STUDY OF ANILINE AND ITS DERIVATIVES AS A CORROSION INHIBITORS IN HYDROCHLORIC ACID SOLUTION

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ABSTRACT

Corrosion is a multi-billion dollar, world-wide problem and the current knowledge of corrosion and corrosion prevention is never adequate and there is a persistent need for further research to complement technical developments. Mild steel is frequently used as a construction material in different industries due to its low cost and high mechanical strength. However, corrosion data are less readily available in many of these environments. The main purpose of this study is to examine effect of acid, strength and additive concentrations on the corrosion resistance of mild-steel. In this study, weight-loss and thermometric techniques have been employed.

Key words: Hydrochloric acid, aniline derivatives, Weight-loss Measurements, Thermometric Measurements

INTRODUCTION

Corrosion behaviour of mild-steel in plain hydrochloric acids has been reported since long. The main purpose of this study is to examine the effect of - (i) acid concentration, (ii) additive concentration on the corrosion resistance of mild-steel, and (iii) mechanism of protective action. For the purpose of study - conventional weight-loss method and thermometric techniques were employed.

Corrosion is a natural phenomenon, which degrades the metallic properties of metal/alloys and renders them to be rejected from the specific structures of industrial importance. Country like India suffers very much in its economical growth due to the destructive phenomena of corrosion because of the tropical climate. The problem of corrosion is very serious in various industries because of the losses that occur due to shut-down and failures of industrial operations are of the colossal properties. Most common constructional of the structural metallic material steel is effectively an alloy of iron and carbon with minor incidental elements like silicon, manganese, sulphur and phosphorous.

However, it is prone to corrosion in aqueous environment, especially acidic solution, which is usually involved in industrial exercises such as acid pickling, industrial acid cleaning, acid descaling and oil well acidizing processes[1,2]. Heterocyclic compounds have been reported as effective corrosion inhibitors because they can easily adsorb on metallic surface via their π- and non-bonding electrons, aromatic rings and polar functional groups, which act as adsorption centers[3,4,5,6,7,8,9].

EXPERIMENTAL

(1) Weight-loss Measurements:

Mild-steel with the composition of S-0.05%, P-0.02%, Mn-0.70%, C-0.27%, Si-0.35% is used. For complete immersion test the test specimens of size 5.5 cms x 2.5 cms x 0.2 cms were completely immersed in 250 ml of corrosive electrolyte solution. The concentration of plain hydrochloric acid solution studied were 0.1 M, 0.5 M, 1.0 M and 2.0 M. The effect of different concentrations (1, 5, 10 and 25 mM) of substituted derivatives i.e. p-toluidine, o-toluidine, p-chloroaniline, o-chloroaniline, aniline, p-nitroaniline and m-nitroaniline were

studied to understand the corrosion behaviour in presence of these compounds. The immersion period was ranging from 60 minutes to 24 hours in different acid concentrations. Total immersion tests were carried out at 30°C with and without aniline and its derivatives. All the chemicals used were of Analytical Reagents (A.R) grade. From the results of weight-loss measurements - (i) corrosion rate (mdd), (ii) inhibition efficiency (IE%), (iii) surface coverage (θ) were calculated.

(2) Thermometric Measurements:

Test specimen of size 2.5 cms x 1.0 cm x 0.2 cm was immersed in 20 ml of acid solution for the thermometric study. The test were carried out in the concentration of 1.0 M and 2.0 M acid solutions, using 1, 5, 10 and 25 mM of aniline and its derivatives. Digital thermometer with 0.01°C precision was used in Dewar flask. The changes in temperature were recorded at the regular interval of time. The results were used to calculate reaction number (RN) and inhibition efficiency (IE%).

RESULTS:

Weight-loss Measurements:

Corrosion behaviour of mild-steel in hydrochloric acid solution at different concentration were studied by weight-loss measurements. It has been observed that the corrosion rate increases with increase in the acid concentration. The corrosion rate increases from 603.25 mdd (0.1 M HCl) to 120.23×10^2 mdd (2.0 M HCl). The values of corrosion rate (mdd) and inhibition efficiency (IE%) for the inhibitors were calculated and reported in tables-1.

Addition of aniline and its derivatives reduces the corrosion rate.

The value of surface coverage was calculated directly from percentage inhibition efficiency by weight-loss method.

Thermometric Measurements:

Results of thermometric technique are presented in tables-2. It can be seen from the data that time to reach maximum temperature (T_{max}) has increased gradually and the temperature difference (ΔT) of the system has gradually decreased with increase in additive concentration.

The plots of time (minute) versus temperature (°C) are given in figures-1 and 3 and reaction number (°C min^{-1}) versus log C (M) is given in figures-2 and 4. Table 2 also include the comparison of inhibition efficiency arrived by thermometric and weight-loss method.

DISCUSSION:

Corrosion in hydrochloric acid solution is of great importance in many chemical processes. The present work was carried out in different concentrations of hydrochloric acid. As it is evident from the result presented that there was considerably low corrosion rate in lower concentration of acid solution and the corrosion rate gets increased with increase in acid concentration. It has already been established that at higher concentration of acid solution, corrosion behaviour of mild-steel can be considered to be predominantly chemical in nature. The dissolution rate for steel in various acids depends on the surface finish of the steel, type and concentration of the acid, temperature and the presence or absence of

impurities that can either promote or inhibit corrosion. Generally, the corrosion rate of mild-steel in hydrochloric acid increases with increase in acid concentration.

Decrease in corrosion rate with increase in additive concentration may be attributed to the decrease in the transport of oxygen and other reducible species which otherwise affect cathodic reaction adversely. At lower concentration, adsorbed layer of the additive may be incomplete. Inhibitive action of aniline and its derivatives on the dissolution character of ferrous material can be attributed to interaction between the additive and the metal surface. Though that may be the first stage of inhibition process. These aniline and its derivatives might have formed a bond with metal and the molecule might have been chemisorbed at the metal surface.

The results presented in tables-1 and 2 and figures-2 and 4 indicate successive decrease in reaction number (RN) and temperature difference (ΔT). Which suggest decrease in corrosion rate in presence of aniline and its derivatives. Higher reaction number (RN) in plain acid solution suggests dissolution of mild-steel. Decrease in reaction number (RN) with increase in aniline and its derivatives concentration suggest adsorption of the compound on the corroding surface. Furthermore, temperature difference (ΔT) values also decrease which suggest inhibition in presence of the additives used. The extent of inhibition depends on the degree of the coverage of the metal surface with the adsorbate. It can be said that when inhibitor is added, induction period is increased. It can also be

concluded that strongly adsorbed inhibitors caused increase in time to reach T_{max}. Inhibitor efficiency can be very well judged by knowing the extent to which reaction number (RN) is affected. It is clear from the figures-2 and 4, that the curves are characterized by an initial period during which the temperature remain constant or varies vary slightly. The 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 suggests time required the break-down of the film and start of attack. Plots of reaction number (RN) versus log C give straight lines indicating the fact that all the compounds used form chemisorbed monolayer protective film on the corroding surface.

The narrow difference in percentage inhibition on comparison of thermo- metric data with weight-loss measurements established the usefulness of this method.

Generally, inhibition efficiency of aniline can be correlated to its basic character by virtue of the amino group. In acid solutions, nitrogen atom of the amino group with its lone pair of electrons neutralizes acidic character of corrosive solutions to some extent and this is responsible for the corrosion inhibiting behaviour of aniline.

Introduction of a nitro group into the aniline molecule reduces its efficiency as an inhibitor. This could be due to the electron withdrawing tendency of the nitro group which weakens the basic nature of the parent compound as is evident from their pKb values. Among the nitro derivatives of aniline examined, p-nitroaniline was found to be a relatively

better corrosion inhibitor than m-nitroaniline. Presence of nitro group at meta-position to the amino group in the case of m-nitroaniline retards its portion not only due to electron withdrawing tendency but also due to steric hinderance. In p-nitroaniline steric hinderance is much reduced due to the greater separation of the amino group and nitro groups, undergoes protonation relatively easily and thereby neutralizing a greater amount of the acid than its meta isomer. P-Nitroaniline is hence more effective as an inhibitor compared to m-nitroaniline and its inhibition efficiency increases with increase in concentration.

Introduction of chlorine atom into aniline molecule was found to improve its inhibition efficiency. As is known, that any factor that enhances the basic character of aniline boosts its ability to reduce the concentration of the corroding acid through neutralization and promotes its inhibitive capacity. The trend observed for the chloro derivatives of anilines were thus as expected. Chlorine with its (+) I-inductive effect enable the enhancement of electron density over the amino nitrogen atom of aniline and thereby increasing its basic character.

The different isomeric toluidines viz. o-toluidine and p-toluidine showed a trend similar to what as observed for the corresponding chloroanilines. Toluidines were found to be more efficient inhibitors compared to the chloroanilines under similar experimental conditions. This was expected considering the greater electron donating tendency [(+) I-inductive effect] of methyl group with respect to that of the chlorine atom in chloroanilines. The following order of corrosion inhibition

capacity in acidic media was observed for the isomeric toluidines:

p-toluidine > o-toluidine > p-chloroaniline > o-chloroaniline > aniline >p-nitroaniline > m-nitroaniline.

CONCLUSION:

From the above discussion, the following conclusions can be drawn:

(1)   The corrosion rate of mild-steel increases with increase in acid concentration. The behaviour is predominantly chemical in nature.

(2)   The corrosion rates are affected by nature of complex reaction taking place and also by the nature of the protective film.

(3)   The extent of inhibition by aniline derivatives increases with the increase in concentration of additives.

(4)   p-toluidine is found more effective compared to other organic additives.

(5)   The order of inhibition efficiency the compounds examined can be given as under:
p-toluidine > o-toluidine > p-chloroaniline > o-chloroaniline > aniline >
p-nitroaniline > m-nitroaniline.

(6)   Linearity of the plots of log (θ/1-θ) versus log C in presence of all the organic compounds suggests that they function through adsorption which can be explained using Langmuir isotherm model.

(7)   Somewhat less anodic polarization, but more cathodic polarization in inhibited acid suggests that these compounds function through general adsorption at cathodic as

well as anodic region of the metal surface.

(8) There was good agreement in the value of inhibition efficiency calculated using polarization technique and thermometric results.

(9) Reaction number (RN) drops to a considerable extent and time to reach T_{max} gets prolonged in presence of the all inhibitor studied.

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TABLE- 1: **Influence of different concentration of aniline and its derivatives on corrosion rate (mdd), inhibition efficiency (IE%) and surface coverage (θ) of mild-steel in 2.0 M HCl solution.**   Specimen area : 30.70 sq.cm.   Immersion period : 1 hr.

Temperature : $30 \pm 1^{\circ}$C

Inhibitor and its concentration (mM)	Corrosion Rate (mdd) (mgm/dm^2/day)	Inhibition Efficiency (IE%)	Surface Coverage (θ)	Log (θ/1-θ)
Blank	12023.45	-	-	-
1. p-Toluidine 1	6340.06	47.24	0.4724	-0.0479
5	5573.94	53.61	0.5361	0.0628
10	5269.05	56.12	0.5612	0.1068
25	4792.18	60.08	0.6008	0.1775
2. o-Toluidine 1	6973.28	41.98	0.4198	-0.1405
5	6058.62	49.57	0.4957	-0.0079
10	6575.57	52.79	0.5279	0.0485
25	5136.15	57.23	0.5723	0.1264
3. p-Chloroaniline 1	7637.78	36.42	0.3642	-0.2419
5	6762.21	43.71	0.4371	-0.1098
10	6363.51	47.05	0.4705	-0.0513
25	5863.19	51.18	0.5118	0.0205
4. o-Chloroaniline 1	8302.28	30.89	0.3089	-0.3497
5	7356.35	38.81	0.3881	-0.1977
10	6918.56	42.42	0.4242	-0.1327
25	6355.70	47.13	0.4713	-0.0499
5. Aniline 1	8990.22	25.22	0.2522	-0.4720
5	8044.29	33.07	0.3307	-0.3061
10	7614.33	36.61	0.3661	-0.2384
25	7051.46	41.32	0.4132	-0.1532
6. p-Nitroaniline 1	9357.65	22.14	0.2214	-0.5461
5	8677.52	27.78	0.2778	-0.4149
10	8302.28	30.91	0.3091	-0.3493
25	7911.40	34.16	0.3416	-0.2849
7. m-Nitroaniline 1	9834.52	18.17	0.1817	-0.6535
5	9201.30	23.45	0.2345	-0.5138
10	8935.50	25.66	0.2566	-0.4619
25	8544.62	28.88	0.2888	-0.3913

TABLE- 2 :   Influence of aniline and its derivatives on temperature difference (ΔT), time to reach maximum temperature (Δt), reaction number (RN) and inhibition efficiency (IE%) during corrosion of mild-steel in 2.0 M HCl solution.

Surface area of specimen : 3.2 sq.cm.   Temperature : $30 \pm 1°C$

Inhibitor and its concentration (mM)	Temp. difference T_{max} (ΔT) °C	Time to reach (Δt) Min.	Reaction number (RN) °C Min^{-1}	Inhibition Efficiency (IE%) calculated from	
				Thermo-metric method	Weight-loss method
Blank	26.3	150	0.1754	-	-
1. p-Toluidine 1	19.8	215	0.0925	47.26	47.24
5	17.8	220	0.0812	53.70	53.67
10	17.6	230	0.0766	56.33	56.31
25	16.8	240	0.0700	60.10	60.09
2. o-Toluidine 1	21.3	210	0.1015	42.13	42.12
5	19.1	215	0.0889	49.53	49.30
10	18.5	225	0.0824	53.02	52.67
25	17.2	230	0.0749	57.30	57.28
3. p-Chloroaniline 1	22.3	200	0.1115	36.43	36.41
5	20.6	210	0.0984	43.90	43.87
10	19.9	215	0.0927	47.14	47.13
25	18.8	220	0.0855	51.25	51.25
4. o-Chloroaniline 1	22.9	190	0.1204	31.36	31.33
5	21.3	200	0.1066	39.22	39.20
10	20.5	205	0.1004	42.75	42.74
25	19.1	210	0.0912	48.00	47.96
5. Aniline 1	23.5	180	0.1304	25.66	25.61
5	22.2	190	0.1171	33.24	33.22
10	21.6	195	0.1110	36.72	36.67
25	20.6	200	0.1033	41.11	41.05
6. p-Nitroaniline 1	23.7	175	0.1355	22.75	22.71
5	22.6	180	0.1255	28.45	28.42
10	22.8	190	0.1201	31.53	31.50
25	22.3	195	0.1146	34.66	34.62
7. m-Nitroaniline 1	24.2	170	0.1428	18.59	18.53
5	23.4	175	0.1342	23.49	23.48
10	23.9	185	0.1297	26.05	26.00
25	23.5	190	0.1242	29.19	29.15