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Study of Corrosion inhibition efficiency of synthesized ligands of Aluminium and Mild steel in Trichloroacetic acid

Lalita Saini[1] and R.K. Upadhyay[1*]

[1] *Synthesis and surface science Laboratory, Department of Chemistry, Govt. College Ajmer, Raj (India)*

ABSTRACT: Mass loss and thermometric methods have been used to study the corrosion inhibition efficiency of synthesized ligands i.e. N-Benzylidene aniline (CI_1) and N-Benzylidene 4-methylaniline (CI_2) on Aluminium and Mild steel in Trichloroacetic acid (TCA). Further study reveals that corrosion inhibition efficiency increase with increasing concentration of inhibitors as well as that of TCA. Both inhibitor are more effective for mild steel than for Al in same concentration of TCA.

Keywords: corrosion inhibition, mass loss, inhibition efficiency, surface coverage, thermometric, corrosion rate, reaction number.

INTRODUCTION

Corrosion is a destructive phenomenon of metal. It involves Chemical and electrochemical reactions due to thermodynamic instabilities of metals in the environment[1]. The corrosion process can be described as electrochemical phenomenon in which exposed surface of metal decays due to a galvanic reaction on the metal in an aqueous or acidic solution. Oxidation occurs on the anode i.e. loss of material (a) and reduction occurs on the cathode. The reduction reaction can be of different types but the common reduction reaction is formation of hydrogen in acidic medium (b)[2].

$$M \rightarrow M^{n+} + ne^- \quad (a)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (b)$$

Many workers have studies corrosion and inhibition of Al and its alloys in various acids[3-11] But much studies have not been done on corrosion of Al and it alloys in chlorosubstituted acetic acid. According to Talati and Patel[12] these acids are more corrosive than acetic itself. In TCA under a variety of conditions corrosion of metals and alloys like Al, mild steel, copper, brass, galvanized iron and tin plated metals have been studied[13]. The various aspects of corrosion behavior of different metals and alloys in mixtures of acetic and formic acid and their vapors have been investigated.[14-16]

Corrosion of aluminium and its alloys has been a subject of numerous studies due to their high technological demand and large range of industrial applications due to presence of a thin, adherent film of aluminium oxide on aluminium. It is highly reactive metal that has high resistance to corrosion in many environments .Aluminium and its alloys however are reactive materials and are prone to corrosion, therefore the inhibition of aluminium and its alloys by organic compounds in acids has been studied by many workers.

Due to its easy availability and its excellent physical properties mild steel is one of the best materials for industries. Most of the efficient inhibitors used in industry are organic compounds. The organic compounds which have hetero atom like O,N,S are effective corrosion inhibitor[17-20]. Efficiency of these compounds depends on the electron density around the heteroatom[21]. Inhibition efficiency also depends upon the number of adsorption active centres in the molecule, their charge density, size of adsorption mode, size of molecule and formation of metallic complexes[22].

Present investigation deals with the efficiency of organic compounds synthesised in laboratory having nitrogen as hetero atom on two metals i.e. aluminum and mild steel in a highly corrosive organic acid TCA.

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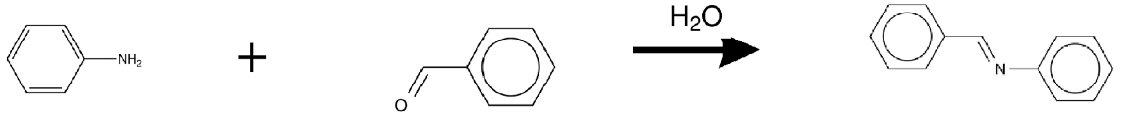
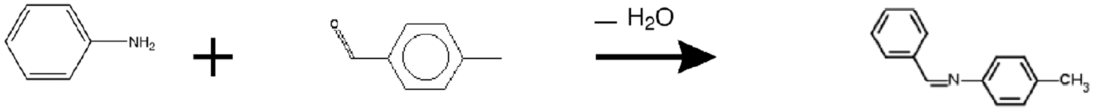
[*] *To whom correspondence be made:*
E-mail: alwayz_rajesh@yahoo.co.in

MATERIAL AND METHODS

Square shaped specimens of aluminium and mild steel of 1mm thickness and 2.5 × 2.5 cm dimensions containing a small hole of about 2 mm diameter near the upper edge were used for studying corrosion rate. Specimen of mild steel and aluminium were cut from a sheet of respective metals. Specimens were cleaned by buffing to produce immaculate finish and then degreased. Solutions of TCA were prepared using double distilled water. Hetero atom containing ligands were synthesized by conventional method[23-25]. All chemicals used were of analytical reagent grade.

Synthesis of hetero atom containing ligands: Hetero atom containing ligands were synthesized by refluxing respective amine with respective aromatic aldehyde in in ethanol for about 6 hours in 1:1 molar ratio.





For the synthesis of N-Benzylidene aniline (CI_1), equimolar quantities of anilne and benzaldehyde were taken in a 250 mL RB flask and were dissolved in minimum quantity of ethanol . The mixture was refluxed for about 7-8 hours then it was cooled to get the crystals of product then compound was recrystallized with ethanol.Thus pure crystal were obtained. Similar process was adopted for the synthesis of N-Benzylidene-4 methyliline (CI_2) by taking respective aldehyde with aniline.

Each specimen of aluminum and mild steel were suspended by a V- shaped glass hook and immersed into corrosive acid solution at room temperature. The time of exposure was varied for individual cases. After the exposure specimens were cleaned by first running tape water and then dried in hot air. The loss in mass was determined with a digital balance having accurancy upto 0.0001 gram.

The corrosion rate (CR) in milli meter per year (mm /yr) can be obtained by the following equation[26]

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

Where ΔM is the mass loss of specimen in mg, A is the area of exposure of specimen in square cm, T is the time in hours and D is the density of specimen in g/cm^3

The percentage inhibition efficiency was calculated as[27]

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

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

The degree of surface coverage q can be calculated as[28]

$$Q = \frac{(M_U - M_i)}{\Delta M_U}$$

Inhibition efficiency (η%)was also determined by using the thermometric technique. This involved the Immersion of single specimen measuring 2.5×2.5 cm in an insulated reaction chamber containing 250 mL of solution at room temperature. Temperature changes were measured at intervals of 5 minute using a digital thermometer with precision of 0.10C. The temperature increased slowly at first then rapidly and attained a maximum value before falling. The maximum temperature was recorded.

Percentage inhibition efficiency (η%) was calculated as[29]

$$\eta\% = \frac{100(RN_U - RN_i)}{RN_U}$$

where RN_U and RN_i are the reaction number uninhibited solution and in inhibited solution in the absence and in presence of inhibitor respectively where RN is defined as.

$$RN = \frac{Tm - Ti}{t}$$

Where:

Tm → maximum temperature of solution

Ti → Initial temperature of solution

t → time required to reach the maximum temp. (in min)

RESULTS AND DISCUSSION

Table 1 shows mass loss (ΔM), percentage inhibition efficiency (η%) for 0.1N, 0.5N, 1N, 2N trichloroacetic acid for mild steel. From the table it is observed that the inhibition efficiency increases with increase in the concentration of inhibitor for given concentration of TCA. It is also clear from the table 1 that each inhibitor has higher efficiency at higher concentration of inhibitor. The maximum efficiency 99.13% was shown by CI_1 whereas CI_2 shows maximum efficiency 82.13%. It means CI_1 is a better corrosion inhibitor than CI_2. Table 2 shows the variation of surface coverage q and log q (1-q) along with h% in different concentration of TCA. It is also clear from the table that surface coverage also increases with increasing concentration of acid.

Loss in mass and percentage inhibition efficiency and surface coverage for various concentrations of TCA and inhibitors are given in table 3 and 4 for aluminium. Same trends are observed for aluminium also. More efficiency was shown at an inhibitor concentration of 40 PPM in 2N TCA.

Inhibition efficiency were also determined using the thermometric method. Temperature changes for mild steel in 1N, 2N and 3N TCA were recorded with various inhibitor. Since no significant temperature changes were observed for lower concentrations of TCA so observation were taken at higher concentration. The maximum efficiency is obtained with the highest concentration of acid (3N TCA). From the table it is clear that η% increases with concentration of TCA. CI_1 shows maximum efficiency 79.41% and C_2 shows maximum efficiency 86.76% these results indicate that CI_2 show more inhibition efficiency than CI_1. Same trends are also observed for Al also as shown in table 6. It means η% increases from low concentration to high concentration for each acid strength, simultaneously η% increase with increasing concentration of TCA. From the table it is obvious that CI_1 shows maximum efficiency 79.86% whereas CI_2 shows maximum efficiency

Table 1

Mass loss (DM) and inhibition efficiency (h%) for mild steel in TCA solution with given inhibitor addition at 298K

Surface Area: 6.25cm^2

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	—	1597.26
CI_1												
10 PPM	144.0	48.97	2.78	201.2	28.7	7.08	103.2	46.7	55.68	422.4	78.88	337.34
20 PPM	122.5	56.59	2.36	74.2	73.7	2.61	39.3	79.7	21.2	403	79.85	321.84
30 PPM	109.2	61.30	2.19	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
CI_2												
10 PPM	221.2	21.61	4.27	215.4	23.67	7.58	129.2	33.23	69.75	610.1	69.49	487.24
20 PPM	216.8	23.17	4.18	213.9	24.2	7.53	120.6	37.66	65.12	537.7	73.11	429.42
30 PPM	215.4	23.67	4.16	75.9	73.1	2.67	96.8	49.98	52.25	417.8	79.11	333.66
40 PPM	213.9	24.2	4.13	69.7	75.3	2.45	43.7	77.41	23.59	357.3	82.13	285.35

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

Surface Area: 6.25cm^2

Inhibitor addition	*0.1 N TCA (93 hrs.)*			*0.5N TCA (51 hrs.)*			*IN TCA (3.33 hrs.)*			*2N TCA (2.25 hrs.)*		
	$\eta\%$	θ	$\log\left(\frac{\theta}{I-\theta}\right)$	$\eta\%$	θ	$\log\left(\frac{\theta}{I-\theta}\right)$	$\eta\%$	θ	$\log\left(\frac{\theta}{I-\theta}\right)$	$\eta\%$	θ	$\log\left(\frac{\theta}{I-\theta}\right)$
Uninhibited	—	—	—	—	—	—	—	—	—	—	—	—
CI_1												
10 PPM	48.97	0.4897	-0.0177	28.34	0.2834	-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	0.5979
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	0.684	99.13	0.9913	2.0566
CI_2												
10 PPM	21.61	0.2161	-0.5596	23.67	0.2367	-0.5084	33.23	0.3323	-0.303	69.44	0.6944	0.3565
20 PPM	23.17	0.2317	-0.5206	24.20	0.2420	-0.4958	37.66	0.3766	-0.2188	73.11	0.7311	0.4343
30 PPM	23.67	0.2367	-0.5084	73.10	0.7310	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	0.7749	0.5368	82.13	0.8213	0.6623

Table 3
Mass loss (DM) and inhibition efficiency (h%) for Aluminium in TCA solution with given inhibitor addition at 298K

Surface Area: 6.25cm^2

Inhibitor addition	*0.1 N TCA (94hrs)*			*0.5 N TCA (48hrs)*			*1 N TCA (3hrs)*			*2 N TCA (1.30hrs)*		
	ΔM, (mg)	$\eta\%$	*C.R.*	ΔM, (mg)	$\eta\%$	*C.R*	ΔM, (mg)	$\eta\%$	*C.R.*	ΔM, (mg)	$\eta\%$	*C.R.*
Uninhibited	188.7		10.42	189		20.44	439.2		759.97	259.2		1035.02
CI_1						15.27						
10 PPM	156.1	17.27	8.627.7	141.2	25.29	15.10	273.5	37.72	473.25	33.3	87.15	132.97
20 PPM	140.2	25.70	47.07	139.7	26.08	10.69	148.0	66.30	256.09	25.1	90.31	100.22
30 PPM	128.1	32.11	6.57	98.9	47.67	7.02	110.6	74.81	191.37	7.1	97.26	28.35
40 PPM	119.0	36.93		65.0	65.60		5.0	98.86	8.65	0.5	99.88	1.99
CI_2		18.49	8.49			13.17			423.42			351.39
10 PPM	153.8	21.19	8.21	121.8	35.55	12.19	244.7	44.28	407.84	88.00	66.04	316.65
20 PPM	148.7	25.06	7.8	112.8	40.31	10.64	235.7	46.33	253.15	79.3	69.40	228.80
30 PPM	141.4	27.50	7.55	98.4	47.93	8.42	146.3	66.68	150.02	57.3	77.89	164.11
40 PPM	136.8			77.9	58.78		86.7	80.25		41.1	84.14	

84.72% for alumniium.It means CI_2 is a better corrosion inhibitor than CI_1

The results revealed that CI_1 work as better corrosion inhibitor in mass loss method because its lone pair electrons facilitate the adsorption process. CI_2 may be less effective due to presence of bulky i.e. methyl group along with two phenyl groups. On other hand in thermometric method CI_2 is a better corrosion inhibitor than CI_1. It may be due to a possible reason that in CI_2,-CH_3 group exerts a positive inductive (+I) effect which increase the electron density at the nitrogen Atom. It has been observed that the inhibition efficiency increases as the acid concentration increases and at high concentration of acid +I effect of -CH_3 groups in CI_2 is more dominant than steric hindrance of -CH_3 group.

Table -4
Inhibition efficiency (η%) and surface coverage (θ) for Aluminum in TCA solution with given inhibitor addition at 298K

Surface Area: 6.25cm^2

Inhibitor addition	*0.N TCA (94 hrs.)*			*0.5N TCA (48 hrs.)*			*I N TCA (3 hrs.)*			*2N TCA (1.30 hrs.)*		
	η%	*θ*	$\log\left(\frac{\theta}{I-\theta}\right)$	*η%*	*θ*	$\log\left(\frac{\theta}{I-\theta}\right)$	*η%*	*θ*	$\log\left(\frac{\theta}{I-\theta}\right)$	*η%*	*θ*	$\log\left(\frac{\theta}{I-\theta}\right)$
Uninhibited												
CI_1												
10 PPM	17.27	0.1727	-0.6803	25.27	0.2527	-0.4708	37.72	0.3772	-0.2177	87.15	0.8715	0.8313
20 PPM	25.70	0.2570	-0.461	26.08	0.2608	-0.4524	66.30	0.6630	0.2938	90.31	0.9031	0.9694
30 PPM	32.93	0.3293	-0.3251	47.67	0.4767	-0.0405	74.81	0.7481	0,4727	97.26	0.9726	1.5501
40 PPM	36.93	0.3693	-0.2324	65.60	0.6560	0.2803	98.07	0.9807	1.7059	99.88	0.9988	2.9202
CI_2												
10 PPM	23.79	0.2379	-0.5056	35.55	0.3555	-0.2583	44.28	0.4428	-0.0998	66.04	0.6604	0.2888
20 PPM	29.67	0.2967	-0.3748	40.31	0.4031	-0.1704	46.33	0.4633	-0.6386	69.4	0.694	0.3556
30 PPM	32.48	0.3248	-0.3178	47.13	0.4713	-0.0499	66.68	0.6668	0.3012	77.89	0.7789	0.5468
40 PPM	38.27	0.3827	-0.2075	58.78	0.5878	0.1541	91.64	0.9164	1.0398	84.14	0.8414	0.7246

Table 5
Reaction Number (RN) and percentage inhibition (η%) for Mild Steel in TCA solution with inhibitor additions

Inhibitor	*1N TCA (4 hrs)*		*2N TCA (2.5 hrs)*		*3N TCA (85 min)*	
	RN	*η%*	*RN*	*η%*	*RN*	*η%*
Uninhibited	5.25		11.23		0.68	
CI_1						
10 PPM	3.75	28.57	5.6	50.13	0.49	27.94
20 PPM	2.25	57.14	5.41	51.82	0.24	64.7
30 PPM	2.05	60.95	4.80	57.25	0.21	69.11
40 PPM	1.75	66.66	3.23	71.23	0.14	79.41
CI_2						
10 PPM	2.25	57.14	6.05	46.12	0.44	35.29
20 PPM	1.75	66.66	5.20	53.69	0.3	55.88
30 PPM	1.50	71.42	4.63	58.77	0.12	82.35
40 PPM	1.12	78.57	2.00	82.19	0.09	86.76]

Table 6
Reaction Number (RN) and percentage inhibition (h%) for Aluminium in TCA solution with inhibitor additions

Inhibitor	*1N TCA (1.5 hrs)*		*2N TCA (1.25 hrs)*		*3N TCA (45 min)*	
	RN	*η%*	*RN*	*η%*	*RN*	*η%*
Uninhibited	20.66		46.41		1.44	
CI_1						
10 PPM	14	32.23	20.81	55.16	1.06	26.38
20 PPM	11.33	45.15	18.4	60.35	0.57	60.41
30 PPM	10	51.59	14.44	68.88	0.66	54.16
40 PPM	7.33	64.5	10.45	77.48	0.29	79.86
CI_2						
10 PPM	18.03	12.72	16.8	63.8	0.62	56.94
20 PPM	14.64	29.13	12.83	72.35	0.52	63.88
30 PPM	12.01	41.86	11.2	75.86	0.35	75.69
40 PPM	6.02	70.86	8.42	81.85	0.22	84.72

Fig. 1 to 4 show the variation of inhibition efficiency with concentration of inhibitor for mild steel whereas Fig. 5 to 8 show the variation of inhibition efficiency (η%) with concentration for Al.

CONCLUSION

The present study shows that compounds having hetero atoms like N are good corrosion inhibitors in organic acids like TCA. N containing inhibitors have sufficient electron density due to presence of lone pair of electrons. When these inhibitors come in contact of acids they dissociate and are adsorbed on the surface and cover active sites of metal, thus retard the attack of acid on metal surface. On increasing the concentration of inhibitor the inhibition efficiency in acid increases due to more adsorption on the metallic active sites. Similarly on increasing the concentration of acid more dissociation of inhibitor takes place which block the active sites of metal thus efficiency of inhibitor is higher in higher concentration of acid.

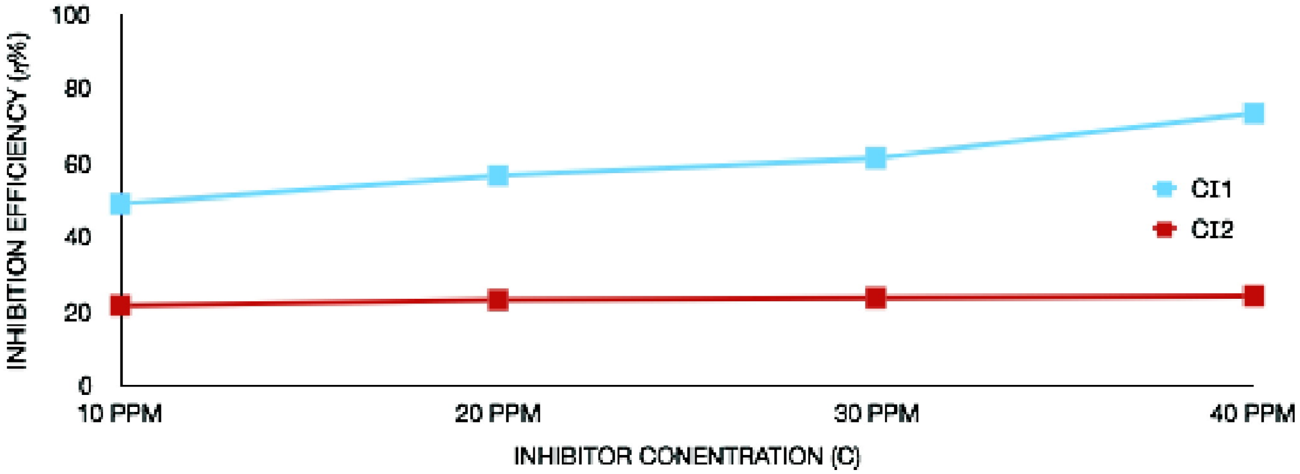


Figure 1: Variation of inhibition efficiency with concentration of inhibitor for Mild steel in 0.1 N TCA

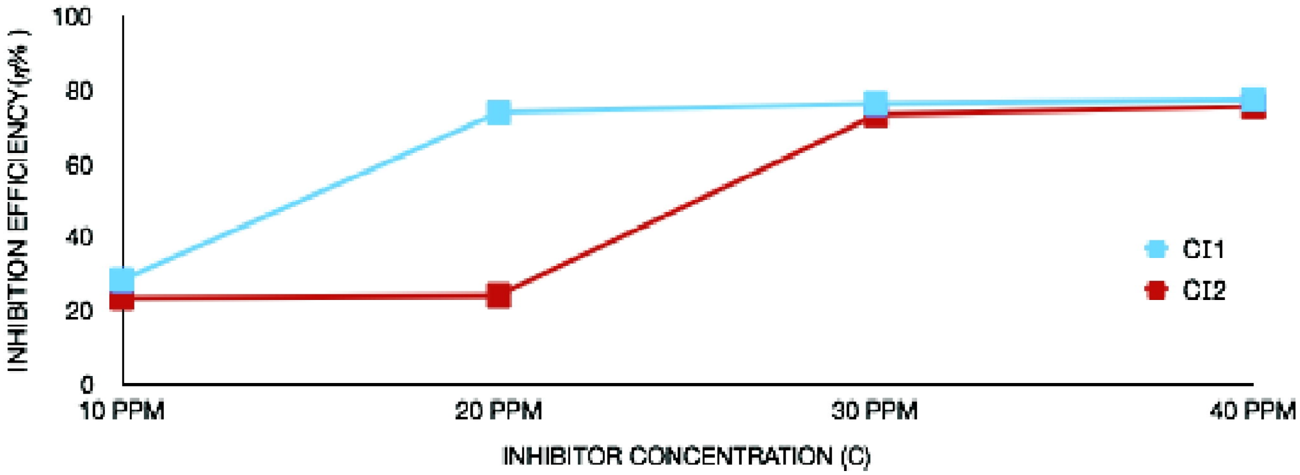


Figure 2: Variation of inhibitor efficiency with concentration of inhibitor for Mild steel in 0.5 N TCA

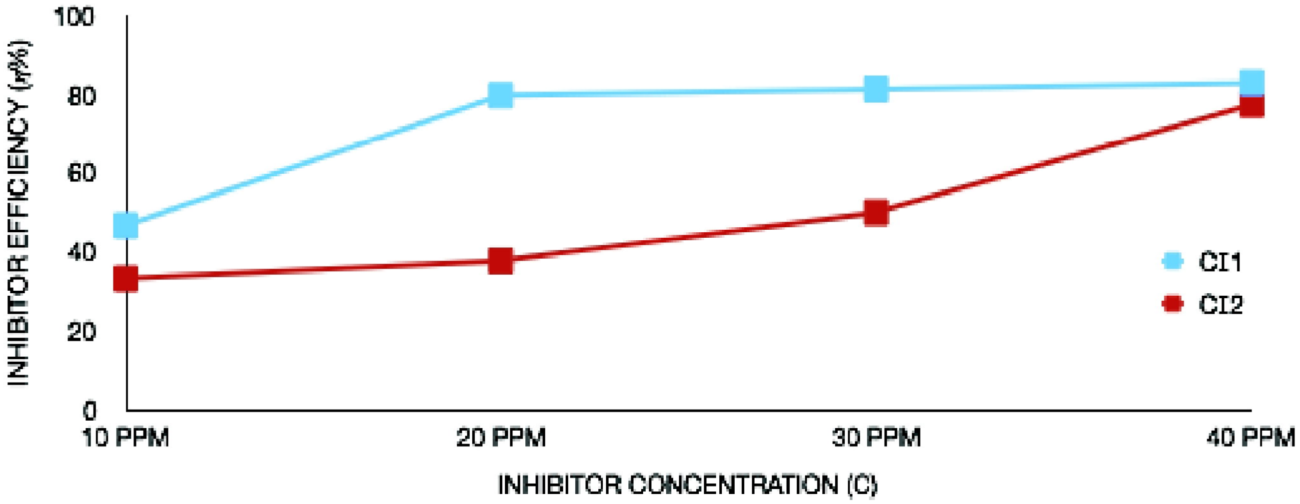


Figure 3: Variation of inhibitor efficiency with concentration of inhibitor for Mild steel in 1N TCA

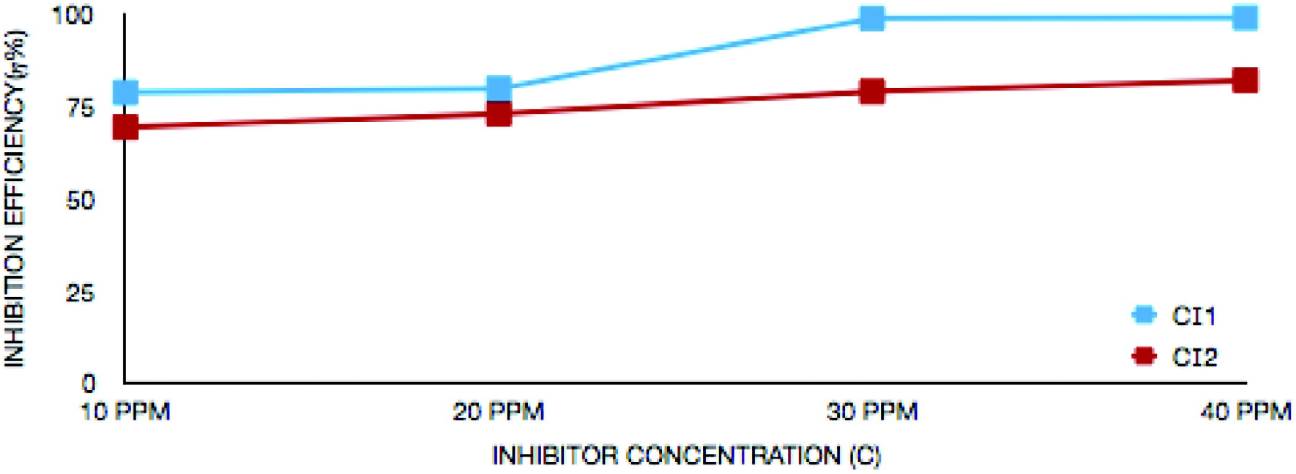


Figure 4: Variation of inhibition efficiency with concentration of inhibitor for Mild steel in 2 N TCA

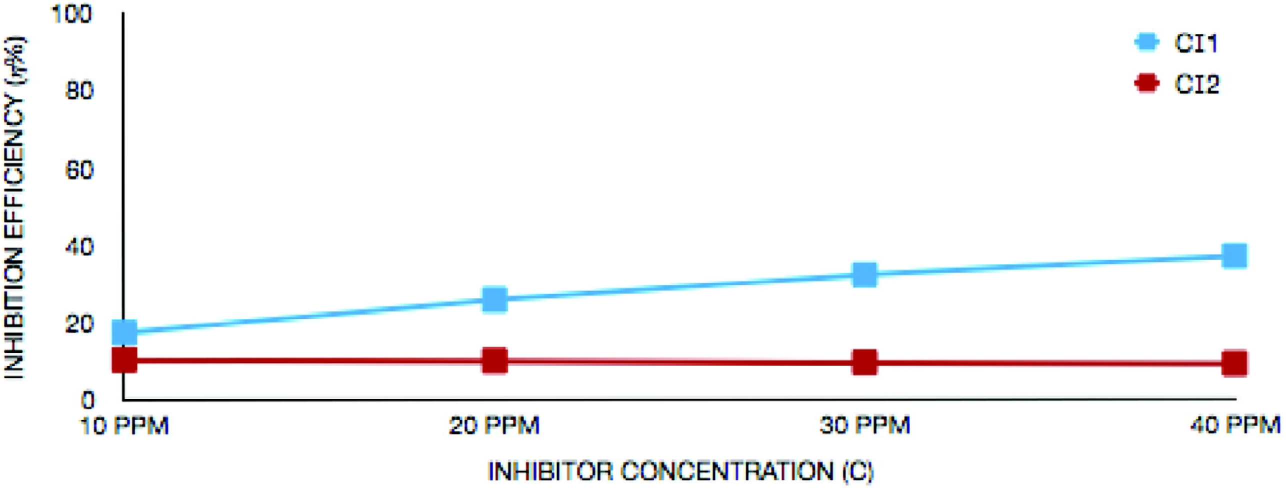


Figure 5: Variation of inhibition efficiency with concentration of inhibitor for Aluminium in 0.1 N TCA

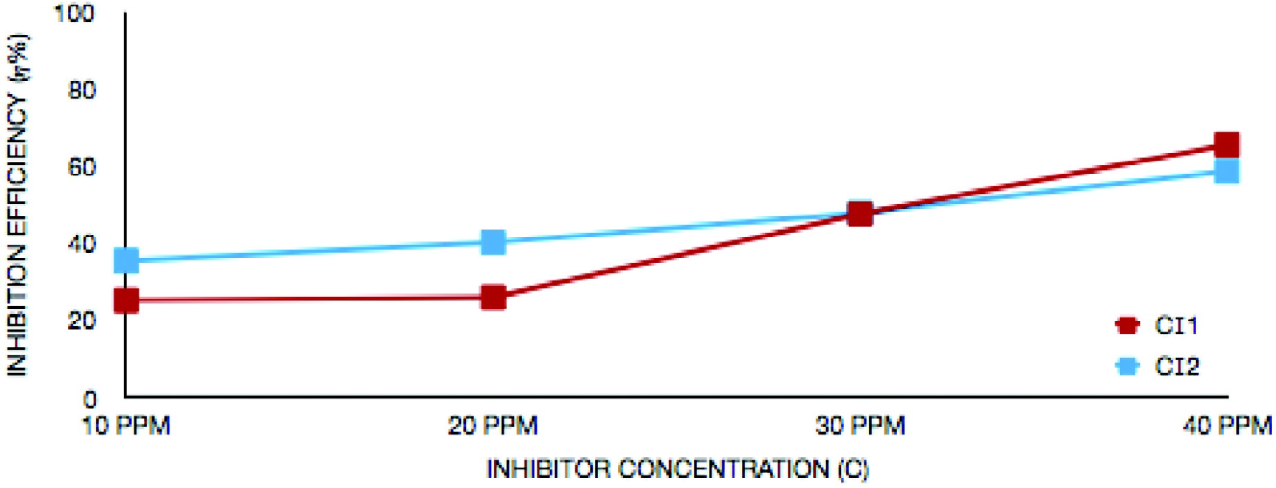


Figure 6: Variation of inhibition efficiency with concentration of inhibitor for Aluminium in 0.5 N TCA

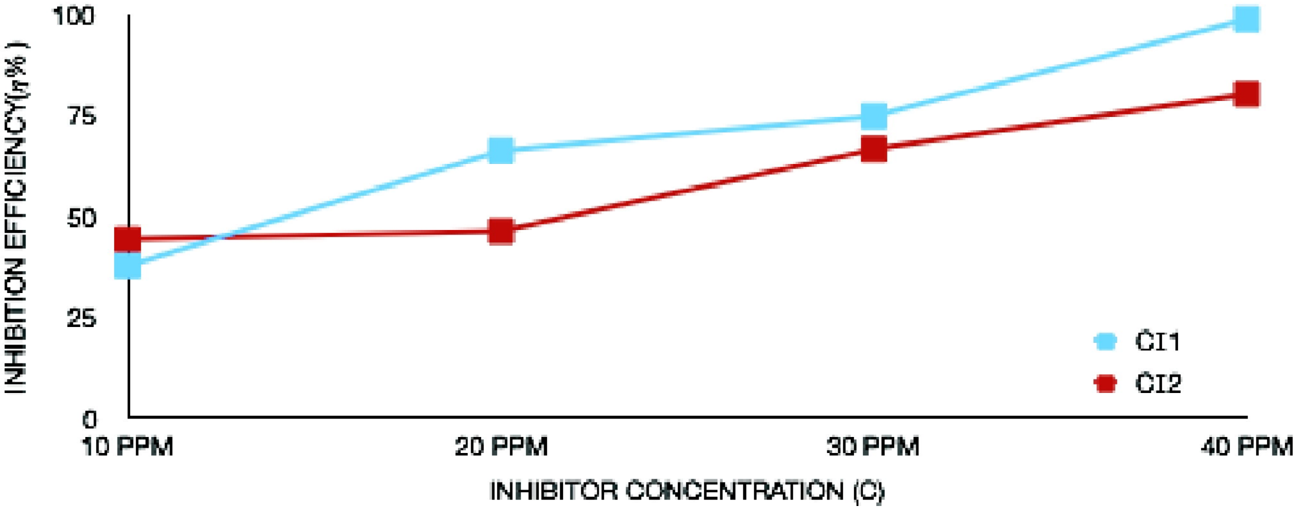


Figure 7: Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 1 N TCA

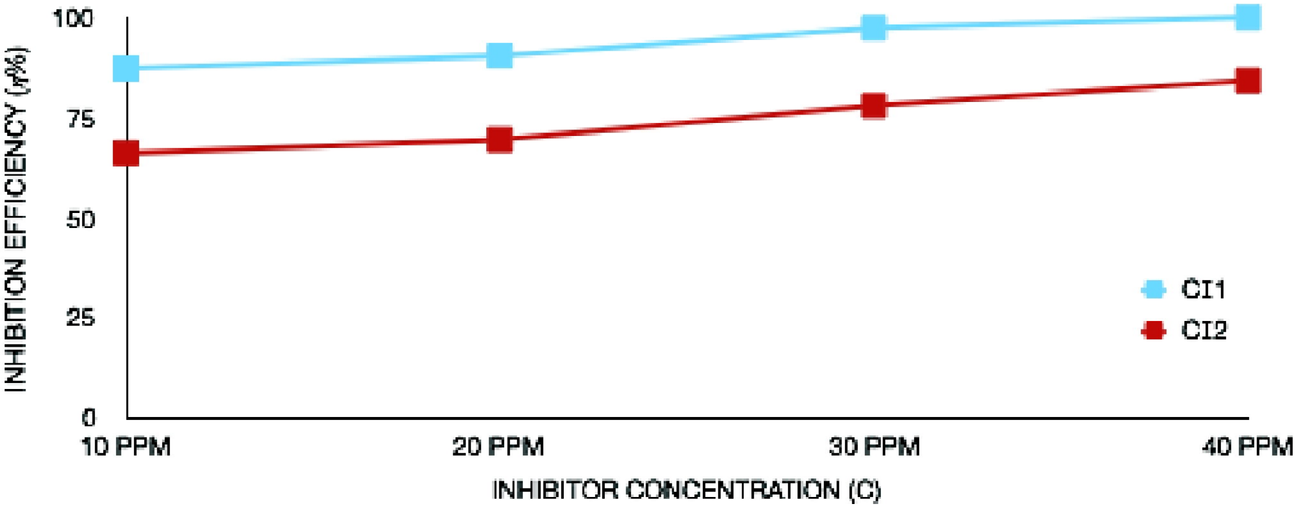


Figure 8: Variation of inhibition efficiency with concentration of inhibitor for Aluminium in 2 N TCA

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