5.0×10^{-3}	1000	60	120	0.26	0.32
313	Zero	984	70	130	0.71	–
	1.0×10^{-3}	992	66	110	0.53	0.15
	3.0×10^{-3}	886	60	140	0.46	0.29
	5.0×10^{-3}	1008	68	135	0.39	0.35
323	Zero	990	56	110	0.89	–
	1.0×10^{-3}	1000	80	120	0.64	0.17
	3.0×10^{-3}	1004	75	120	0.50	0.35
	5.0×10^{-3}	1014	65	122	0.43	0.43
333	Zero	998	90	118	1.13	–
	1.0×10^{-3}	996	70	120	0.60	0.20
	3.0×10^{-3}	1010	60	130	0.53	0.41
	5.0×10^{-3}	1004	60	130	0.46	0.51

TABLE 2
VARIATION OF INHIBITOR EFFICIENCY OF HEXAMETHYLENETETRAMINE IN 0.1 N H_2SO_4 WITH INHIBITOR CONCENTRATION AND TEMPERATURE

Concentration of hexamethylene-tetramine mole	Inhibitor efficiency (%)			
	303 K	313 K	323 K	333 K
1.0×10^{-3}	23.0	25.6	28.9	46.9
3.0×10^{-3}	33.1	38.5	44.0	53.1
5.0×10^{-3}	40.6	45.2	52.4	59.4

The degree of surface coverage, θ, may be evaluated from the linear parallel portion of the cathodic curves at a given potential by the expression

$$\theta = 1 - \frac{i_{cp}}{i_{ca}}$$

where i_{cp} and i_{ca} are the corrosion currents in the presence and absence of inhibitor at the same potential.[10] The degree of surface coverage increases with the additive concentration and temperature. The thermal energy activates the adsorption process. The degree of surface coverage varies linearly with log C where C is the concentration of the inhibitor. This shows that the inhibitor obeys the Temkins adsorption isotherm[11] according to which θ increases linearly with log C.

The polarization curves for zinc in H_2SO_4 containing 3.0×10^{-3} M - hexamethylenetetramine with acid concentration in the range of 0.01 N to 0.1 N are given in Fig. 6. The corrosion current and the inhibitor efficiencies for various acid concentrations are summarized in Table 3. It is seen that the inhibitor efficiency increases with decrease of acid concentration.

TABLE-3
VARIATION OF CORROSION PARAMETERS AND INHIBITOR EFFICIENCY OF 3.0×10^{-3} M HEXAMETHYLENETETRAMINE FOR ZINC IN DIFFERENT SULPHURIC ACID CONCENTRATIONS

Solution	Corrosion Parameters				Inhibitor efficiency (%)
	$-E_{corr}$	b_a mV	b_c mv	i_{corr} mA/cm^2	
0.01 N H_2SO_4	946	56	120	0.25	
0.01 N H_2SO_4 + Hexamethylenetetramine	956	54	116	0.07	72.0
0.05 N H_2SO_4	960	58	124	0.33	
0.05 N H_2SO_4 + Hexamethylenetetramine	971	52	120	0.15	54.5
0.1 N H_2SO_4	972	60	120	0.46	
0.1 N H_2SO_4 + Hexamethylenetetramine	984	54	118	0.28	38.5

TABLE-4

VARIATION OF CORROSION PARAMETERS AND INHIBITOR EFFICIENCY OF THIOUREA AND PROPARGYL ALCOHOL FOR ZINC IN 0.1 N H_2SO_4

Solution mole	Corrosion Parameters				Inhibitor efficiency (%)
	-E Corr	b_a mV	b_c mV	i_{corr} mA/cm^2	
Thiourea					
1.0×10^{-3}	978	75	120	0.15	67
5.0×10^{-3}	1000	60	120	0.17	63
7.0×10^{-3}	966	56	110	0.35	23
Propargyl Alcohol					
5.0×10^{-3}	1010	54	122	0.17	63
7.0×10^{-3}	1006	58	126	0.21	54
1.0×10^{-2}	998	56	130	0.24	47

Polarization measurements were carried out for zinc in 0.1 N H_2SO_4 containing different concentrations of thiourea and propargyl alcohol at 303 K (Figs. 7, 8).

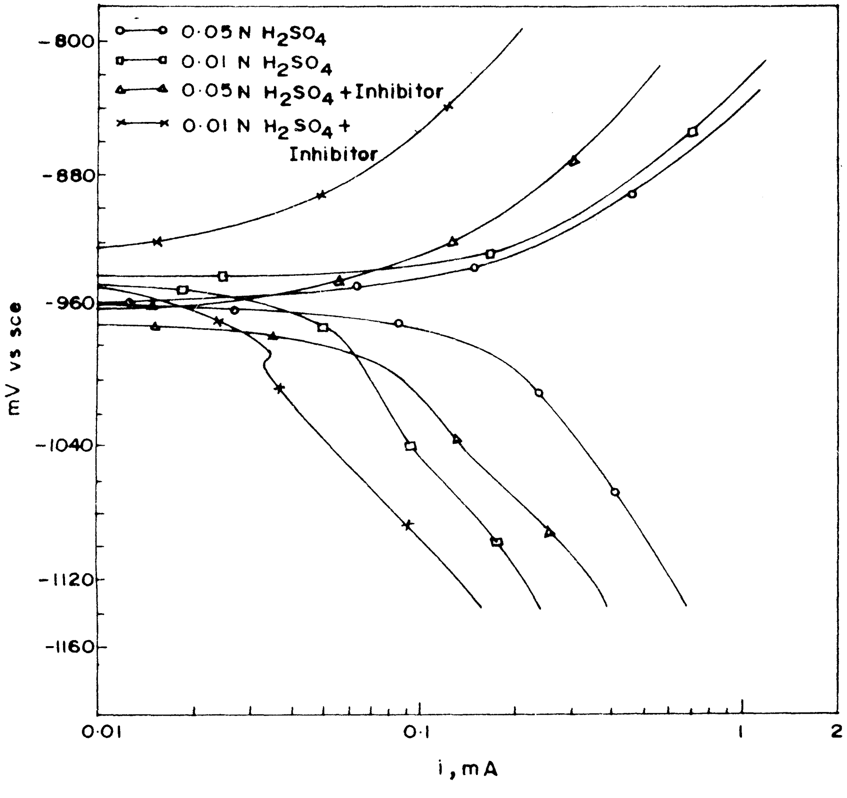

Fig. 6 Polarization curves for zinc in different H_2SO_4 concentrations containing 3×10^{-3} M hexamethylenetetramine

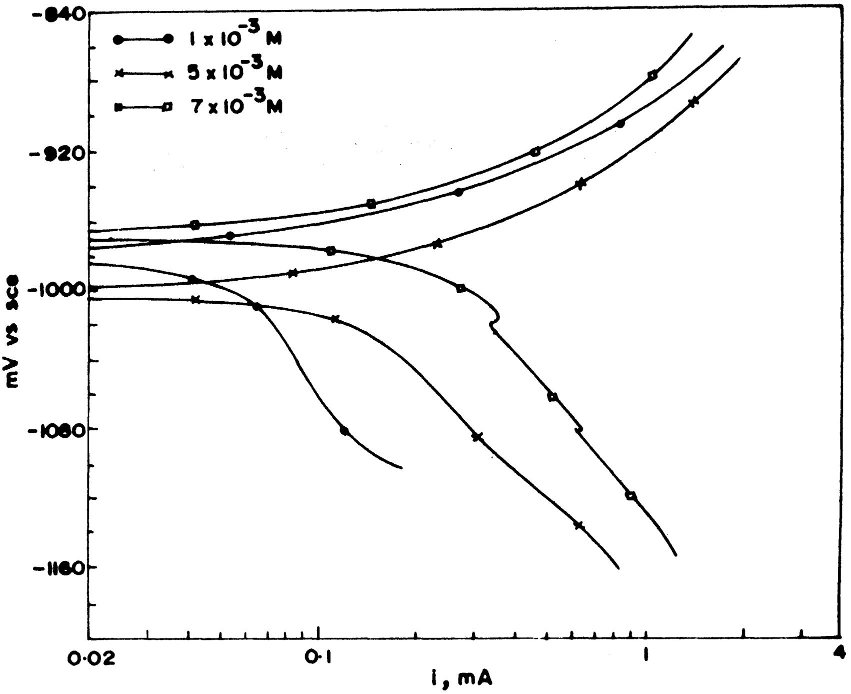

Fig. 7 Polarization curves for zinc in 0.1 N H_2SO_4 containing various amount of thiourea

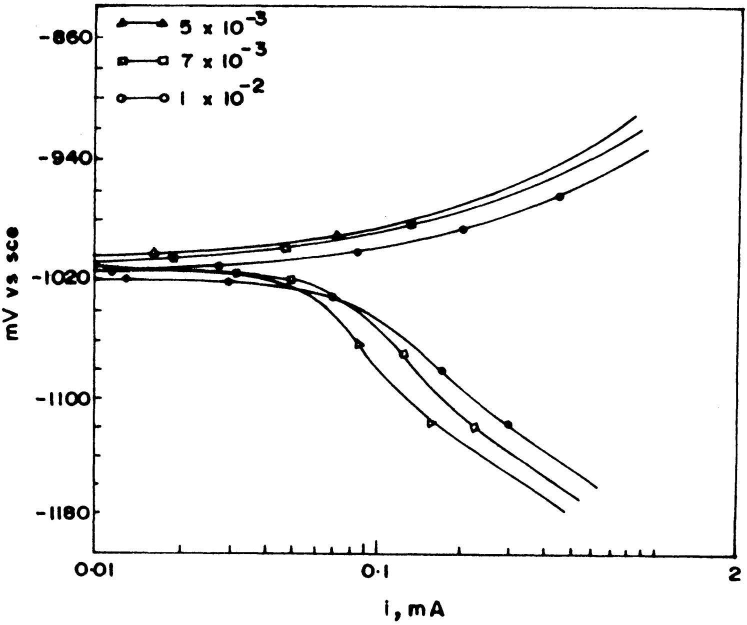

Fig. 8 Polarization curves for zinc in 0.1 N H_2SO_4 containing various amounts of propargyl alcohol

The corrosion currents and inhibitor efficiency for various inhibitor concentrations are given in Table 4. It is seen that the corrosion current increases with increase of thiourea and propargyl alcohol concentrations. This indicates that thiourea and propargyl alcohol accelerate the zinc dissolution reaction in H_2SO_4.

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