

## A Study Of Some Nitrogen Containing Ligands As potential corrosion Inhibitor For Aluminium In Trichloroacetic Acid And Monochloroacetic Acid

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### ABSTRACT:

Mass loss and thermometric methods have been used to study the corrosion inhibition efficiency of synthesized ligands i.e. N-Benzylidene aniline (corrosion inhibitor,  $CI_1$ ) and N-Benzylidene 4-methylaniline (corrosion inhibitor,  $CI_2$ ) on Aluminium in Trichloroacetic acid (TCAA) and Monochloroacetic acid (MCAA). Study shows that both synthesized ligands are effective corrosion inhibitors on metal in both acids. Further study reveals that corrosion inhibition efficiency increases with increasing concentration of inhibitors as well as that of both acids TCAA and MCAA. Both inhibitors are more effective for Aluminium in TCAA than for in MCAA.

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

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### I. INTRODUCTION

Corrosion is destructive attack on the metal due to its reaction with environment. Corrosion word derived from the latin word "Corrodere" (meaning to eat away) occurs when a metal or alloy undergoes a chemical or electrochemical reactions that find due to thermodynamic instabilities in the environment (1). The process of corrosion may be fast, slow or medium (average). The corrosion of metals or alloys can be considered as reverse of metallurgy. Metals corrode because we use them in environment where they are chemically unstable (2). Many structural alloys corrode only from exposure to moisture in the air but the process can be severely affected by exposure to certain substances. Corrosion and inhibition of Al and its alloys in various acids many workers have been studied by studied. (3-11) But corrosion of Al and its alloys in Chlorosubstituted acetic acid like Trichloroacetic acid (TCAA), Dichloroacetic acid (DCAA), Monochloroacetic acid (MCAA), has not been widely studied. According to Talati and Patel (12) these acids are more corrosive than acetic acid itself. Metals like aluminium, copper, mild steel, brass, galvanized iron and tin plated metals were studied for their corrosion by chlorosubstituted acetic acids under a variety of conditions. (13) Aluminium and its alloys show good resistivity towards a wide variety of corrosive environments. Aluminium and its alloys however are reactive materials and are prone to corrosion, therefore the inhibition of aluminium and its alloys by organic

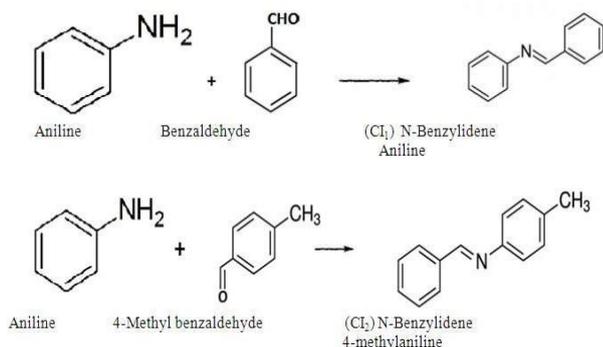
compounds in acids has been studied by many workers.

The use of corrosion inhibitors constitutes one of the most economical ways to mitigate the corrosion role to protect metal surface against corrosion and preserve industrial facilities (14). Inhibitors are chemical compounds added in small quantities in order to reduce the corrosion rate (15). The organic compounds which have hetero atom like O, N and S are effective corrosion inhibitor (16-18).

Present investigation deals with the efficiency of nitrogen containing organic compounds synthesized in laboratory on metal i.e. aluminium in a highly corrosive organic acid TCAA and MCAA.

### II. MATERIAL AND METHODS

Square shaped specimens of aluminium of 1mm thickness and  $2.5 \times 2.5$  cm dimensions containing a small hole of about 2 mm diameter near the upper edge were used for studying corrosion rate. Specimen of aluminium were cut from a sheet of respective metal. Specimens was cleaned by buffing to produce immaculate finish and then degreased. Solutions of TCAA and MCAA were prepared using double distilled water. Hetero atom containing ligands were synthesized by conventional method (19-21). All chemicals used were of analytical reagent grade.



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 milli meter per year (mm /yrs.) can be obtained by the following equation(22).

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

Where  $\Delta M$  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<sup>3</sup>. The percentage inhibition efficiency was calculated as (23).

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

Where  $\Delta M_u$  and  $\Delta M_i$  are the mass loss of the specimen in uninhibited acid and in inhibited solution respectively. The degree of surface coverage  $\theta$  can be calculated as (24).

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

Inhibition efficiency ( $\eta\%$ ) 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 0.1°C. The temperature increased slowly at first then rapidly and attained a maximum value before falling. The maximum temperature was recorded.

Percentage inhibition efficiency ( $\eta\%$ ) was calculated as (25).

$$\eta\% = \frac{100 (RNU - RNi)}{RNU}$$

Where RNU and RNi are the reaction number in uninhibited solution and in inhibited solution respectively where RN is defined as.

$$RN = \frac{T_m - T_i}{t}$$

Where:

$T_m$  → maximum temperature of solution

$T_i$  → Initial temperature of solution

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

### III. RESULTS AND DISCUSSION

Corrosion behavior of aluminium in different concentrations of trichloroacetic acid and Monochloroacetic acid in different concentrations of newly synthesized corrosion inhibitors (Cl<sub>1</sub> and Cl<sub>2</sub>) have been studied and the results are depicted in table 1-6 respectively.

Table -1 shows mass loss ( $\Delta M$ ), percentage inhibition efficiency ( $\eta\%$ ) for 0.1N, 0.5N, 1N, 2N trichloroacetic acid for aluminium. From the table it is observed that the inhibition efficiency increases with increase in the concentration of inhibitor for given concentration of TCAA. It is also clear from the table.1 that each inhibitor has higher efficiency at higher concentration of inhibitor. The maximum efficiency 99.88% was shown by Cl<sub>2</sub> whereas Cl<sub>1</sub> shows maximum efficiency 84.14%. It means Cl<sub>1</sub> is a better corrosion inhibitor than Cl<sub>2</sub>. Table.2 shows the variation of surface coverage  $\theta$  and  $\log \theta / (1-\theta)$  along with  $\eta\%$  in different concentration of TCAA. 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 MCAA and inhibitors are given in table.3 and 4 for aluminium. Same trends are observed for MCAA also. More efficiency was shown at an inhibitor concentration of 40 ppm in 2NMCAA.

Corrosion inhibition behavior of two synthesized corrosion inhibitor for aluminum in TCAA and MCAA solutions were determined by thermometric method. Temperature changes for Aluminum in 1N, 2N and 3N TCAA and MCAA were recorded with various inhibitor concentrations. Since no significant temperature changes were observed for lower concentrations of both acids so observation were taken at higher concentration. The maximum efficiency was obtained with the highest concentration of acids (3N TCAA and 3N MCAA). From the table it is clear that  $\eta\%$  increases with concentration of acids.  $CI_1$  shows maximum efficiency 79.86% and  $CI_2$  shows maximum efficiency 84.72% these results indicate that  $CI_2$  show more inhibition efficiency

It may be due to a possible reason that in  $CI_2$ , -CH<sub>3</sub> 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<sub>3</sub> groups in  $CI_2$  is more dominant than steric hindrance of -CH<sub>3</sub> group.

Fig. 1 to 4 show the variation of inhibition efficiency with concentration of inhibitor for aluminium in TCAA whereas Fig.5 to 8 show the variation of inhibition efficiency ( $\eta\%$ ) with concentration for Al in MCAA.

#### IV. CONCLUSION

The present study shows that aluminium have tendency to be corroded in acid media.

than  $CI_1$ . Same trends are also observed for Al also as shown in table.

It means  $\eta\%$  increases from low concentration to high concentration for each acid strength, simultaneously  $\eta\%$  increase with increasing concentration of acids. From the table it is obvious that  $CI_1$  shows maximum efficiency 79.86% whereas  $CI_2$  shows maximum efficiency 84.72% for aluminium. 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  $CI_1$ . Corrosion rate of aluminium is maximum in TCAA in comparison to MCAA compounds having hetero atoms like N are good corrosion inhibitors in organic acids like TCAA and MCAA. 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.

**Table -1**  
 Mass loss ( $\Delta M$ ) and inhibition efficiency ( $\eta\%$ ) for Aluminium in TCAA solution with given inhibitor addition at 298K  
 Surface Area:  $6.25\text{cm}^2$

Inhibitor addition	0.1 N TCAA (94hrs)			0.5 N TCAA (48hrs)			1 N TCAA (3hrs)			2 N TCAA (1.30hrs)		
	$\Delta M$ , (mg)	$\eta\%$	C.R.	$\Delta M$ , (mg)	$\eta\%$	C.R.	$\Delta M$ , (mg)	$\eta\%$	C.R.	$\Delta M$ , (mg)	$\eta\%$	C.R.
Uninhibited $CI_1$	188.7		10.42	189.0		20.44	439.2		759.97	259.2		1035.02
10 ppm	156.1	17.27	8.62	141.2	25.29	15.27	273.5	37.72	473.25	33.3	87.15	132.97
20 ppm	140.2	25.70	7.74	139.7	26.08	15.10	148.0	66.30	256.09	25.1	90.31	100.22
30 ppm	128.1	32.11	7.07	98.9	47.67	10.69	110.6	74.81	191.37	07.1	97.26	28.35
40 ppm	119.0	36.93	6.57	65.0	65.60	07.02	005.0	98.86	8.65	00.5	99.88	01.99
$CI_2$												
10 ppm	153.8	18.49	8.49	121.8	35.55	13.17	244.7	44.28	423.42	88.00	66.04	351.39
20 ppm	148.7	21.19	8.21	112.8	40.31	12.19	235.7	46.33	407.84	79.3	69.40	316.65
30 ppm	141.4	25.06	7.80	98.4	47.93	10.64	146.3	66.68	253.15	57.3	77.89	228.80
40 ppm	136.8	27.50	7.55	77.9	58.78	8.42	86.7	80.25	150.02	41.1	84.14	164.11

**Table -2**  
 Inhibition efficiency ( $\eta\%$ ) and surface coverage ( $\theta$ ) for Aluminum in TCAA solution with given inhibitor addition at 298K  
 Surface Area:  $6.25\text{cm}^2$

Inhibitor addition	0.1 N TCAA (94hrs)			0.5 N TCAA (48hrs)			1 N TCAA (3hrs)			2 N TCAA (1.30 hrs)		
	$\eta\%$	$\theta$	$\log\left(\frac{\theta}{1-\theta}\right)$	$\eta\%$	$\theta$	$\log\left(\frac{\theta}{1-\theta}\right)$	$\eta\%$	$\theta$	$\log\left(\frac{\theta}{1-\theta}\right)$	$\eta\%$	$\theta$	$\log\left(\frac{\theta}{1-\theta}\right)$
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	-0.4610	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	69.40	0.6940	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 -3**  
**Mass loss ( $\Delta M$ ) and inhibition efficiency ( $\eta\%$ ) for Aluminum in MCAA solution with given inhibitor addition at 298K**  
**Surface Area: 6.25cm<sup>2</sup>**

Inhibitor addition	0.1 N MCAA (240 hrs.)			0.5 N MCAA (240hrs.)			1N MCAA (240 hrs.)			2N MCAA (240 hrs.)		
	$\Delta M$ , (mg)	$\eta\%$	C.R.	$\Delta M$ , (mg)	$\eta\%$	C.R.	$\Delta M$ , (mg)	$\eta\%$	C.R.	$\Delta M$ , (mg)	$\eta\%$	C.R.
Uninhibited	31.8	---	0.69	38.3	---	0.83	40.2	---	0.87	42.1	---	0.91
CI <sub>1</sub>												
10 ppm	28.0	11.94	0.60	27.8	27.41	0.60	17.3	56.96	0.37	17.0	59.61	0.37
20 ppm	26.3	17.29	0.57	25.1	34.46	0.54	16.0	60.19	0.35	14.1	66.50	0.30
30 ppm	25.3	20.44	0.54	21.0	45.16	0.45	14.3	64.67	0.31	10.1	74.58	0.22
40 ppm	23.9	24.84	0.51	20.1	47.51	0.43	13.5	66.41	0.29	09.9	76.48	0.21
CI <sub>2</sub>												
10 ppm	31.5	00.94	0.68	36.9	03.65	0.80	23.1	42.53	0.50	30.5	27.55	0.66
20 ppm	31.3	01.57	0.68	30.8	19.58	0.67	22.5	44.09	0.49	24.0	42.99	0.52
30 ppm	29.8	06.28	0.64	29.1	24.02	0.63	20.2	49.75	0.44	20.9	50.35	0.45
40 ppm	27.1	14.77	0.59	27.1	29.24	0.59	19.9	50.49	0.43	18.0	57.24	0.39

**Table -4**  
**Inhibition efficiency ( $\eta\%$ ) and surface coverage ( $\theta$ ) for Aluminum in MCAA solution with given inhibitor addition at 298K**  
**Surface Area: 6.25cm<sup>2</sup>**

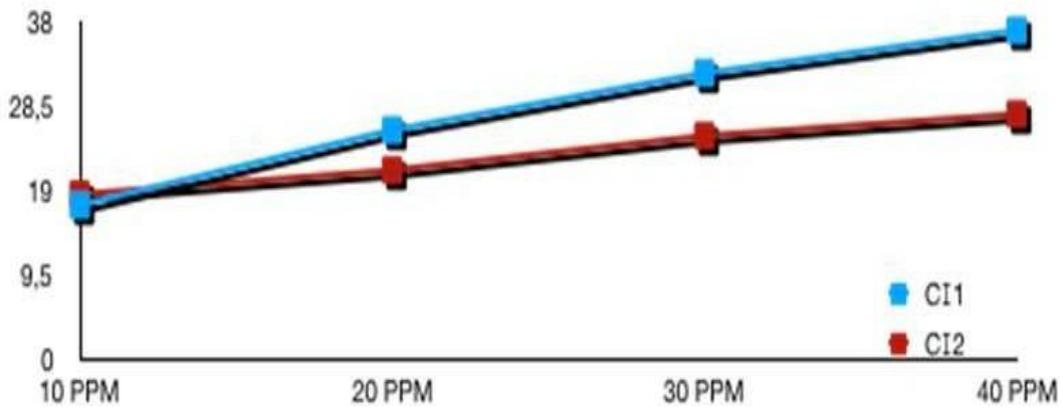
Inhibitor addition	0.1 N MCAA (240 hrs.)			0.5 N MCAA (240 hrs.)			1N MCAA (240 hrs.)			2N MCAA (240 hrs.)		
	$\eta\%$	$\theta$	$\log(\frac{\theta}{1-\theta})$	$\eta\%$	$\theta$	$\log(\frac{\theta}{1-\theta})$	$\eta\%$	$\theta$	$\log(\frac{\theta}{1-\theta})$	$\eta\%$	$\theta$	$\log(\frac{\theta}{1-\theta})$
Uninhibited	----	----	----	----	----	----	----	----	----	----	----	----
CI <sub>1</sub>												
10 ppm	11.94	0.1194	-0.8677	03.65	0.0365	-1.4215	42.53	0.4253	-0.1307	27.55	0.2755	-0.4199
20 ppm	17.29	0.1729	-0.6797	19.58	0.1958	-0.6135	44.09	0.4409	-0.1031	42.99	0.4299	-0.1225
30 ppm	20.44	0.2044	-0.5902	24.02	0.2402	-0.5001	49.75	0.4975	-0.0043	50.35	0.5035	0.0060
40 ppm	24.84	0.2484	-0.4808	29.24	0.2924	-0.3838	50.49	0.5049	0.0085	57.24	0.5724	0.1297
CI <sub>2</sub>												
10 ppm	00.94	0.0094	-2.0227	27.41	0.2741	-0.4229	56.96	0.5696	0.1216	59.61	0.5961	0.1690
20 ppm	01.57	0.0157	-1.7972	34.46	0.3466	-0.2753	60.19	0.6019	0.1795	66.50	0.6650	0.2977
30 ppm	06.28	0.0628	-1.1738	45.16	0.4516	-0.0843	64.67	0.6467	0.2625	74.58	0.7458	0.4674
40 ppm	14.77	0.1477	-0.7612	47.51	0.4751	-0.0432	66.41	0.6641	0.2960	76.48	0.7648	0.5121

**Table :5**  
**Reaction Number (RN) and percentage inhibition ( $\eta\%$ ) for Aluminium in TCAA solution with inhibitor additions**

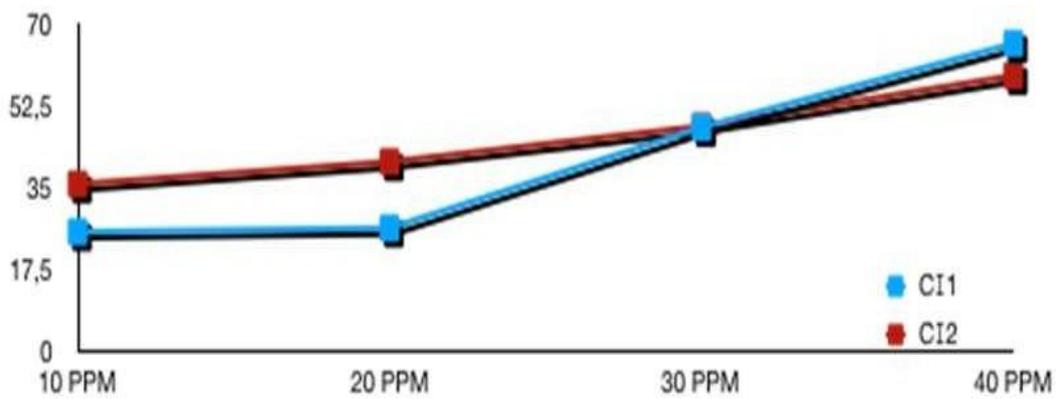
Inhibitor	1N TCAA		2N TCAA		3N TCAA	
	RN	$\eta\%$	RN	$\eta\%$	RN	$\eta\%$
Uninhibited	20.66		46.41		1.44	
Cl <sub>1</sub>						
10 ppm	14.00	32.23	20.81	55.16	1.06	26.38
20 ppm	11.33	45.15	18.40	60.35	0.57	60.41
30 ppm	10.00	51.59	14.44	68.88	0.66	54.16
40 ppm	07.33	64.50	10.45	77.48	0.29	79.86
Cl <sub>2</sub>						
10 ppm	18.03	12.72	16.80	63.80	0.62	56.94
20 ppm	14.64	29.13	12.83	72.35	0.52	63.88
30 ppm	12.01	41.86	11.20	75.86	0.35	75.69
40 ppm	06.02	70.86	08.42	81.85	0.22	84.72

**Table :6**  
**Reaction Number (RN) and percentage inhibition ( $\eta\%$ ) for Aluminium in MCAA solution with inhibitor additions**

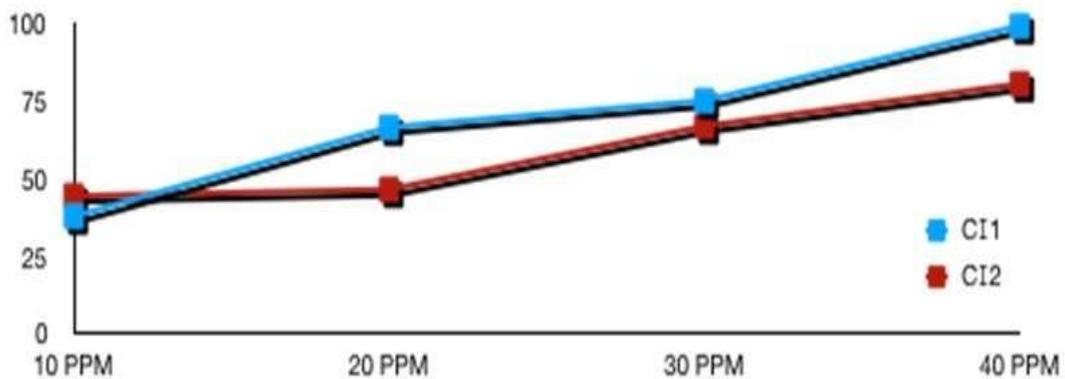
Inhibitor	1N MCAA		2N MCAA		3N MCAA	
	RN	$\eta\%$	RN	$\eta\%$	RN	$\eta\%$
Uninhibited	1.56		3.23		2.51	
Cl <sub>1</sub>						
10 ppm	1.26	19.23	2.31	26.48	1.93	23.10
20 ppm	1.20	23.07	2.20	31.88	1.42	43.42
30 ppm	0.93	40.32	2.08	35.60	1.25	50.19
40 ppm	0.86	44.74	1.98	38.69	0.91	63.74
Cl <sub>2</sub>						
10 ppm	1.23	21.15	0.61	81.11	1.64	34.66
20 ppm	1.19	23.71	0.20	38.08	1.33	47.01
30 ppm	0.89	42.94	2.30	28.79	1.04	58.56
40 ppm	0.82	47.43	1.53	52.63	0.73	70.91



**Fig.1:** Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 0.1 N TCAA



**Fig.2:** Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 0.5 N TCAA



**Fig.3:** Variation of inhibition efficiency with concentration of inhibitor for Aluminium in 1N TCAA

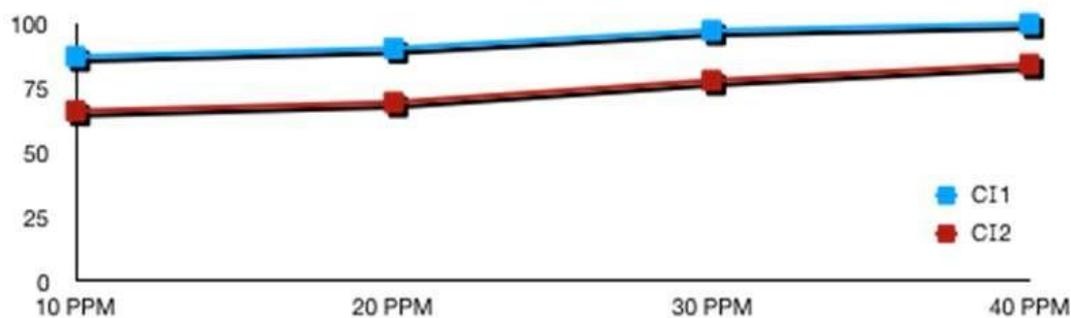


Fig.4: Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 2 N TCAA

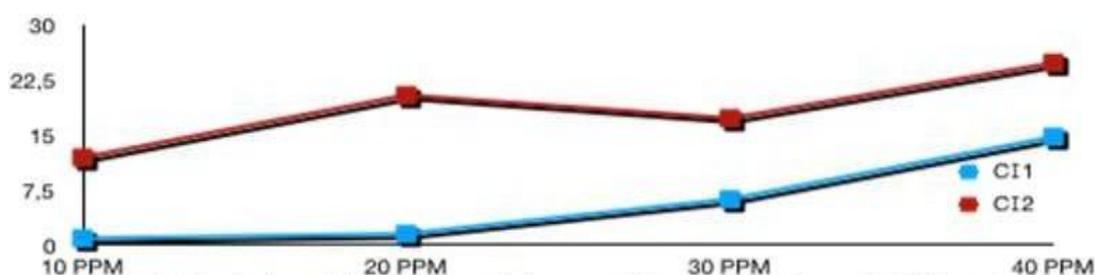


Fig.5: Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 0.1 N MCAA

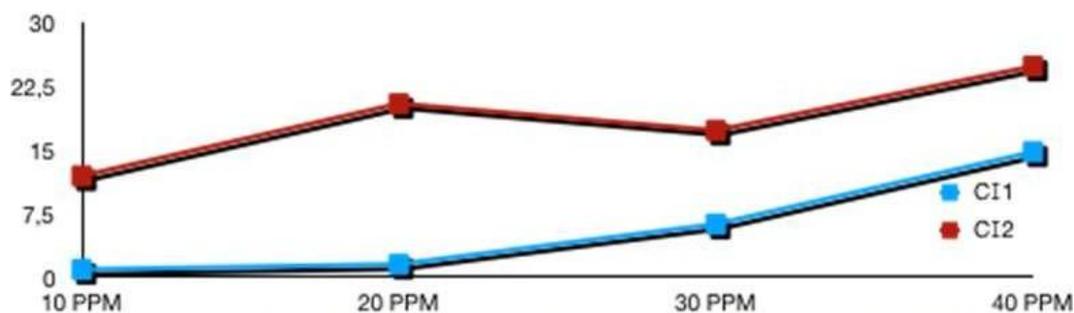


Fig.5: Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 0.1 N MCAA

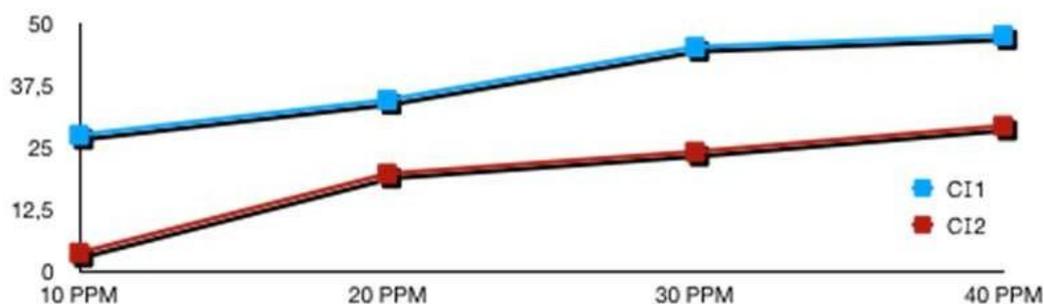


Fig.6: Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 0.5 N MCAA

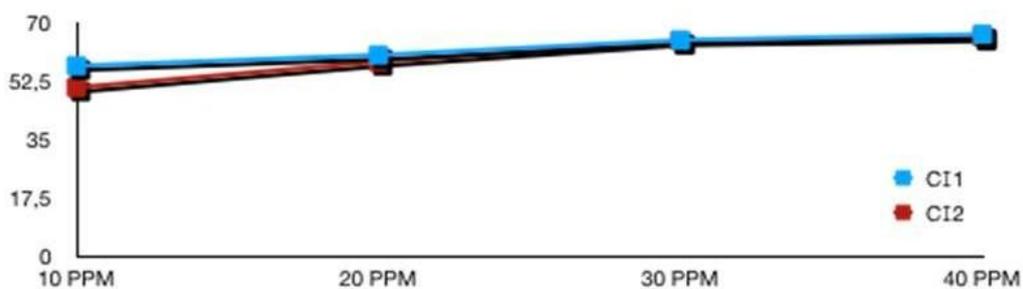


Fig.7: Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 1 N MCAA

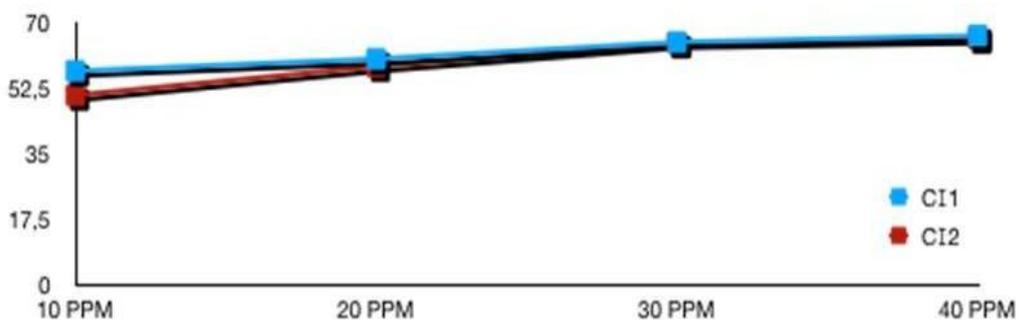


Fig.7: Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 1 N MCAA

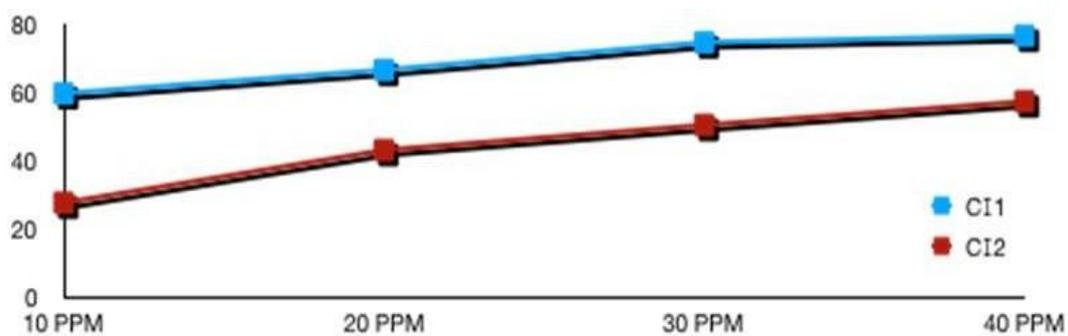


Fig.8: Variation of inhibition efficiency with concentration of inhibitor for Aluminum in 2 N MCAA

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