

## Inhibition of Corrosion of Zinc in Sulphamic Acid

R.T. VASHI\* and V.A. CHAMPANERI

*Department of Chemistry*

*Navyug Science College, Rander Road, Surat-395 009, India*

The inhibition by sulphanilamide and phenyl diamine tetraacetic acid of the corrosion of zinc in sulphamic acid solution has been studied in relation to the concentrations of inhibitors and temperature. In plain sulphamic acid, the corrosion increases with the temperature. Inhibition efficiency increases as the concentration of inhibitor increases. At 15 mM inhibitor concentration in 0.1 M sulphamic acid, the efficiency of sulphanilamide was found to be 78%, whereas 75% for phenyl diamine tetraacetic acid. The mode of inhibition action appears to be the chemisorption because the plot of  $\log \frac{\theta}{1-\theta}$  versus  $\log C$  giving a straight line suggests that the inhibitors cover both the anodic as well as cathodic regions through general absorption Langmuir isotherm. Galvanostatic polarization curves show both anodic and cathodic polarization in both inhibitors studied.

### INTRODUCTION

Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coatings. Zinc, like aluminium, is amphoteric in its behaviour towards acids and alkalies.<sup>1</sup> Sulphamic acid is a strong acid ( $\text{NH}_2\text{SO}_3\text{H}$ ) and it is used as a cleaner for rust, algae and hard water scales from cooling tower and condensers.<sup>2,3</sup> Desai<sup>4</sup> studied the effect of anisaldehyde and ethylene diamine as inhibitors for the corrosion of zinc in sulphamic acid. Crotty<sup>5</sup> stated that in cleaning zinc surface with sulphamic acid the corrosive action of the acid is inhibited by cinnamaldehyde and heptaldehyde. Water<sup>6</sup> stated that corrosion of zinc and zinc plated surfaces, like boilers or pipe systems during scale removal by treatment with sulphamic acid was inhibited by addition of benzylquinolinium chloride and cinnamic acid. In the present work, the corrosion of zinc by sulphamic acid containing sulphanilamide and phenyl diamine tetra acetic acid has been reported.

### EXPERIMENTAL

Rectangular specimens ( $5.5 \times 2.5 \times 0.2$  cm) of zinc with a small hole of ca. 3 mm diameter near the upper edge were used for the determination of the corrosion rate. The chemical composition of specimen was found to be 98.5% Zn, 0.03% Pb, 0.02% Cd and 0.01% Fe. All the specimens were cleaned by buffing to obtain a mirror-like finish.

A specimen, suspended by a glass hook, was immersed in each beaker containing 230 mL of test solution at  $303 \pm 1$  K for a period of 24 h. After the exposure period, the test specimens were derusted by using a solution made up by dissolving 10%  $\text{CrO}_3$  and about 0.2 g  $\text{BaCO}_3$  in distilled water for a period of about 2 minutes<sup>7</sup>. Duplicate experiments were performed in each case and the mean values of corrosion loss were calculated.

To determine the effect of temperature on corrosion, weight loss was measured in 0.1 M sulphamic acid containing 5 mM of the inhibitor concentration at solution temperature of 313, 323 and 333 K for a period of 3 h.

For polarization study, metal specimens of circular design, having an area of 7.7 cm<sup>2</sup> were immersed in 100 mL corrosive media. Auxiliary platinum electrode was also placed in a corrosive media through which external current was supplied from a regulated power supply. A silver-silver chloride reference electrode, placed in a saturated KCl solution, remained in contact with the corrosive solution *via* salt bridge. The change in potential was measured by potentiostat/galvanostat (Model-273) against reference electrode (Ag/AgCl).

## RESULTS AND DISCUSSION

To assess their protective value, sulphanilamide and phenyl diamine tetraacetic acid are added as inhibitors in 5, 10 and 15 mM concentration in 0.1 M sulphamic acid for an immersion period of 24 h. It is clear from the data of Table-1 that both the inhibitors decrease corrosion. In 0.1 M acid concentration, the inhibition efficiency increases with the increase in inhibitor concentration.

TABLE-1  
CORROSION RATE AND INHIBITION EFFICIENCY (IE, %)

Effective area of specimen: 30.74 cm<sup>2</sup>, Temperature: 303 ± 1 K  
Acid concentration: 0.1 M

No.	Inhibitor	Inhibitor Concentration mM	Corrosion loss mg/dm <sup>2</sup>	I.E. %
1.	Sulphamic acid only	—	163.0	—
		5	52.0	68
		10	46.0	72
2.	Acid + Sulphanilamide	15	36.0	78
		5	65.0	60
		10	55.5	66
3.	Acid + Phenyl diamine tetraacetic acid	15	40.0	75

The inhibition efficiency (IE,%) due to inhibitors has been calculated on a percentage basis.<sup>8</sup>

$$IE, \% = \frac{W_u - W_i}{W_u} \times 100$$

where,  $W_u$  is the weight loss of the metal in uninhibited acid and  $W_i$  is the weight loss of metal in inhibited solution.

### Effect of Temperature

The results show in Table-2 that as the temperature is increased, the extent of corrosion also increases, *viz.*, 196.1, 336.0 and 750.0 mg/dm<sup>2</sup> at 313, 323 and 333 K respectively. However, from Table-2, it is apparent that the inhibitive efficiency of all the inhibitors decreases with a rise in temperature. Sul-

TABLE-2  
EFFECT OF TEMPERATURE

Acid concentration: 0.1 M, Inhibitor concentration: 5 mM, Immersion period : 3h, Effective area of specimen : 30.74 cm<sup>2</sup>

S. No.	Inhibitor	Temp. (in K)				Mean E <sub>a</sub> From eq. 1	E <sub>a</sub> from Arrhenius plot	Q <sub>ads.</sub>		Mean ΔG <sub>a</sub> <sup>o</sup>
		313		323				333		
		mg/dm <sup>2</sup>	I.E. (%)	mg/dm <sup>2</sup>	I.E. (%)			mg/dm <sup>2</sup>	I.E. (%)	
1.	Sulphamic acid (only)	196.1	—	336.0	—	750.0	—	—	—	
2.	Acid + sulphanilamide	74.2	62	218.4	35	566.4	24	-92.5	-9.9	
3.	Acid + PDTA acid	82.0	58	240.4	28	606.7	19	-180.1	-9.8	

PDTA acid = Phenyl diamine tetraacetic acid.

TABLE-3  
POLARIZATION DATA

Acid concentration: 0.1 M, Temp.: 303 ± 1K, Inhibitor concentration: 5 mM

S. No.	System	E <sub>corr</sub> mV	I <sub>corr</sub> (μA/cm <sup>2</sup> )	Tafel slope (mV/decade)			I.E. (in %)		
				Cathodic -B <sub>a</sub>	Anodic +B <sub>a</sub>	B (mV)	R <sub>p</sub> (ohm/cm <sup>2</sup> )	From TI method	From weight loss method
1.	Sulphamic acid (only)	-918	1.18	-11	+14	2.67	2.26	—	—
2.	Sulphamic acid + sulphanilamide	-922	0.40	-35	+15	4.56	11.40	66	68
3.	Sulphamic acid + PDTA acid	-930	0.51	-99	+7	2.84	5.57	57	60

PDTA acid = Phenyl diamine tetraacetic acid

phanilamide shows 62, 35 and 24% inhibition efficiency at 313, 323 and 333 K respectively in 0.1 M sulphamic acid.

The values of the energy of activation ' $E_a$ ' have been calculated from the slopes of plots of  $\log \zeta$  versus  $1/T$  ( $\zeta$  = corrosion rate,  $T$  = absolute temperature) (Fig. 1) and also with the help of the Arrhenius equation.<sup>9, 10</sup>

$$\log \zeta_2/\zeta_1 = E_a/2.303[(1/T_1) - (1/T_2)] \quad (1)$$

where  $\zeta_1$  and  $\zeta_2$  are the corrosion rates at temperatures  $T_1$  and  $T_2$  (K) respectively.

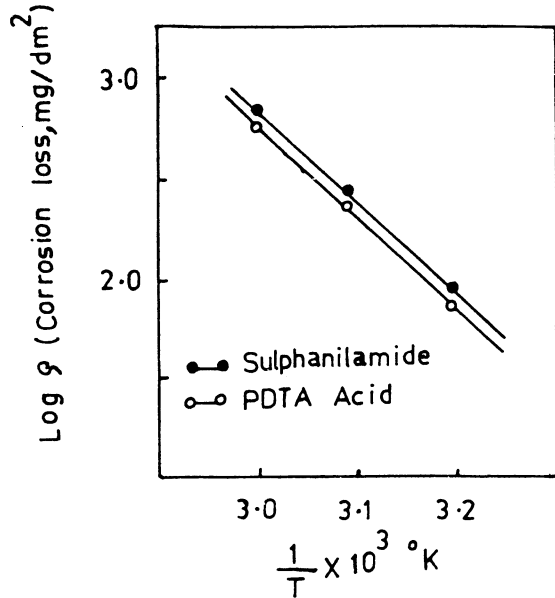


Fig. 1. Arrhenius plots for corrosion of zinc in 0.1 M sulphamic acid in presence of 5 mM inhibitor concentration

The  $E_a$  values, given in Table-2 show that the energy of activation for the corrosion of zinc in 0.1 M sulphamic acid is *ca.* 58.4 kJ mol<sup>-1</sup>. In acid containing 5 mM inhibitors, the  $E_a$  values are found to be higher, *i.e.*, 87.7 kJ mol<sup>-1</sup> for sulphanilamide and 86.5 kJ mol<sup>-1</sup> for phenyl diamine tetraacetic acid. The almost similar value of  $E_a$  for both the inhibitors (within  $\pm 2$  kJ mol<sup>-1</sup>) suggest that the inhibitors are similar in their mechanism of action.<sup>11</sup>

The values of heat of adsorption,  $Q_{ads}$ ,<sup>9</sup> and free energy of adsorption,  $\Delta G^0$ ,<sup>12</sup> were calculated from the equation

$$Q = 2.303R \left( \log \frac{\theta_2}{1 - \theta_2} - \log \frac{\theta_1}{1 - \theta_1} \right) \left( \frac{T_1 \times T_2}{T_2 - T_1} \right) \quad (2)$$

where,  $\theta_1$  and  $\theta_2$  are the fractions of the metal surface covered by the inhibitors at temperatures  $T_1$  and  $T_2$  respectively.

$$\log C = \log \{ \theta / (1 - \theta) \} - \log B \quad (3)$$

where  $\log B = -1.74 - (\Delta G^0 / 2.303 RT)$  and  $C$  is the inhibitor concentration.

Table-2 indicates that 'Q' values are negative in all cases and range from  $-43.2$  to  $-108.1$   $\text{kJ mol}^{-1}$ . The negative Q values show that the adsorption and hence the inhibition efficiency decrease with rise in temperature.

The mean values of  $\Delta G_a^0$  given in Table-2 are negative, *i.e.*,  $-9.9$   $\text{kJ mol}^{-1}$  for sulphanilamide and  $-9.8$   $\text{kJ mol}^{-1}$  for phenyl diamine tetraacetic acid.

### Polarization behaviour

Anodic and cathodic galvanostatic polarization curves for zinc in 0.1 M sulphamic acid, alone and containing 5 mM concentration of both the inhibitors are shown in Fig. 2. The curves show polarization of both, the anodes as well as

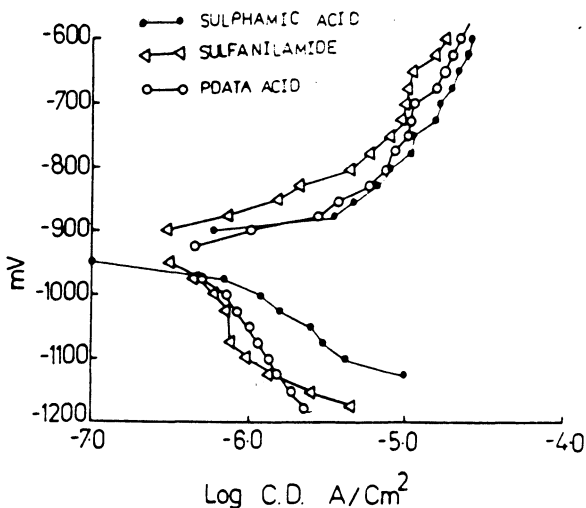
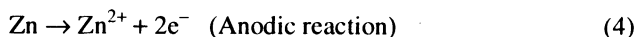


Fig. 2. Polarisation curves for corrosion of zinc in 0.1 M sulphamic acid in absence and presence of inhibitors.

cathodes. Inhibitive efficiency, calculated from corrosion currents obtained by extrapolation of the Tafel lines, are also given in Table-3. In almost all the cases, the Tafel plot efficiency agrees well (within  $\pm 5\%$ ) with the values obtained from weight loss data.

### Mechanism of corrosion

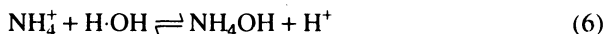
Zinc dissolved in sulphamic acid is shown by eq. (4).



Sulphamic acid acts as a strong acid which may hydrolyse in aqueous media as shown by the following equation:



$\text{NH}_4^+$  may on further hydrolysis gives  $\text{H}^+$  ions in solution by the following reactions:



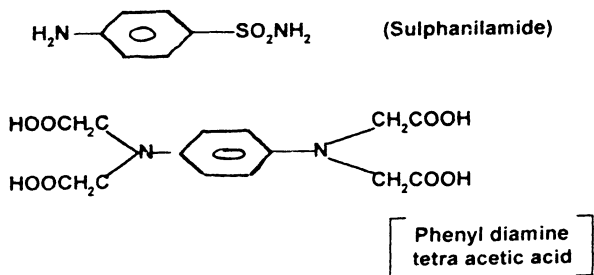
Different cathodic reactions can also occur simultaneously on a corroding surface as shown below:



or



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. It appears that nitrogen atom of amino group ( $-\text{NH}_2$ ) in sulphanilamide acts as the reaction centre (polar function) because of its higher electron density. This reaction centre forms a monolayer on the zinc surface. Moreover, sulphanilamide assumes a small positive charge in acid solution due to protonation of amino group; higher electron density of the N-atom facilitates the protonation. The increase in protonation may be responsible for the enhancement of inhibition efficiency. Structures of both the inhibitors are as follows:



Further, when  $\log \theta/(1 - \theta)$  is plotted against  $\log C$  straight lines are obtained in case of sulphanilamide and phenyl diamine tetraacetic acid (Fig. 3). This suggests that the inhibitors cover both anodic as well as cathodic regions through general adsorption following Langmuir isotherm.

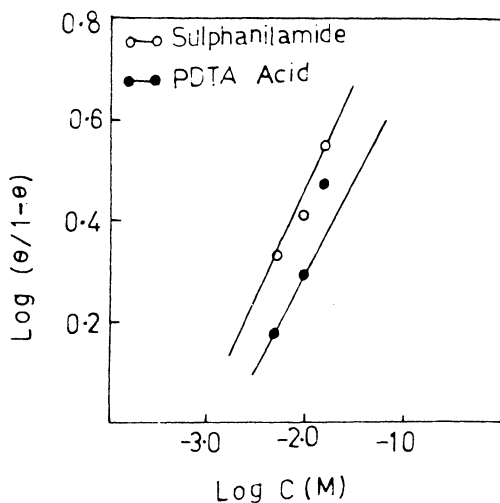


Fig. 3. Plot of  $\log (\theta/1 - \theta)$  versus  $\log C$  for inhibitors in 0.1 M sulphamic acid.

### ACKNOWLEDGEMENTS

Authors are very much thankful to Department of Chemistry, Navyug Science College, Surat for providing laboratory facilities.

### REFERENCES

1. L.L. Shreir, Corrosion, George Newnes Ltd., London, p. 37 (1983).
2. N.I. Sax and R.J. Lewis, Harvey's Condensed Chemical Dictionary, Eleventh edn., CBS Publ., Delhi, p. 1104 (1990).
3. S.A. Rajkumar, Encyclopaedia Dictionary of Chemistry, Anmol Publ., New Delhi, Vol. 1, p. 264 (1990).
4. M.N. Desai and S.T. Desai, *J. Electrochem. Soc., India*, **32**, 397 (1983).
5. H.F. Crotty, U.S. Pat. 3/325/410; *Chem. Abstr.*, **68**, 5773 (1961).
6. B. Water, Ger. Pat. 2/405; *Chem. Abstr.*, **82**, 76842 (1975).
7. E.G. Stroud, *J. Appl. Chem.*, **1**, 93 (1951).
8. J.D. Talati and D.K. Gandhi, *Indian J. Technol.*, **29**, 277 (1991).
9. N. Subramanian and K. Ramkrishna, *Indian J. Tech.*, **8**, 369 (1970).
10. R.A. Alberty, Physical Chemistry, 7th ed., John Wiley and Sons, New York, p. 694 (1987).
11. I.N. Putilova, V.P. Barannik and S.A. Balezin, *Metallic Corrosion Inhibitors*, Pergamon, Oxford, pp. 30-32 (1960).
12. A.M.S. Abdel and A. El-Saied, *Trans. SAEST*, **16**, 197 (1981).

(Received: 28 August 1997; Accept.ed: 27 October 1997)

AJC-1379