# INHIBITION OF ACID CORROSION OF MILD STEEL WITH 1,3-DIAMINOPROPANE

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# **Abstract**

The influence of 1,3-diaminopropane on corrosion inhibition of mild steel in 1N HNO<sub>3</sub> and 1N H<sub>2</sub>SO<sub>4</sub> has been studied using weight loss study and galvanostatic polarization study. Galvanostatic study indicates that compound act as mixed type corrosion inhibitor. The rate of corrosion of mild steel rapidly increases with temperature over the temperature range of 298K to 328K both in absence and presence of inhibitor. Thermodynamic parameters for adsorption process have been calculated using the Langmuir's adsorption isotherm.

Key words: Corrosion, Inhibition, 1,3-diaminopropane, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>.

## 1. Introduction

Corrosion is a type of surface chemical process in which metallic material is lost as oxides, hydrids and carbonates due to its direct chemical, biochemical and electrochemical reactions with environment. There are several ways to prevent atmospheric corrosion. Among the available methods of preventing corrosion, the use of inhibitor is the most promising method particularly for closed systems. The inhibitors find wide application in the industrial field. Most of the organic compounds that mainly contain nitrogen, sulpher atom and multiple bonds in the molecules is act as inhibitor. The inhibition by organic additives on metals in acids has been studied [1-12]. The selection of an inhibitor for a given system depends on the corrosive medium, the nature of metal, the magnitude of charge at metal solution interface and the cathodic relation [13]. The aim of present investigation is to examine the inhibitive action of 1,3-diaminopropane towards the corrosion of mild steel in both acid solutions (1N HNO<sub>3</sub> and1N H<sub>2</sub>SO<sub>4</sub>) by chemical and electrochemical technique.

# 2. Experimental

The mild steel coupons of composition(C=0.20%, Mn=1.00%, Si=0.05%, S=0.025%, P=0.25% and Fe=98%) and of size (i.e. 0.8×0.8×3.0 cms) have been used for weight loss measurements. These coupons were given mechanical polishing and then degreased before use. Weight loss study was carried out as described in literature [14]. The inhibition efficiency for different concentrations of inhibitor was calculated from weight loss values. For polarization studies a cylindrical mild steel rod of it composition embedded ion araldite was used. The electrodes were polished with emery papers and degreased. AR grade of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> acids were used for preparing solutions. Double distilled water was used to prepare all solutions. For accurate measurements of potential and current densities, galvanostatic polarization studies were carried out at different temperatures. A platinum foil and saturated calomel electrode were used as counter and reference electrode respectively. Polarization was carried out in 1N

HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in the absence and presence of inhibitor of various concentrations and temperatures.

#### 3. Results and Discussion

## 3.1 Weight loss measurements

Tables 1 & 2 give the values of inhibition efficiencies for different concentrations of 1,3-diaminopropane in 1N HNO $_3$  and 1N H $_2$ SO $_4$  obtained from weight loss measurements. The percentage inhibition were calculated using the following equation

$$I\% = \frac{Wo - Wi}{Wo} \times 100$$

where Wo and Wi are weight losses in the absence and in the presence of inhibitor respectively. The results in Table 1 & 2 show that the inhibition efficiency increases with increasing the concentration of inhibitor in both acids at lower temperature. As the temperature increases the inhibition efficiency decreases. The inhibition efficiency is some much higher i.e. 90.66% in case of  $H_2SO_4$  acid in presence of  $10^{-1}M$  concentration at 298K temperature.

# 3.2. Galvanostatic polarization measurements

Table 3 & 4 give the electrochemical parameters such as corrosion potential (E<sub>corr</sub>), Tafel's slopes (b<sub>a</sub> and b<sub>c</sub>), corrosion current (i<sub>corr</sub>) and inhibition efficiency (I%) for corrosion of mild steel in 1N HNO<sub>3</sub> and 1N H<sub>2</sub>SO<sub>4</sub> in absence and presence of 1,3-diaminopropane inhibitor in different concentrations and temperatures. Figures 1 to 4 show the effect of compound concentration on the current potential curves for both the cathodic and anodic reactions at different temperatures in 1N HNO<sub>3</sub>. The potential curves for the same temperature and concentration in 1N H<sub>2</sub>SO<sub>4</sub> acid medium are shown in Figs. 5 to 8. As the concentration increases there is an increase in the values of both the Tafel's slopes in both the acid. The value of Tafel's slopes (cathodic and anodic) is more in case of 1N H<sub>2</sub>SO<sub>4</sub> in comparison to 1N HNO<sub>3</sub>. But in 1N H<sub>2</sub>SO<sub>4</sub> the values of cathodic Tafel's slope is larger than anodic values. So inhibition of corrosion of mild steel

in 1N H<sub>2</sub>SO<sub>4</sub> acid is under mixed control but predominately under anodic control. The percentage inhibition curve of 1,3- diaminopropane on mild steel in 1N H<sub>2</sub>SO<sub>4</sub> solution shows that the corrosion inhibition efficiency reached about 90% with solution containing 10<sup>-1</sup>M inhibition whereas at the lower concentration (10<sup>-1</sup> M), the percentage inhibition was about 55.33% at temperature 298K. The percentage inhibition of 1,3-diaminopropane in 1N HNO<sub>3</sub> is about 87% having concentration 10<sup>-1</sup>M while at lower concentration 10<sup>-7</sup>M the percentage inhibition was about 66.1% at 298K temperature. At lower concentration the inhibition efficiency is more in case of 1N HNO<sub>3</sub> at all temperatures except 318K. The value of I<sub>corr</sub> is found to be little more in case of lowest concentrations of compound in both the acids. As the concentration increases there is decrease in the values of I<sub>corr</sub>. The inhibition efficiency of 1,3-diaminopropane depends on many factors including number of adsorption active center in the molecule and their charge density, which are affected by amino (-NH2) group. The values of inhibition efficiency obtained by weight loss method and galvanostatic polarization studies show fairly good agreement in both acids. It is also found that compound performs better in 1N H<sub>2</sub>SO<sub>4</sub> acid.

# 3.3. Adsorption Kinetics

From polarization measurements, surface coverage  $\theta$  values have been obtained for various concentration of inhibitor. The data were tested graphically for fitting a suitable adsorption isotherm. A straight line is obtained by plotting a graph between log  $\theta/1$ -  $\theta$  vs. 1/T in both the acids (Figs 9&10). This clearly proves that the adsorption of 1,3-diaminopropane on mild steel surface from both the acids obey Langumir's adsorption isotherm.

To calculate the activation energy of corrosion process, corrosion current densities at various temperatures in the absence and presence of various concentrations of inhibitor were put in Arrhenius equation.

$$\log K = \log A - \frac{E_a}{2.303RT}$$

where K is the specific corrosion rate constant,  $E_a$  is the activation energy, T is absolute temperature and A is the exponential factor. Plotting of log K against 1/T in absence and presence of inhibitor give straight line as shown in Figs.11&12. The activation energy is calculated from this graph. The activation energy is 72.18 Kcal/mol in 1N HNO<sub>3</sub> solution while it is 74.11Kcal/mol in case of  $H_2SO_4$ . The results show that the rate of corrosion increases as the temperature increases. This indicates that corrosion inhibition takes place by adsorption of inhibitor at electrode surface.

## 4. Conclusion

- 1,3-diaminopropane inhibits the corrosion of mild steel in both the acids (1N HNO<sub>3</sub> and 1N H<sub>2</sub>SO<sub>4</sub>).
- 2. The performance of this compound as an inhibitor in both the acid is very much encouraging.
- The inhibition efficiency increases with increase in concentration in both the acid.
- 4. The inhibition efficiency decrease with increase in temperature in both the acids.
- 5. The inhibition of corrosion of mild steel by 1,3-diaminopropane in both the acids is of mixed type.
- 6. The adsorption of 1,3-diaminopropane on mild steel surfaces from both the acids obey Langumir's adsorption isotherm.

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# **Caption of Figures**

- 1. Galvanostatic polarization curves of mild steel in 1N HNO<sub>3</sub> solution containing different concentrations of 1,3-diaminopropane at 298K.
- 2. Galvanostatic polarization curves of mild steel in 1N HNO<sub>3</sub> solution containing different concentrations of 1,3-diaminopropane at 308K.
- 3. Galvanostatic polarization curves of mild steel in 1N HNO<sub>3</sub> solution containing different concentrations of 1,3-diaminopropane at 318K.
- 4. Galvanostatic polarization curves of mild steel in 1N HNO<sub>3</sub> solution containing different concentrations of 1,3-diaminopropane at 328K.
- 5. Galvanostatic polarization curves of mild steel in 1N H<sub>2</sub>SO<sub>4</sub> solution containing different concentrations of DAP at 298K.
- 6. Galvanostatic polarization curves of mild steel in 1N H<sub>2</sub>SO<sub>4</sub> solution containing different concentrations of DAP at 308K.
- 7. Galvanostatic polarization curves of mild steel in 1N H<sub>2</sub>SO<sub>4</sub> solution containing different concentrations of DAP at 318K.
- 8. Galvanostatic polarization curves of mild steel in 1N H<sub>2</sub>SO<sub>4</sub> solution containing different concentration of DAP at 328K.
- 9. Variation of surface coverage vs. concentration at different temperatures of DAP in 1N HNO<sub>3</sub>.
- 10. Variation of surface coverage vs. concentration at different temperatures of DAP in 1N H<sub>2</sub>SO<sub>4</sub>.
- 11. Variation of corrosion current vs. reciprocal of temperature at different concentrations of DAP in 1N HNO<sub>3</sub>.
- 12. Variation of corrosion current vs. reciprocal of temperature at different concentrations of DAP in  $1N\ H_2SO_4$ .



Table1:

Inhibition efficiency of mild steel in presence of different concentrations of 1-3-diaminopropane from weight loss at various temperatures in 1N HNO<sub>3</sub>

Temperature	Solution/mol (L <sup>-1</sup> )	Weight loss/gram	%I	
298K	1N HNO <sub>3</sub>	0.5701	-	
	$10^{-7}$	0.1385	75.7	
	$10^{-5}$	0.1450	74.5	
	$10^{-3}$	0.1440	74.7	
	$10^{-1}$	0.0698	87.7	
308K	1N HNO <sub>3</sub>	0.8900	_	
	$10^{-7}$	0.5100	42.6	
	$10^{-5}$	0.3400	61.7	
	$10^{-3}$	0.2300	74.1	
	$10^{-1}$	0.1700	80.8	
318K	$1N HNO_3$	0.8350	-	
	$10^{-7}$	0.4280	48.7	
	$10^{-5}$	0.3320	60.2	
	$10^{-3}$	0.2550	69.4	
	$10^{-1}$	0.2050	75.4	
328K	1N HNO <sub>3</sub>	0.7500	-	
	$10^{-7}$	0.6000	20.0	
	$10^{-5}$	0.5300	29.3	
	$10^{-3}$	0.3400	54.6	
	$10^{-1}$	0.3000	60.0	



Table2: Inhibition efficiency of mild steel in presence of different concentrations of 1-3-diaminopropane from weight loss at various temperatures in  $1N\ H_2SO_4$ 

Temperature	Solution/mol (L <sup>-1</sup> )	Weight loss/gram	%I	
298K	1N H <sub>2</sub> SO <sub>4</sub>	0.0786	_	
	$10^{-7}$	0.0384	56.10	
	$10^{-5}$	0.0275	65.01	
	$10^{-3}$	0.0231	70.61	
	$10^{-1}$	0.0074	90.58	
308K	$1N H_2SO_4$	0.1568	-	
	$10^{-7}$	0.0728	53.57	
	$10^{-5}$	0.0658	58.03	
	$10^{-3}$	0.0518	66.96	
	$10^{-1}$	0.0189	87.94	
318K	$1N H_2SO_4$	0.5467	-	
	$10^{-7}$	0.3091	43.46	
	$10^{-5}$	0.2394	56.20	
	$10^{-3}$	0.2075	62.04	
	$10^{-1}$	0.1374	74.86	
328K	$1N H_2SO_4$	1.1891	-	
	$10^{-7}$	0.9105	23.42	
	$10^{-5}$	0.6113	48.59	
	$10^{-3}$	0.5913	50.27	
	$10^{-1}$	0.4692	60.54	

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Table 3: Electrochemical parameters of mild steel in 1N HNO<sub>3</sub> in presence of 1,3-diaminopropane as additive

Temp.	Solution/mol (L <sup>-1</sup> )	E <sub>corr</sub> mV	Log i <sub>corr</sub> μA/cm <sup>2</sup>	b <sub>c</sub> mV/dec	b <sub>a</sub> mV/dec	%I
298K	1N HNO <sub>3</sub>	410	3.57	29	40	-
	$10^{-7}$	451	3.10	21	29	66.1
	$10^{-5}$	439	2.99	30	32	73.6
	$10^{-3}$	390	2.80	20	20	83.0
	$10^{-1}$	407	2.68	75	45	87.1
308K	1N HNO <sub>3</sub>	474	3.40	21	22	-
	$10^{-7}$	427	3.06	18	18	54.2
	$10^{-5}$	437	3.04	16	17	56.3
	$10^{-3}$	420	2.88	13	20	69.8
	$10^{-1}$	442	2.59	22	24	84.5
318K	1N HNO <sub>3</sub>	478	3.39	28	28	-
	$10^{-7}$	451	3.19	14	16	36.9
	$10^{-5}$	431	3.00	16	16	59.2
	$10^{-3}$	420	2.90	20	20	67.6
	$10^{-1}$	450	2.80	25	20	74.2
328K	$1N HNO_3$	493	3.37	20	11	-
	$10^{-7}$	442	3.19	17	16	33.9
	$10^{-5}$	441	3.09	12	12	47.5
	$10^{-3}$	457	3.01	18	08	56.3
	10 <sup>-1</sup>	440	2.90	31	32	66.1

Table 4: Electrochemical parameters of Mild Steel in  $1N\ H_2SO_4$  in presence of 1,3-diaminopropane (DAP) as additive:

Temp.	$\begin{array}{c} Solution/mol\\ (L^{-1}) \end{array}$	$\begin{array}{c} E_{corr} \\ mV \end{array}$	Log i <sub>corr</sub> μA/cm <sup>2</sup>	b <sub>c</sub> mV/dec	b <sub>a</sub> mV/dec	% I
298K	1N H <sub>2</sub> SO <sub>4</sub>	512	3.45	99	141	-
	$10^{-7}$	471	3.10	53	72	55.33
	$10^{-5}$	453	3.00	36	97	64.51
	$10^{-3}$	481	2.90	36	52	71.81
	$10^{-1}$	483	2.42	163	297	90.66
308K	$1N H_2SO_4$	522	3.38	111	151	=
	$10^{-7}$	478	3.05	59	72	53.22
	$10^{-5}$	481	3.00	49	48	58.31
	$10^{-3}$	472	2.89	49	73	67.59
	$10^{-1}$	485	2.48	123	170	87.41
318K	$1N H_2SO_4$	500	3.35	75	73	-
	$10^{-7}$	480	3.10	50	59	43.76
	$10^{-5}$	464	2.98	30	78	57.34
	$10^{-3}$	470	2.93	30	71	61.98
	$10^{-1}$	470	2.75	55	121	74.88
328K	$1N H_2SO_4$	480	3.29	41	93	-
	10 <sup>-7</sup>	471	3.17	46	32	24.14
	$10^{-5}$	470	3.00	50	39	48.71
	$10^{-3}$	472	2.99	47	88	49.88
	$10^{-1}$	476	2.89	35	59	60.18



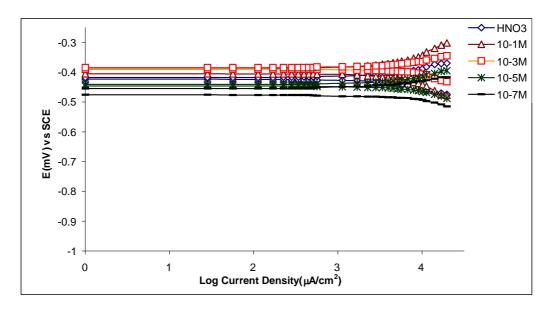


Fig. 1. Galvanostatic polarization curves of mild steel in 1N HNO<sub>3</sub> containing different concentrations of 1,3-diaminopropane at 298K.

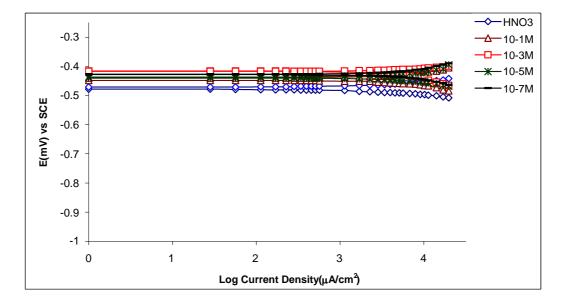


Fig. 2. Galvanostatic polarization curves of mild steel in 1N HNO<sub>3</sub> solution containing different concentrations of 1,3-diaminopropane at 308K.

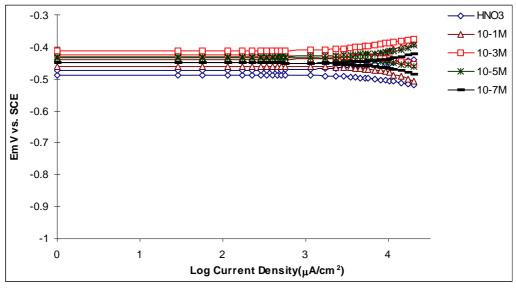


Fig. 3. Galvanostatic polarization curves of mild steel in 1N HNO<sub>3</sub> solution containing different concentrations of 1,3-diaminopropane at 318K.

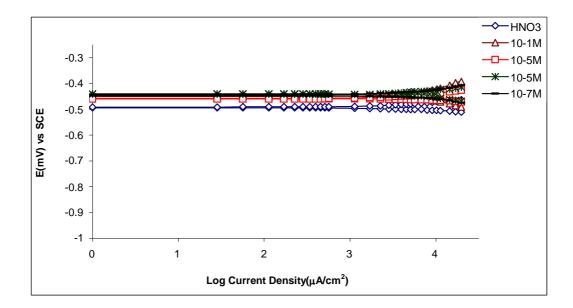


Fig. 4. Galvanostatic polarization curves of mild steel in 1N HNO<sub>3</sub> solution containing different concentrations of 1,3-diaminopropane at 328K.

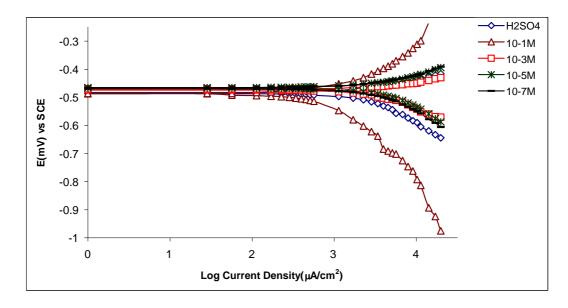


Fig. 5. Galvanostatic polarization curves of mild steel in 1N H<sub>2</sub>SO<sub>4</sub> solution containing different concentrations of DAP at 298K.

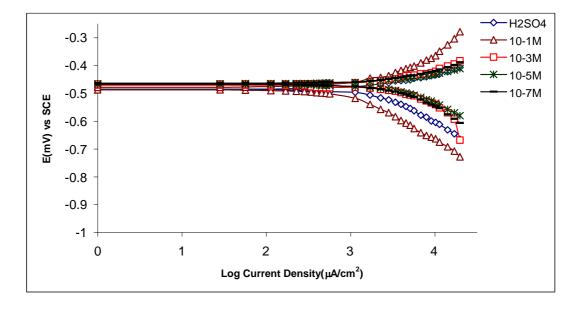


Fig.6. Galvanostatic polarization curves of mild steel in 1N H<sub>2</sub>SO<sub>4</sub> solution containing different concentrations of DAP at 308K.



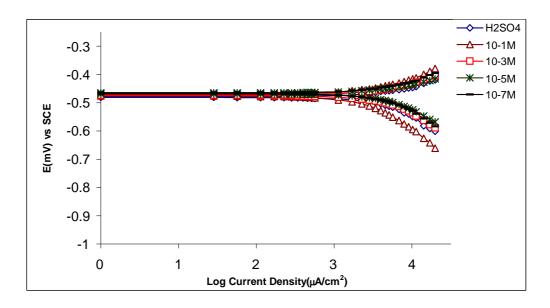


Fig. 7. Galvanostatic polarization curves of mild steel in 1N H<sub>2</sub>SO<sub>4</sub> solution containing different concentrations of DAP at 318K.

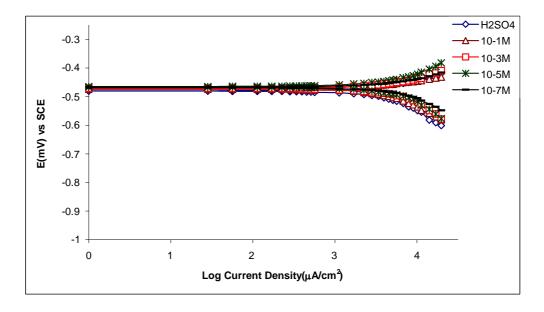


Fig. 8. Galvanostatic polarization curves of mild steel in 1N H<sub>2</sub>SO<sub>4</sub> solution containing different concentration of DAP at 328K.



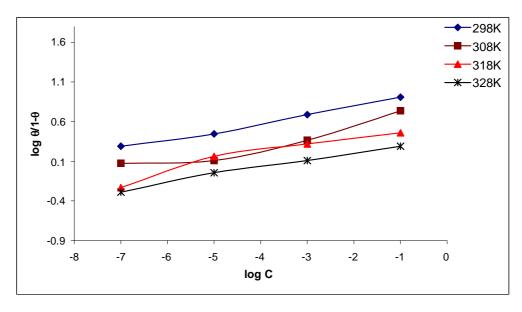


Fig. 9. Variation of surface coverage vs concentration at different temperatures of DAP in 1N HNO<sub>3</sub>.

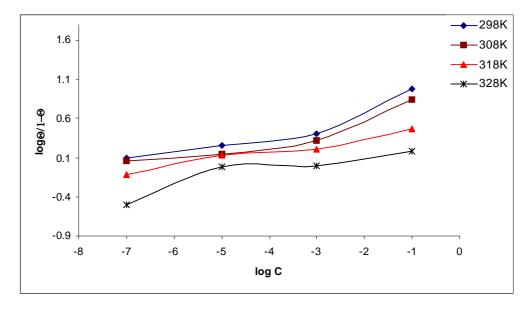


Fig.10. Variation of surface coverage vs. concentration at different temperatures of DAP in 1N H<sub>2</sub>SO<sub>4</sub>.

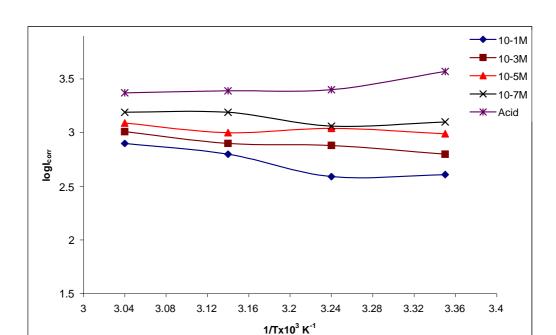


Fig. 11. Variation of corrosion current vs. reciprocal of temperature at different concentrations of DAP in 1N HNO<sub>3</sub>

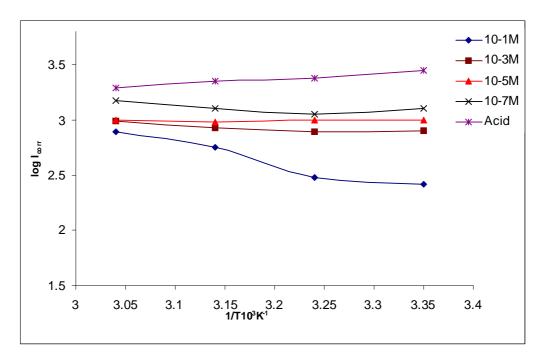


Fig.12. Variation of corrosion current vs. reciprocal of temperature at different concentrations of DAP in  $1N\ H_2SO_4$ .