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Corrosion Behaviour of Mild-Steel in Binary Acid (HCl+H₂SO₄) Mixture in Presence of Aniline & its Derivatives

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ABSTRACT: Corrosion behaviour of mild-steel in binary acid (HCl+H₂SO₄) mixture have been examined using conventional weight-loss and thermometric techniques in presence of aniline and its derivatives. viz, o-anisidine, o-chloroaniline, o-nitroaniline and aniline. All These inhibitors obey Langmuir Adsorption Isotherm equation (i) Reaction Number(RN), (ii) temperature difference as well as (iii) time to reach T_{max} were calculated by thermometric technique. Inhibition efficiency determined from the result of weight-loss and thermometric techniques are in good agreement for all the compounds used in the binary acid mixture. The mode of inhibitive action appears to be chemisorption. Aniline and its derivatives can be arrange in the following order of efficiency in inhibiting corrosion of mild-steel. o-Anisidine > o-Chloro aniline > o-Nitroaniline > Aniline. Presence of -OCH₃ group in o-Anisidine, Cl⁻ in o-Chloroaniline, -NO₂ group in o-Nitroaniline can be considered responsible for the higher ability of these compounds to provide protection against corrosive action of binary acid mixtures studied.

KEYWORDS : Reaction Number (RN), Inductive Effect, Resonance States, Chemisorption.

I. INTRODUCTION

Annual losses due to corrosion in many developed countries are about 4% their GNP and estimate under Indian context puts this loss to about 24,000 crore per annum, which is colossal figure. Leakage of pipe-lines, distress in bridges and structures, leakage of valves etc. may either be due to the faulty corrosion resistance of mild-steel. The awareness of corrosion its periodic monitoring, timely detection followed by maintenance and repairs is very important especially for buildings, structures and plants which are in contact with inflammable toxic chemicals. Proper corrosion control can save loss to the order of 20,000 crore or more and industrial accident can be averted^[1]. Iron and ferrous alloys have been extensively used under different conditions in chemical and allied industries in handling alkalies, acids and salt solutions. Mild-steel is one major material of construction, which is extensively used in such situations^[2]. Corrosion behaviour of mild-steel in sulphuric acid in presence of simple amines was investigated by the polarization, electrochemical impedance spectroscopy(EIS) and X-ray photoelectron spectroscopy (XPS)^[3]. Mylius thermometric technique has been successfully used to study the effect of some Schiff bases and moreover the data has been treated mathematically^[4-5]. New synthesized Guanidine Derivative as a Green corrosion inhibitor for mild-steel in acidic solutions^[6]. Inhibition of the corrosion of mild-steel in H₂SO₄ by Penicillin-G has been discussed by Eddy N.O. *et al.*^[7]. Metol(N-methyl p-amino phenol sulphate) as corrosion inhibitor for steel.(mild-steel in HCl & H₂SO₄) has been reported by Pravin B.N *et al.*^[8]. Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors^[9-11]. Vashi *et al.* studied ethanolamines¹² and ethylamines¹³ as corrosion inhibitors for zinc in phosphoric acid. Hexamine was reported as effective corrosion inhibitor for various metals in acid.^[14-16]. Corrosion behaviour of brass in binary acid mixture by thermometric technique has been investigated by Oza and others^[17]. Vashi *et al.* studied Aniline as Corrosion Inhibitor for Zinc in Hydrochloric Acid^[19], “ Corrosion Inhibition of Aluminium in Hydrochloric Acid by Lawsonia intermis Leaves Extract ”^[20]. N. I. Prajapati studied “Cuminum Cyminum (Jeera) seed extract as an Efficient Inhibitor for Aluminium Corrosion in 0.75 M Hydrochloric Acid ”^[21]. Here corrosion behaviour of mild-steel in binary acid mixture (HCl+H₂SO₄) and inhibitive power of aniline and its derivatives have been examined.



II. EXPERIMENTAL

Weight loss measurement

The corrosion rate of mild-steel having the composition S = 0.05%, P = 0.02%, Mn = 0.7%, C = 0.27%, Si = 0.35%, was studied in binary acid mixture in presence of aniline and its derivatives using weight-loss technique. Inhibitor efficiencies were determined from weight-loss measurements using standard expressions [18]. The concentration of mixed acid studied was (3.0 M HCl + 3.0 M H₂SO₄).

Thermometric technique

For the purpose of thermometric study, the specimens of the 2.5 x 1.0 x 0.2 (l,b,t)cm were immersed in 20 ml of corrosive solution. Temperature rise recorded was not significant with lower concentrations of hydrochloric acid and hence the tests were carried out in binary acid mixture (3.0 M HCl + 3.0 M H₂SO₄) in absence and presence of 1,5,10 and 25mM of aniline and its derivatives. Digital temperature recorder with 0.01 °C precision was used in Dewar's flask thermometer bulb and the test specimens were completely immersed in the test solution. Changes in temperature were recorded at the successive intervals of five minutes. The results were used to calculate reaction number (RN) and inhibition efficiency (IE%) as under,

$$RN = \frac{T_{(max)} - T_{(i)}}{t} \quad \longrightarrow \quad (1)$$

where, T_(max) and T_(i) are the maximum and initial temperature respectively and 't' is the time in minutes in the experiments to attain T_(max).

The inhibition efficiency was calculated as,

$$IE \% = \frac{RN_{(b)} - RN_{(inh)}}{RN_{(b)}} \times 100 \quad \longrightarrow \quad (2)$$

Where, RN_(b) and RN_(inh) are the reaction numbers in blank and inhibited system respectively. Results are presented in table 2 and Fig. 1.

Table 1. Influence of different concentrations of aniline and its derivatives on corrosion rate (mdd), inhibition efficiency (IE%) and surface coverage(θ) of mild steel in mixed acid (3.0 M HCl +3.0 M H₂SO₄) solution

Specimen area : 30.70 sq.cm

Immersion period : 1 hr.

Density : 7.86 Kgm/m³

Temperature : 27 ± 1 °C

Inhibitor and its concentration (C) (mM)	Corrosion rate (mdd) x 10 ² (mgm/dm ² day)	Inhibition Efficiency (IE%)	Surface coverage(θ)	Log (θ/1- θ)
Blank	212.87	-	-	-
1.o-Anisidine 1	101.3	52.36	0.5236	0.0409
5	69.2	67.46	0.6746	0.3166
10	59.3	72.12	0.7212	0.4127
25	43.8	79.39	0.7939	0.5856
2.o-Nitroaniline 1	109.9	48.36	0.4836	-0.0285
5	73.8	65.29	0.6529	0.2743
10	62.6	70.54	0.7054	0.3792
25	48.3	77.30	0.7730	0.5321
3.o-Chloroaniline 1	114.5	46.19	0.4619	-0.0663
5	80.7	62.06	0.6206	0.2137
10	68.7	67.62	0.6762	0.3197



		25	52.6	75.24	0.7524	0.4826
4.Aniline	1		133.5	37.23	0.3723	-0.2268
		5	108.1	49.17	0.4917	-0.0144
	10	25	99.0	53.47	0.5347	0.0603
			85.0	60.04	0.6004	0.1768

Fig.1 : Reaction Number(RN) as a function of inhibitor concentration (log C) for mild-steel in mixed acid (3.0 M HCl+3.0 M H₂SO₄) solution containing aniline and its derivatives.

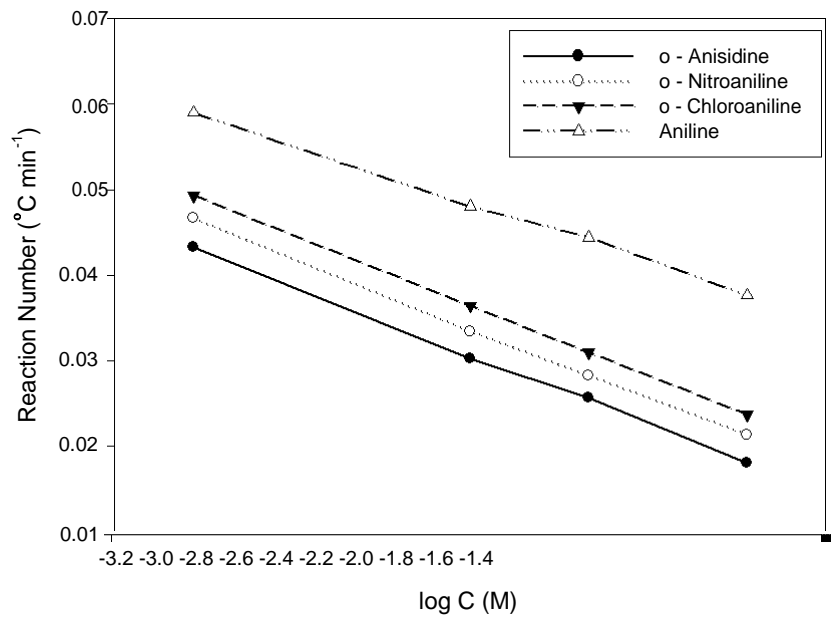


Fig.2 : Langmuir adsorption isotherms for corrosion of mild-steel in binary acid (3.0 M HCl+3.0 M H₂SO₄) mixture containing aniline and its derivatives.

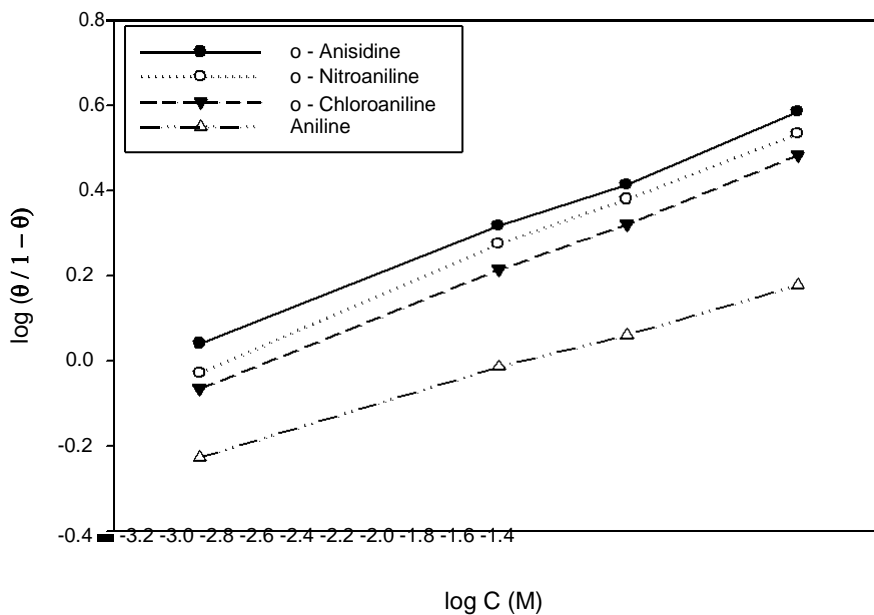




Table 2. Influence of aniline and its derivatives on temperature difference (ΔT), time to reach T_{max} , reaction number (RN) and inhibition efficiency (IE%) during corrosion of mild-steel in mixed acid (3.0 M HCl + 3.0 M H_2SO_4) solution.

Specimen area : 3.2 cm²

Temperature: 26.4 °C.

Inhibitor and its concentration (C) (mM)	Temperature Difference (ΔT) °C	Time to reach T_{max} (Δt) min.	Reaction number (RN) ° C Min ⁻¹	Inhibition Efficiency (IE%) calculated from	
				Thermometric method	Weightloss method
Blank	14.8	160	0.0925	--	--
1.o-Anisidine	1	10.6	245	0.0432	53.29
	5	8.0	265	0.0302	67.35
	10	7.3	285	0.0256	72.32
	25	5.6	310	0.0180	80.54
2.o-Nitroaniline	1	11.2	240	0.0466	49.62
	5	8.7	260	0.0334	63.89
	10	7.9	280	0.0282	69.51
	25	6.4	300	0.0213	76.97
3.o-Chloroaniline	1	11.6	235	0.0493	46.70
	5	9.1	250	0.0364	60.65
	10	8.5	275	0.0309	66.59
	25	7.0	295	0.0237	74.38
4.Aniline	1	13.0	220	0.0590	36.21
	5	11.3	235	0.0480	48.10
	10	11.1	250	0.0444	52.00
	25	9.8	260	0.0376	59.35

III. RESULTS AND DISCUSSIONS

Data on corrosion rate, inhibition efficiency and surface coverage during static immersion of mild-steel in binary acid mixture (3.0 M HCl + 3.0 M H_2SO_4) are presented in Table 1.

The results presented in Fig.1 and in Table 2 indicate successive decrease in reaction number (RN) and temperature difference (ΔT) which suggest decrease in corrosion rate in presence of aniline and its derivatives. This decrease in RN and ΔT can be correlated with inhibitive action of the compounds studied. Decreases in RN with addition of the inhibitors suggest adsorption of the compound on the corroding surface. Decrease in ΔT also indicates the effect of the added compounds. It is clear from the curves that the behaviour is characterised by an initial period during which the temperature remains constant or varies very slightly. This part of the curves can be described as incubation period in which pre-immersion oxide film protects the metal from acid attack or an induction period representing the breakdown of the film and start of attack. Inhibition efficiency can be arrived at by knowing the extent to which reaction number is affected. Variation in delay time as a function of log molar concentration has resulted in parabolic curves which indicates that all the compounds form chemisorbed monolayer protective film on the corroding surface. Similar conclusion can be drawn from the plots of RN Vs log C. However, adsorption may be of weak type since the time necessary to reach T_{max} clearly establishes good amount of inhibition particularly when higher inhibitor concentrations were employed.

It is seen from the results that corrosion rate in general decreases with increase in inhibitor concentration. o-Anisidine, provided somewhat better protection which may be due to presence of electron repelling methoxy group on the benzene ring which in turn might have increased electron density on nitrogen atom. In o-chloroaniline, substitution of electron attracting Cl^- group increases the contribution of the positively charged resonance state of aniline. This increases its adsorbability at the surface of mild-steel in contrast to ring substituted methyl aniline. In case of o-nitroaniline, the introduction of electron withdrawing $-NO_2$ group (especially in the ortho position) has remarkably increased the inhibitive efficiency because of the additional reaction centre established by N and O atoms of $-NO_2$ group. **Chemisorption of the additives is shown by linearity of $\log(0/1-0)$ Vs. log C (plot Fig.-2)**



From the results presented in Table-2, it is evident that thermometric technique can be satisfactorily employed to study corrosion behaviour of mild-steel in binary acid mixture in absence and presence of aniline and its derivatives.

IV. CONCLUSION

- 1) Linearity of the plot of $\log (\theta/1-\theta)$ Vs. $\log C$ (inhibitor concentration) in presence of all the organic compounds suggests that they function through adsorption by Langmuir isotherm.
- 2) The order of inhibition efficiency is observed to be o-anisidine > o-chloroaniline > o-nitroaniline > aniline.
- 3) Thermometric technique is simple and quick. However, it is found more useful when reactions are highly exothermic i.e. particularly in more aggressive acid solution.
- 4) Inhibition efficiency results obtained with thermometric technique are in fair agreement with those obtained with weight-loss method.
- 5) Variation in delay time as a function of log molar concentration has resulted in parabolic curves indicating that all the compounds form chemisorbed monolayer protective film on the corroding surface.

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