



Corrosion Combating Effect of Some Nitrogen Containing Inhibitors on Mild Steel in Trichloroacetic Acid

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Abstract:

Mass loss method has been used to study the corrosion inhibition of Mild Steel in Trichloroacetic acid solution by two newly synthesised Corrosion Inhibitors viz N-benzylidene aniline (CI₁) and N-(p-methyl benzylidene) aniline (CI₂). Results Show that inhibition efficiencies of inhibitors increase with increase in their concentration. Efficiency also increases with increase in the concentration of Trichloroacetic acid. Study shows that CI₁ is better corrosion inhibitor than CI₂ in identical condition.

Keywords: corrosion inhibition, mass loss, inhibition efficiency, surface coverage.

INTRODUCTION

Mild Steel is an industrial important metal which has variety of applications and is used in many mechanical industries and works like building material, steam engine, automobile containers and in many other systems. It's application and uses are due to it's low cost, easy availability and strong mechanical strength but it's applications are restricted due to it's chemical affinity with inorganic acids like HCl, H₂SO₄ and in some cases with organic acids like acetic acid, formic acid and trichloroacetic acid etc.¹

Corrosion is an electrochemical phenomenon which affects the surface of a metal or even alloys and nonmetals adversely in the presence of oxygen and moisture. There are two process occurring simultaneously in this processes i.e. oxidation at anodic site and reduction at cathodic site on metallic surface in acidic medium where H⁺ ion are liberated from acids.

The reduction process is responsible for the corrosion. Corrosion inhibitors reduce or prevent these reactions. They adsorb on the anodic and cathodic sites and thus make a barrier for oxygen and moisture by complexing with metal



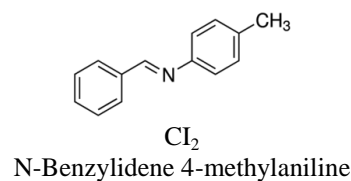
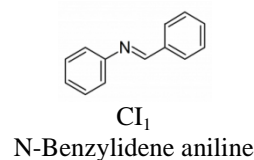
ion. Some inhibitors form a passive film on the metallic surface.

Generally the organic compounds containing hetero atoms such as N, O, S, Se etc. are found to be very effective corrosion inhibitors²⁻⁷. The efficiency of these compounds depends upon electron density of hetero atoms⁸. Inhibition efficiency also depends upon the number of adsorption active centres in the molecule and their charge density, molecular size, mode of adsorption and formation of metallic complexes.

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EXPERIMENTAL

Corrosion Inhibitors were synthesised by conventional method i.e. by refluxing equimolar quantities of ethanolic solution of corresponding aniline and benzaldehyde (for CI₁) and aniline and 4-methyl benzylidene (for CI₂) in a round bottom flask (250mL) for about 8-9 hours and then pouring the reaction mixture in ice cold water. Resulting crystals were filtered and then recrystallised by alcohol which were dried and collected.



Square shaped specimens of mild steel of dimensions 2.5cm × 2.5 cm and 1mm thickness containing a small hole of about 2mm diameter near the upper edge were used for studying of corrosion rate. The solutions of TCA were prepared using double distilled water. All chemicals used were of analytical reagent grade.

Each specimen was suspended by glass hook made of fine glass capillary tube in a beaker containing 50 mL of the test solution at 298K. After the sufficient exposure the specimens were cleaned by running water. Duplicate experiments were performed in each case and mean values of the mass loss were calculated.

The Corrosion rate (CR) in mm/yr can be obtained by the following equation⁹

$$\text{Corrosion rate (mm/yr)} = \frac{87.6\Delta M}{ATd}$$

Where ΔM is mass loss in mg, A is area of specimen in cm², T is time of exposure in hours, d is density of metal in g/cm³.

The percentage inhibition efficiency was calculated as¹⁰

$$\eta\% = \frac{100 (\Delta M_u - \Delta M_i)}{\Delta M_u}$$

Where ΔM_u and ΔM_i are the mass loss of the metal in uninhibited acid and in inhibited solution respectively.

The degree of surface coverage θ can be calculated as¹¹

$$\theta = \frac{(\Delta M_u - \Delta M_i)}{\Delta M_u}$$

Where ΔM_u and ΔM_i are the mass loss of the metal in uninhibited acid and in inhibited solution respectively.

Result and Discussion

Mass loss (ΔM), percentage inhibition efficiency ($\eta\%$) for 0.1N, 0.5N, 1.0N and 2N trichloroacetic acid are shown in Table 1 at 298K. From the table it is clear that $\eta\%$ increases with increase in the concentration of inhibitor for a given concentration of TCA. It means $\eta\%$ increases from 10 PPM to 40 PPM for each acid strength. Simultaneously $\eta\%$ increases

with increasing concentration of TCA i.e. inhibitor shows maximum efficiency in 2N TCA and minimum in 0.1 N TCA. Same trends are observed for Cl_2 i.e. this inhibitor is also more effective when it's concentration is 40 PPM and also when concentration of acid is 2N. From the table it is obvious that Cl_1 shows maximum efficiency of 99.13% whereas, Cl_2 shows maximum efficiency 82.13%. It means Cl_1 is a better corrosion inhibitor than Cl_2 . Table 2 shows the surface coverage (θ), $\log\left(\frac{\theta}{1-\theta}\right)$ with corresponding inhibition efficiencies for 0.1N, 0.5N, 1.0N and 2.0 N TCA for Cl_1 and Cl_2 .

Surface (θ) indicates the surface coverage of metallic surface by inhibitor and $\log\left(\frac{\theta}{1-\theta}\right)$ indicates the logarithmic of ratio of fraction of covered surface and uncovered surface. More surface coverage means less sites are available for acid to attack on metallic surface. It means more the surface covered by inhibitor, more will be it's efficiency. Fig1 to Fig4 show the variation of inhibition efficiency with concentration of inhibitor for mild steel in different concentration of TCA.

Generally organic inhibitors work on the principle of adsorption on metallic surface. Inhibitors having hetero atoms like N, S, O, P etc. have sufficient electron density due to presence of lone pairs on these atoms. When these inhibitors come in contact of acids they dissociate and are adsorbed on the surface of metallic surface and cover active sites of metal, thus retard the attack of acid on metal surface. More is the concentration of acid, more will be the dissociation of corrosion inhibitors and more will be the adsorption of inhibitor on metallic surface. That is why inhibitors are more effective at higher concentration of acids.

Cl_1 is better corrosion inhibitor than Cl_2 . The possible reason is that Cl_2 may be less effective due to presence of bulky i.e. methyl group along with two phenyl groups.

The present study shows that compounds having hetero atoms like N are good corrosion inhibitors in organic acids like trichloroacetic acid and such inhibitors can be used to protect metals in corrosive media like organic acids.

Table -1

Mass loss (ΔM) and inhibition efficiency ($\eta\%$) for mild steel in TCA solution with given inhibitor addition at 298K
Surface Area: 6.25cm²

Inhibitor addition	0.1 N TCA (93 hrs.)			0.5 N TCA (51 hrs.)			1N TCA (3.33 hrs.)			2N TCA (2.25 hrs.)		
	ΔM , mg	η %	C.R.	ΔM , mg	η %	C . R	ΔM , mg	η %	C.R.	ΔM , mg	η %	C . R .
Uninhibited	282.2	-	5.45	282.2	-	9.94	193.6	-	104.46	2000.0	-	1597.26
Cl_1												
10 PPM	144.0	48.97	2.78	201.2	28.70	7.58	103.2	46.70	55.68	422.4	78.88	337.34
20 PPM	122.5	56.59	2.36	74.2	73.70	2.53	39.3	79.70	21.20	403.0	79.85	321.84
30 PPM	109.2	61.30	2.10	67.3	76.15	2.37	36.4	81.19	19.64	20.3	98.98	16.21
40 PPM	75.1	73.38	1.45	64.3	77.21	2.26	33.2	82.85	17.91	17.4	99.13	13.89
Cl_2												
10 PPM	221.2	21.61	4.27	215.4	23.67	7.58	129.2	33.23	69.75	610.1	69.44	487.24
20 PPM	216.8	23.17	4.18	213.9	24.20	7.53	120.6	37.66	65.12	537.7	73.11	429.42
30 PPM	215.4	23.67	4.16	75.9	73.10	2.67	96.843	49.98	52.25	417.8	79.11	333.66
40 PPM	213.9	24.20	4.13	69.7	75.30	2.45		77.41	23.59	357.3	82.13	285.35

Table -2
Inhibition efficiency ($\eta\%$) and surface coverage (θ) for mild steel in TCA solution with given inhibitor addition at 298K

Surface Area: 6.25cm²

Inhibitor addition	0.1 N TCA (93 hrs.)			0.5 N TCA (51 hrs.)			1N TCA (3.33 hrs.)			2N TCA (2.25 hrs.)		
	η %	θ	$\log \left(\frac{\theta}{1-\theta} \right)$	η %	θ	$\log \left(\frac{\theta}{1-\theta} \right)$	η %	θ	$\log \left(\frac{\theta}{1-\theta} \right)$	η %	θ	$\log \left(\frac{\theta}{1-\theta} \right)$
Uninhibited	-	-	-	-	-	-	-	-	-	-	-	-
Cl₁												
10 PPM	48.97	0.4897	-0.0177	28.70	0.2870	-0.4028	46.70	0.4670	-0.0574	78.88	0.7888	0.5722
20 PPM	56.59	0.5659	0.1151	73.70	0.7370	0.4475	79.70	0.7970	0.5939	79.85	0.7785	0.5958
30 PPM	61.30	0.6130	0.1998	76.15	0.7615	0.5041	81.19	0.8119	0.6351	98.98	0.9898	1.9869
40 PPM	73.38	0.7338	0.4003	77.21	0.7721	0.5299	82.85	0.8285	0.6840	99.13	0.9913	2.0566
Cl₂												
10 PPM	21.61	0.2161	-0.5596	23.67	0.2367	-0.5084	33.23	0.3323	-0.3030	69.44	0.6944	0.3565
20 PPM	23.17	0.2317	-0.5206	24.20	0.2420	-0.4958	37.66	0.0376	-0.2188	73.11	0.7311	0.4343
30 PPM	23.67	0.2367	-0.5084	73.70	0.7370	0.4342	49.98	0.4998	-0.0003	79.11	0.7911	0.5782
40 PPM	24.20	0.2420	-0.4958	75.30	0.7530	0.4840	77.41	0.7741	0.5368	82.13	0.8213	0.6623

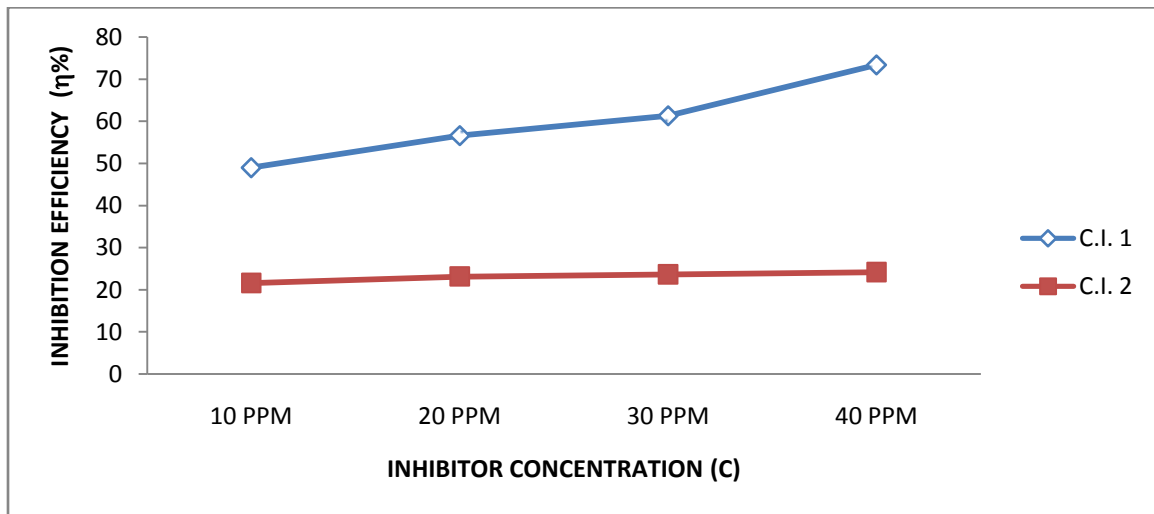


Fig.1: Variation of inhibition efficiency with concentration of inhibitor for mild steel in 0.1 N TCA

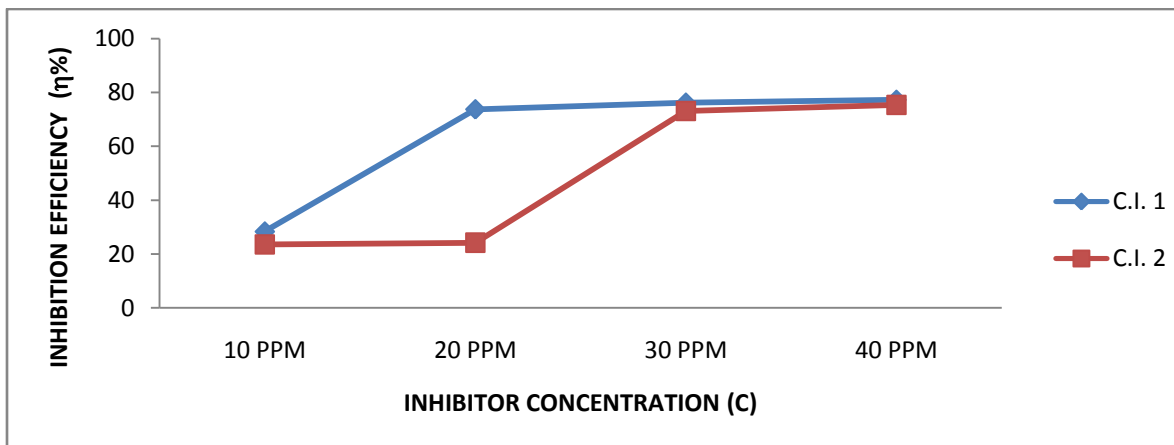


Fig.2: Variation of inhibition efficiency with concentration of inhibitor for mild steel in 0.5 N TCA

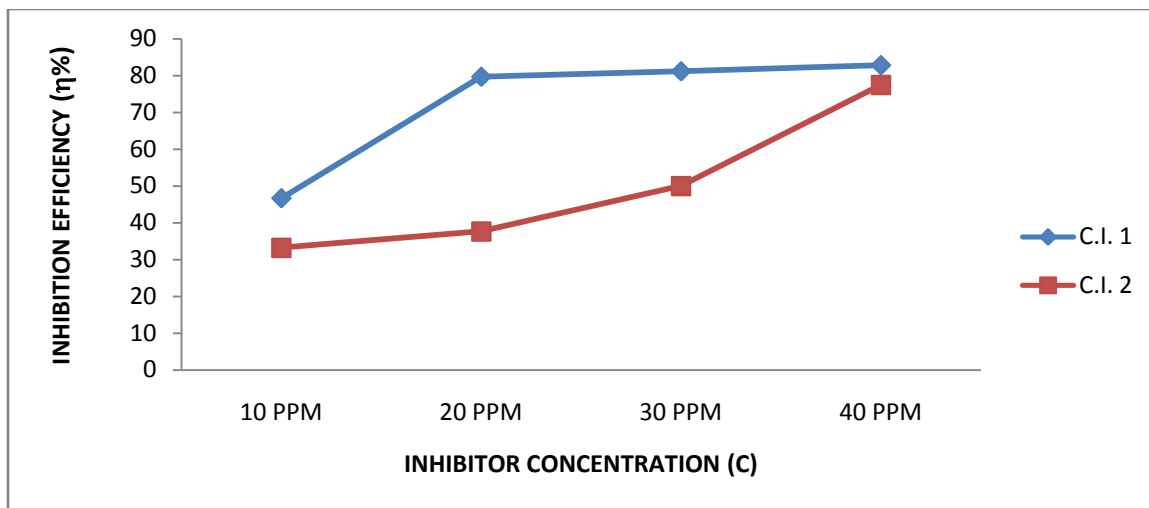


Fig. 3: Variation of inhibition efficiency with concentration of inhibitor for mild steel in 1 N TCA

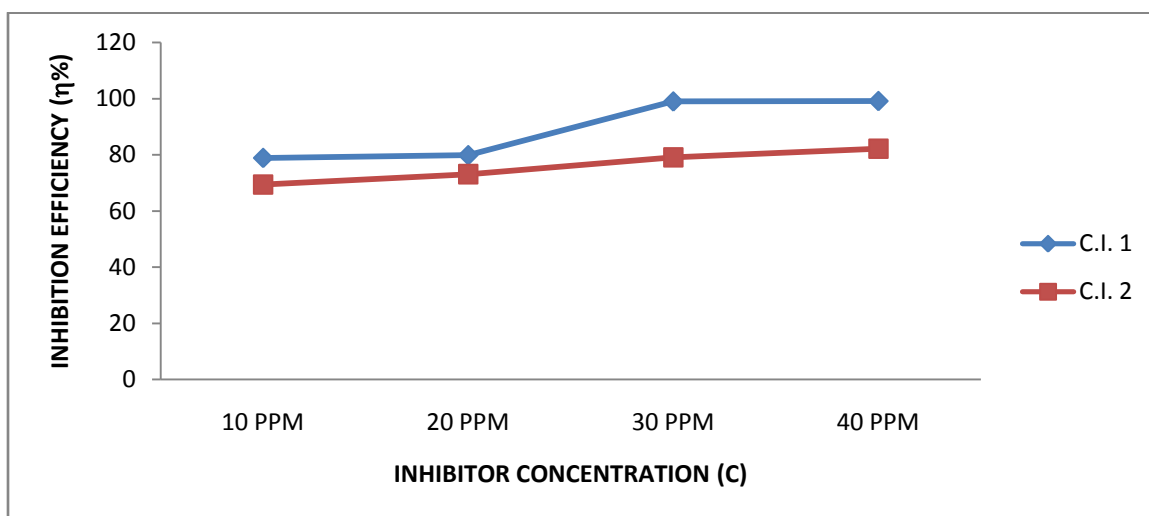


Fig. 4: Variation of inhibition efficiency with concentration of inhibitor for mild steel in 2 N TCA

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