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Aromatic Amines as Corrosion Inhibitors for Zinc in Hydrochloric Acid

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ABSTRACT

The inhibition of corrosion of zinc in hydrochloric acid by aromatic amines like, aniline, o- toluidine, m- toluidine, p- toluidine and p- chloroaniline has been studied with respect to inhibitor concentration and temperature. The inhibition efficiency of aromatic amines increased as the concentration of the inhibitor increased, while decreased with the increase in concentration of the acid and temperature. Weight loss data at different temperatures was used to determine activation energy. The activation energies in inhibited acid are higher than that in plain acid. For all inhibitors, the heat of adsorption (ΔH_{ads}) and free energy of adsorption are negative. The plot of log (θ/1-θ) versus log C results in a straight line, suggest that, the inhibitors appears to function through adsorption following Langmuir isotherm. Galvanostatic polarization curves show polarization of both anodes as well as cathodes.

Keywords: Corrosion, Zinc, Hydrochloric Acid, Aromatic Amine.

INTRODUCTION

Corrosion resistance property of zinc is so important that nearly half the worlds annual consumption of the metal is used to protect steel from rusting. Due to various industrial applications and economic importance of zinc, its protection against corrosion attracted much attention. Acid and alkaline solution, both adversely affect the corrosion behavior of zinc, the corrosion being more sever at P^H values below 6 and above 12.5[1] . Hydrochloric acid is a strong inorganic acid that is used in many industrial processes. Aliphatic, aromatic and heterocyclic amines have been extensively investigated as corrosion inhibitor[2-7]. According to Hackerman et al[8], the percentage of π-orbital of free electron on the nitrogen atom of secondary aliphatic and cyclic amines controls the inhibitive properties of these compounds in acid media. The efficiency of few Schiff bases as corrosion inhibitor [9-10] has also been reported.

In the present work, the effect of aromatic amines like aniline, o-toluidine, m-toluidine, p- toluidine and p-chloroaniline as corrosion inhibitor for zinc in hydrochloric acid has been reported.

EXPERIMENTAL SECTION

To study the corrosion of zinc in hydrochloric acid methods such as weight loss and polarization have been used.

Rectangular specimens (5.25cm x 2.50cm x 0.2 cm) of 99.90% pure zinc with a small hole of about 3 mm diameter just near one end of the specimen have been used. The specimens were polished by buffing, cleaned with distilled water several times, then degreased by acetone and dried by air drier. Each specimen was suspended to the same depth using pyrex glass hook. The volume of corrosive solution taken was 200 ml for all experiment. Only one specimen was suspended in a pyrex beaker of 250 ml capacity. The weight loss experiment were carried out in various concentration of hydrochloric acid with and without inhibitors of different concentration (5 to 25 mM) at temperature 302 ± 1 k, for 24 hours. To study the effect of temperature on corrosion of zinc, the weight loss experiment was carried out in 0.025 N hydrochloric acid at different temperature, for an immersion period of 3 hours with and without inhibitor. After the test, the specimen were cleaned by 10% chromic acid solution having 0.2% $BaCO_3$[11]. After cleaning, the test specimens were washed with distilled water followed by acetone and dried by air drier. The mean value of weight loss was reported as mdd. All the chemicals used were of A. R. grade. The corrosive solution was prepared in double distilled water. From the data, I. E. (%), energy of activation (E_a), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG_a) were calculated.

For polarization study, metal specimens having an area of 1 cm^2 were immersed in 200 ml corrosive solution with and without 25 mM inhibitor concentration in 0.01 N hydrochloric acid. The test cell include the metal specimen as a working electrode, corrosive solution in which the specimen was to be tested and saturated calomel electrode (SCE) as a reference electrode as well as platinum electrode as an auxiliary electrode. The polarization study was made by using Potentio – Galvano – Scan meter. Polarization curves were plotted with potential against log current density (called Tafel plot). Cathodic and anodic polarization curves give cathodic and anodic Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines gives the corrosion current (I_{corr}) and the corrosion potential (E_{corr})[12].

RESULTS AND DISCUSSION

To study the effect of inhibitor concentration on inhibition efficiency of the inhibitor, weight loss were determined in 0.01, 0.025, and 0.050 N hydrochloric acid, containing various concentrations of inhibitor at 29 ± 1 °C for exposure period of 24 hours. The inhibition efficiency (IE%) was calculated as follows:

$$IE\% = \left(\frac{w_u - w_i}{w_i}\right) \times 100 \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_(1)}$$

Where, Wu = weight loss in uninhibited acid and,
Wi = weight loss in inhibited acid.

The results given in table-1, show that the specimen of zinc immersed in plain acid suffers a weight loss of 307.33, 609.88, and 1157.41 mdd in 0.01 N, 0.025 N and 0.050 N HCl respectively.

The results show that for all the three concentrations of the acid, the concentration of the inhibitor is increased the weight loss due to corrosion decreases. The order of efficiency of the different inhibitor at 25 mM concentrations is found to be:

(a) In 0.01 N HCl :

p- chloroaniline (98.45 %) > p-toluidine (97.45 %) > o-touidine (85.48 %) > m- toluidine (83.04 %) >aniline (80.82 %)

(b) In 0.025 N HCl :

p-chloroaniline (93.46%) > p-toluidine (91.17 %) > o-toluidine (84.08 %) > m-toluidine (80.06 %) > aniline (71.23 %)

(c) In 0.05 N HCl :

m-toluidine(71.213 %) > p-toluidine (70.21 %) > aniline (64.53 %)> o-toluidine (59.91 %) p-chloroaniline (44.16 %)

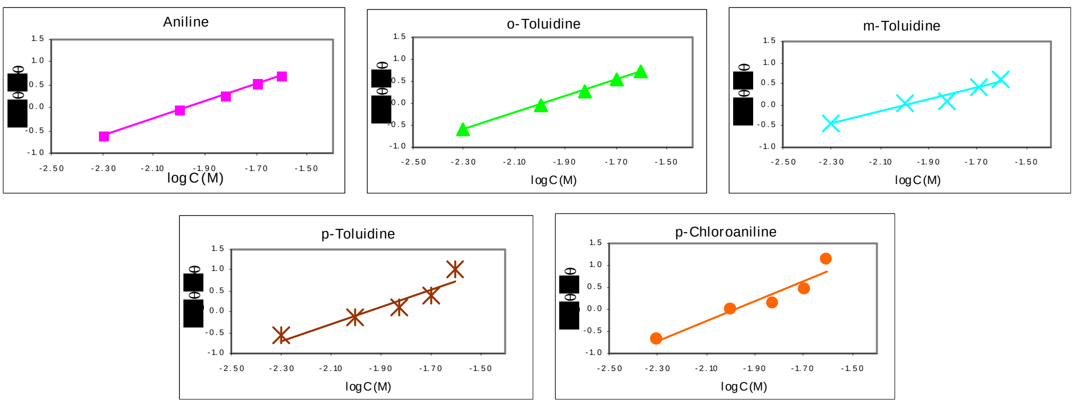

fig. 1: Langmuir Adsorption Isotherm for Corrosion of Zinc in 0.025N HCl solution containing Aromatic Amines.

Table 1 : **Weight Loss Data for Corrosion of Zinc in Hydrochloric Acid Solution: Effect of Aromatic Amines.**

Surface area of specimen : 29.35 cm^2 Temperature: 29 ± 1°C
Immersion period: 24 hrs

Acid concentration		0.01 N		0.025 N		0.050 N	
Inhibitor and its concentration in mM		**Corrosion rate (mdd)**	**Inhibition Efficiency (IE%)**	**Corrosion rate (mdd)**	**Inhibition Efficiency (IE%)**	**Corrosion rate (mdd)**	**Inhibition Efficiency (%)**
Blank		307.33		609.88		1157.4100	
Aniline	**5**	133.56	56.54	491.9900	19.3296	1021.4700	11.75
	10	112.10	63.53	445.6558	26.9274	962.8600	16.81
	15	79.39	74.17	247.0187	59.4972	856.2200	26.02
	20	62.35	79.71	177.1700	70.9500	681.4300	41.12
	25	58.94	80.82	175.4700	71.2300	410.5600	64.53
o-Toluidine	**5**	114.14	62.86	486.5400	20.2200	1009.2000	12.8
	10	96.42	68.63	318.2283	47.8200	912.4400	21.17
	15	69.85	77.27	207.5000	65.9800	875.3000	24.37
	20	50.09	83.70	133.1976	78.1600	745.8300	35.56
	25	44.63	85.48	97.1000	84.0800	464.0500	59.91
m-Toluidine	**5**	122.32	60.20	443.2700	27.3200	1056.9000	8.68
	10	93.01	69.73	288.9300	52.6300	865.7600	25.2
	15	66.10	78.49	271.5500	55.4700	825.8900	28.64
	20	55.88	81.82	164.9063	72.9600	613.9700	46.92
	25	52.13	83.04	121.6400	80.0600	333.2200	71.21
p-Toluidine	**5**	106.98	65.19	481.4300	21.0600	1046.3400	9.5967
	10	78.02	74.61	356.3900	41.5600	987.3900	14.69
	15	31.01	89.91	271.8900	55.4200	814.3100	29.64
	20	9.20	97.01	173.7600	71.5100	613.2700	46.95
	25	7.84	97.45	53.8300	91.1700	344.8000	70.21
p-Chloroaniline	**5**	58.26	81.04	503.9200	17.3700	1066.4400	7.86
	10	42.59	86.14	305.9600	49.8300	982.6200	15.1
	15	32.71	89.35	251.7900	58.7200	925.0400	20.08
	20	7.50	97.56	152.6400	74.9700	819.7600	29.17
	25	4.77	98.45	39.8600	93.4600	646.3400	44.16

When the plot of log (θ/1- θ) versus log C (θ = fraction of the metal surface covered by the inhibitor, C = inhibitor concentration) were drawn, straight lines were obtained (fig.-1).This suggests that the inhibitors get adsorbed on the metal surface following Langmuir adsorption isotherm[13].

To study the effect of temperature on inhibitor efficiency, corrosion rate were determined in 0.025 N hydrochloric acid, plain as well as inhibited solution at temperature of 303, 313 and 323 K.

Energy of activation (E_a) has been calculated with the help of Arrhenius equation[13].

$$\log \frac{\rho_2}{\rho_1} = \frac{A}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (2)$$

Where, ρ_1 and ρ_2 are the corrosion rate (in mdd) at temperature T_1 and T_2 K respectively.

The values of the apparent energy of activation, E_a were also calculated from the slope of log ρ versus 1/T K following the Arrhenius equation,

$\rho = A\ e^{-Ea/RT}$

The values given in the table -2 show that the E_a values are low (8.3467 K Cal. $Mole^{-1}$) in uninhibited acid whereas in inhibited acid they are higher. The higher value of activation energy (E_a) in the presence of inhibitor as compared to the activation energy in the absence of inhibitor in hydrochloric acid indicates that the inhibitor induces the energy barrier for the corrosion reaction, which leads to the decreasing the rate of corrosion of zinc in presence of inhibitor. The activation energy in inhibited acid is ranging from 9.5380 K Cal. $mole^{-1}$ to 19.3638 K Cal. $mole^{-1}$, which indicates that the inhibitors are adsorbed physically. According to O. K. Aiola, B. B. Damaskin [14,15], the value of activation energy less than 19.12 K Cal. $mole^{-1}$ (80 K J $mole^{-1}$) and even smaller than 1.19 K Cal. $mole^{-1}$ (5 K J. $mole^{-1}$) represents physical adsorption.

The value of heat of adsorption (Q_{ads}) were calculated from the following equation[16].

$$Q_{ads} = 2.303R\left[\mathrm{Log}\left(\frac{\theta_2}{1-\theta_2}\right) - \mathrm{Log}\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left[\left(\frac{T_1 T_2}{T_2 - T_1}\right)\right] \qquad \text{\_\_\_\_\_\_\_\_(3)}$$

Where, θ_1 and θ_2 [θ = Wu – Wi / Wi] are the fraction of the metal surface covered by the inhibitors at temperature T_1 and T_2 K respectively.

The value of the free energy of adsorption (ΔG_a) was calculated with the help of the following equation[17].

$$\mathrm{Log}\,C = \mathrm{Log}\left(\frac{\theta}{1-\theta}\right) - \mathrm{Log}\,B \qquad \text{\_\_\_\_\_\_\_\_(4)}$$

Where, $\mathrm{Log}\,B = -1.74 - \left(\frac{\Delta G^o_{ads}}{2.303RT}\right)$ and C is the inhibitor concentration (in mM)

The values given in table -2 show that in all the cases, the corrosion rate increases with temperature. However, the efficiency of inhibitors decreases.

Table 2: **Effect of Tempreature on Corrosion Rate (mdd), Inhibition Efficiency (IE%), Energy of Activation (E), heat of adsorption (Qads) and free energy of adsorption (ΔG_{ads}) for zinc in 0.025 N hydrochloric acid containing Aromatic Amines as inhibitor.**

Surface area of specimen : 29.35 cm^2 Immersion period :3 hours

Inhibitor and its concentration in mM		Temperature (K) 303K		313K		323K		Energy of Activation (E) K Cal. $mole^{-1}$		Heat of Adsorption Qads, K.cal.$mole^{-1}$		Free Energy Of Adsorption ?G°A r K.cal.$mole^{-1}$
		CR	IE	CR	IE	CR	IE	Mean Ea from eq.	E from Arhenius Plot	303-313 K	313-323 K	Mean
Blank		534.24		703.24		1237.48		8.2675	8.3467			
Aniline	5	160.82	69.90	392.50	44.19	1163.88	5.95	19.3284	19.6675	-20.278	-50.772	-5.318
	25	54.51	89.80	81.77	88.37	144.46	88.32	9.5380	9.6839	-2.775	-0.098	-6.077
o-Toluidine	5	158.09	70.41	444.29	36.82	812.27	34.36	15.7990	16.2629	-26.516	-2.157	-5.712
	25	46.34	91.33	73.59	89.53	190.80	84.58	13.9301	14.0632	-3.931	-8.921	-6.069
m-Toluidine	5	174.45	67.35	267.12	62.02	637.82	48.46	12.7590	12.8825	-4.404	-11.091	-6.022
	25	32.71	93.88	65.42	90.69	160.82	87.00	15.5684	15.8258	-8.559	-7.543	-6.214
p-Toluidine	5	149.91	71.94	305.28	56.59	1076.66	12.99	19.3638	19.5910	-12.748	-43.539	-5.625
	25	32.71	93.88	51.79	92.64	125.38	89.87	13.2129	13.3520	-0.674	-7.028	-6.295
p-Chloro aniline	5	166.27	68.88	264.40	62.40	1038.50	16.08	18.1150	18.2035	-5.427	-43.377	-5.698
	25	29.98	94.39	59.97	91.47	158.09	87.22	16.2717	16.5214	-8.490	-9.079	-6.256

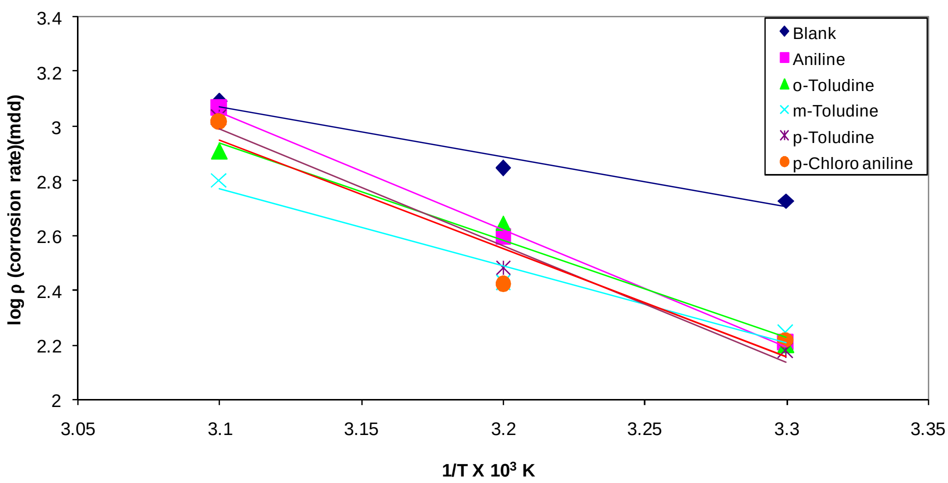

fig 2 Arrhenius Plot for Corrosion of Zinc in 0.025N HCl in Absence and Presence of 5mM of Aromatic Amines.

From the values given in table-2 it is evident that for all the five inhibitors the heat of adsorption and free energy of activation are negative. This suggest that there is a strong interaction of the inhibitor molecules with the metal surface[18], forming a highly adherent film[19]. The lower ΔG_{ads} value in this case further confirms physical adsorption.

Galvanostatic, cathodic and anodic polarization measurements were carried out in 0.01 N HCl solution, in presence and absence of aniline, o-toluidine, m-toluidine, p-toluidine and p-chloroaniline. In 0.01 N HCl solution the values of I_{corr}, Tafel parameters β_a and β_c obtained in presence and absence of aromatic amines, presented in table -3.

Table 3: Tafel Parameters and Inhibition Efficiency (IE%) for Zinc in 0.01 N Hydrochloric Acid Solution containing Aromatic Amines.

Surface area of specimen : 1 cm^2 Temperature : 25°C
Inhibitor Concentration : 25 Mm

Inhibitor	Open circuit potential (mV)	Corrosion current density I_{corr} ($\mu A/cm^2$)	Tafel slope (V/decade)		Inhibition effeciency (IE%) Calculated from	
			Cathodic β_c	Anodic β_a	Polarization method	Weight loss method
Blank	-1030.00	53.50	220.70	109.70		
Aniline	-997.60	13.00	472.90	55.60	75.70	80.82
o-Toluidine	-1005.00	9.91	210.30	58.70	81.48	85.48
m-Toluidine	-993.10	12.20	353.90	52.80	77.20	83.04
p-Toluidine	-1004.00	0.94	100.60	43.60	98.24	97.45
p-Chloro aniline	-985.20	3.09	110.90	80.60	94.22	98.45

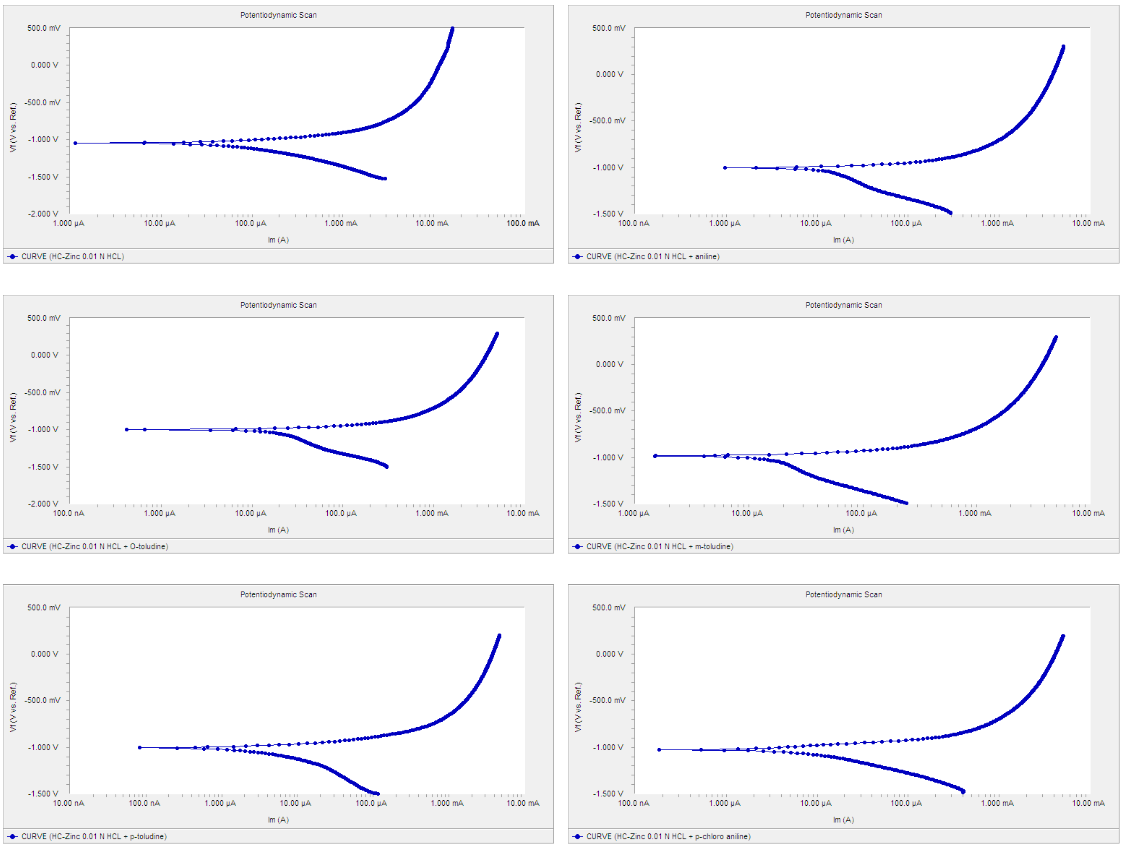

Fig 3 Polarisation Curves for Corrosion of Zinc in 0.01N HCl containing 25 mM Inhibitor Concentration

In 0.01 N HCl solution, the value of I_{corr} obtained by Tafel extrapolation was 53.50 $\mu A/cm^2$ and the β_c and β_a values were 220.70 and 109.70 V/decade respectively. I_{corr} values in presence of aromatic amines have narrow variation but more deviation from that in plain acid. The inhibitor adsorption shifted the corrosion potential E_{corr}, with respect to the blank, but this shift is not more than 85 mV. According to Riggs and others, the classification of a compound as an anodic or cathodic inhibitor is feasible when the potential displacement is at least 85 mV in relation to that measured for the blank solution. So it can be said that the inhibitor are mixed type inhibitor.

Mechanism of Corrosion Inhibition

As evident from the results, the higher inhibition efficiency (IE) at different concentration of aromatic amines can be attributed to the presence of nitrogen atom of amino group (-NH_2). Nitrogen atom in aromatic amines acts as the reaction centre, because of its higher electron density. This reaction centre terms and the same trend is maintained even at higher environment concentrations. The higher electron density of the nitrogen atom facilitates the protonation, the successive increase in protonation may also be responsible for the enhancement of the inhibition efficiency (I.E.).

In aniline, the lone pair present in nitrogen atom is delocalized with benzene ring by resonance, so aniline is weaker base than the primary aliphatic amine, which does not happen in aliphatic amines.

In case of para isomer of toluidine, higher inhibition efficiency is observed. This behavior may be mainly due to position of methyl group which act as electron repelling group and provides more electron density to the nitrogen atom present on the ring and therefore increased electron density on the N atom results in higher inhibition action.

Methyl group present on meta and ortho isomer have a steric hindrance as nitrogen atom has been adsorbed on the metallic surface and this explains the lower inhibition power of the substance compared to p-toluidine.

High efficiency of P-chloroaniline may be attributed to the presense of –Cl group in the vicinity of nitrogen atom of amino group (-NH_2) on the aromatic nucleus. Presence of the chloro (-Cl) group increase the electron charge cloud density on amino group and this increased electron density is responsible for the enhancement of inhibition efficiency (I.E.) of the compound.

CONCLUSION

From the results of the study, the following conclusion may be drawn:
1. The corrosion rate of zinc increase with increase in acid concentration.
2. The extent of inhibition increases with the increase in concentration of inhibitors.
3. All the aromatic amine provides protection through physical adsorption.
4. The change in anodic and cathodic Tafel values in the presence of aliphatic amines indicate their effect on both anodic and cathodic process, however, somewhat less anodic polarization, but greater cathodic polarization occur in plain as well as in inhibited acid, suggest that the inhibitors function by general adsorption at cathodic as well as anodic regions of the metal surface.
5. There was good agreement in the value of inhibition efficiency calculated using polarization technique and weight loss data.

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