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STUDY OF CORROSION INHIBITION EFFICIENCY OF SOME SCHIFF'S BASES ON ALUMINIUM IN TRICHLOROACETIC ACID SOLUTION

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Weight loss and thermometric methods have been used to study the corrosion inhibition of aluminium in trichloroacetic acid (TCA) solution by three newly synthesised Schiff bases viz. *N*-(4-*N*,*N*-dimethylamino)benzylidene-4-methoxyaniline (SB_1),*N*-(4-*N*, *N*-dimethylamino)benzylidene-2-methylaniline (SB_2) and *N*-(4-*N*,*N*-dimethylamino)benzylidene-3-methylaniline (SB_3). Results of inhibition efficiencies obtained from two methods are in good agreement with each other. Efficiency increases with increasing concentration of inhibitors as well as that of TCA solution.

INTRODUCTION

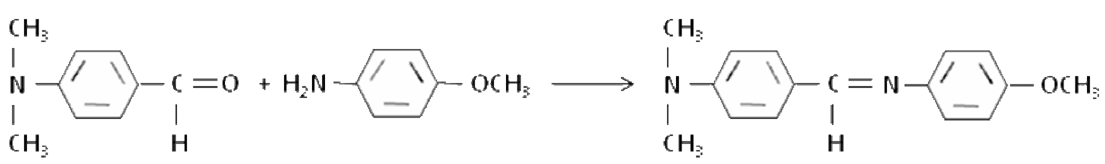
Aluminium, being an industrially important metal, is subjected to corrosion in service by various corrosive agents of which the aqueous acids are the most dangerous. The corrosion of aluminium and its alloys in TCA solution has been extensively studied.[1-4] Some workers have studied corrosion inhibition efficiency of Schiff's bases for aluminium in HCl solution.[5-8] The effect of nitrogen containing compounds such as amines,[9] various aldehydes[10] and heterocyclic compounds[11] on the dissolution of aluminium in TCA solution has also been evaluated. Among the compounds to have received attention as corrosion inhibitors for aluminium are Schiff bases derived from aliphatic and aromatic monoamines and diamines.[12]

In the present investigation, the inhibitive effect of three newly synthesised Schiff's bases viz.*N*-(4-*N*,*N*-dimethylamino)benzylidene-4-methoxyaniline (SB_1),*N*-(4-*N*,*N*-dimethylamino)benzylidene-2-methylaniline (SB_2) and *N*-(4-*N*,*N*-dimethylamino)benzylidene-3-methylaniline (SB_3) have been studied.

EXPERIMENTAL

The Schiff bases were synthesised by conventional methods i.e. by refluxing equimolar quantities of ethanolic solutions of corresponding aldehydes and amines in a round bottom flask (250 mL) for about 4-5 hours and then pouring the reaction mixture in ice cold water. Resulting crystals were filtered and then recrystallised by n-hexane which were dried and collected.

Ar CHO H_2N Ar Ar CH N Ar H_2O



(SB_1)*

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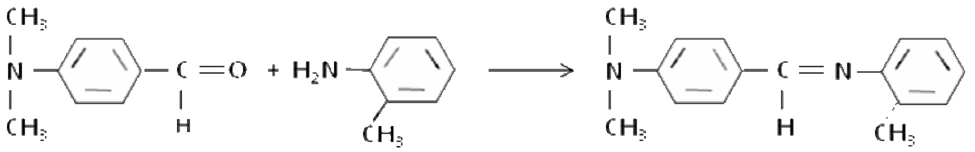
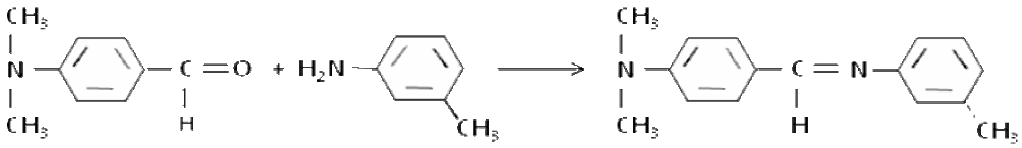


(SB_2)



(SB_3)

Rectangular specimens of aluminium of dimensions 2.0x2.0x0.03 cm containing a small hole of about 2 mm diameter near the upper edge were used for studying of corrosion rate. The chemical composition of the test specimen was 98.5% Al, 0.2% Fe, 0.2% Cu, 0.08% Zn, 0.08% Ti. Specimens were cleaned by buffing to produce a mirror finish and then they were degreased. 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 capillary tube in a beaker containing 50 mL of the test solution at $25 \quad 0.1^{o}C$. After the sufficient exposure, the specimens were cleaned by running water. Duplicate experiments were performed in each case and mean values of the weight loss were calculated.

The percentage inhibition efficiency was calculated[13] as

$$\eta\% \quad \frac{100\,(\ M_u - \ M_i)}{M_u}$$

where ΔM_u and ΔM_i are the weight loss of the metal in uninhibited acid and in inhibited solution respectively.

The degree of surface coverage θ can be calculated as[14]

$$\frac{M_u - \ M_i)}{M_u}$$

where ΔM_u and ΔM_i are the weight loss of the metal in uninhibited acid and in inhibited solution respectively.

Inhibition efficiencies were also determined by using the thermometric technique. This involved the immersion of single specimen measuring $2.0 \quad 2.0 \quad 0.03$ cm in a reaction chamber containing 50 mL of solution at an initial temperature of $25 \quad 0.1^{o}C$. Temperature changes were measured at intervals of 5 min. using a thermometer with a precision of 0.1^{o} C. The temperature increased slowly at first, then rapidly and attained a maximum value before falling. The maximum temperature was recorded.

Percentage inhibition efficiencies (η%) were calculated[15] as

$$\eta\% \quad \frac{100(RN_f - RN_i)}{RN_f}$$

Where RN_f and RN_i are the reaction number in the absence and in presence of inhibitor respectively and RN ($Kmin^{-1}$) is defined as

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

Where T_m and T_i are the maximum and initial temperature respectively, and t is the time (in min.) required to reach the maximum temperature.

RESULT AND DISCUSSION

Loss in weight and percentage inhibition efficiency for various concentrations of acid and inhibitors are given in Table-1. It can be seen that the inhibition efficiency increases with increase in concentration of inhibitor. It is also evident from the Table-1 that inhibition efficiency improves with increasing concentration of acid and that all inhibitors display maximum efficiency at the highest concentration of acid used (i.e. 2N). All the inhibitors reduce corrosion rate to a significant extent. The highest efficiency was shown by SB_1 for which a maximum value of 98.5% was obtained at an inhibitor concentration of 0.8% in 2N TCA. The corresponding values of surface coverage are shown in Table-2.

Inhibition efficiencies were also determined using the thermometric method. Temperature changes for Al in 0.5N, 1N and 2N TCA were recorded with various inhibitor concentrations. Since, no significant temperature changes were recorded in the inhibited 0.1N TCA solution, therefore, use of thermometric method was restricted to 0.5N to 2N TCA solution. The results summarized in Table-3 are in good agreement with those obtained from the weight loss measurements. As in the case of the weight loss data, the maximum efficiency is obtained with the highest concentration of SB_1 (0.8%) in the highest concentration of acid (2N TCA). The variation of reaction number with inhibitor concentration presented graphically in Fig-1 for 2N TCA shows almost linear behaviour, with the negative slope indicating that the reaction number decreases with increasing inhibitor concentration.

Table 1

Weight loss ΔM and inhibition efficiency (η%) for Aluminium in TCA solution with given inhibitor addition at 25 0.1°C

Inhibitor addition	0.1N TCA (24 hr.)		0.5N TCA (70 min.)		1N TCA (23 min.)		2N TCA (14 min.)	
	ΔM,mg	**η%**	**ΔM,mg**	**η%**	**ΔM,mg**	**η%**	**ΔM,mg**	**η%**
Uninhibited	**158**	----	**202**	----	**208**	----	**278**	----
SB_1								
0.2%	86.0	45.5	95.0	52.9	87.0	58.1	7.0	97.4
0.4%	82.0	48.1	92.0	54.4	77.0	62.9	6.0	97.8
0.6%	71.0	55.0	88.0	56.4	60.0	71.1	5.0	98.2
0.8%	59.0	62.6	70.0	65.3	47.0	77.4	4.0	98.5
SB_2								
0.2%	92.0	41.7	107.0	47.0	96.0	53.8	26.0	90.6
0.4%	86.0	45.5	98.0	51.4	84.0	59.6	22.0	92.0
0.6%	77.0	51.2	90.0	55.4	77.0	62.9	21.0	92.4
0.8%	69.0	56.3	83.0	58.9	69.0	66.8	15.0	94.6
SB_3								
0.2%	100.0	36.7	114.0	43.5	101.0	51.4	30.0	89.2
0.4%	95.0	39.8	105.0	48.0	91.0	56.2	26.0	90.6
0.6%	89.0	43.6	93.0	53.9	82.0	60.5	23.0	91.7
0.8%	74.0	53.1	89.0	55.9	71.0	65.8	18.0	93.5

Table 2

Inhibition efficiency (η%) and surface coverage (*θ*) for Aluminium in TCA solution with given inhibitor addition at 25 0.1°C

Inhibitor addition	0.1N TCA (24 hr)			0.5N TCA (70 min)			1N TCA (23 min)			2N TCA (14 min)		
	η%	***θ***	**log** $\frac{}{1}$	**η%**	***θ***	**log** $\frac{}{1}$	**η%**	***θ***	**log** $\frac{}{1}$	**η%**	***θ***	**log** $\frac{}{1}$
Uninhibited	---	---	---	---	---	---	---	---	---	---	---	---
SB_1												
0.2%	45.5	0.455	-0.078	52.9	0.529	0.050	58.1	0.581	0.141	97.4	0.974	1.57
0.4%	48.1	0.481	-0.033	54.4	0.544	0.076	62.9	0.629	0.214	97.8	0.978	1.64
0.6%	55.0	0.550	0.087	56.4	0.564	0.111	71.1	0.711	0.390	98.2	0.982	1.73
0.8%	62.6	0.626	0.223	65.3	0.653	0.274	77.4	0.774	0.534	98.5	0.985	1.81
SB_2												
0.2%	41.7	0.417	-0.145	47.0	0.470	-0.052	53.8	0.538	0.064	90.6	0.906	0.983
0.4%	45.5	0.455	-0.078	51.4	0.514	0.024	59.6	0.596	0.168	92.0	0.920	1.060
0.6%	51.2	0.512	0.020	55.4	0.554	0.094	62.9	0.629	0.229	92.4	0.924	1.08
0.8%	56.3	0.563	0.110	58.9	0.589	0.156	66.8	0.668	0.303	94.6	0.946	1.24
SB_3												
0.2%	36.7	0.367	-0.236	43.5	0.435	-0.113	51.4	0.514	0.024	89.2	0.892	0.916
0.4%	39.8	0.398	-0.179	48.0	0.480	-0.034	56.2	0.562	0.108	90.6	0.906	.0.983
0.6%	43.6	0.436	-0.111	53.9	0.539	0.067	60.5	0.605	.0.184	91.7	0.917	1.04
0.8%	53.1	0.531	0.053	55.9	0.559	0.102	65.8	0.658	.0.283	93.5	0.935	1.15

Table 3

Reaction Number (RN) and inhibition efficiency (η%) for Aluminium in TCA solution with given inhibitor addition at 25 $0.1^{o}C$

Inhibitor addition	0.5N TCA (70min.)		1N TCA (23 min.)		2N TCA (14 min.)	
	RN, $Kmin^{-1}$	η%	RN, $Kmin^{-1}$	η%	RN, $Kmin^{-1}$	η%
Uninhibited	0.168	-----	0.847	-----	0.857	-----
SB_1						
0.2%	0.081	51.7	0.360	57.4	0.050	94.1
0.4%	0.077	54.1	0.330	61.0	0.042	95.0
0.6%	0.075	55.3	0.265	68.7	0.028	96.7
.0.8%	0.062	63.0	0.208	75.4	0.021	97.5
SB_2						
0.2%	0.092	45.2	0.404	52.3	0.092	89.2
0.4%	0.084	50.0	0.352	58.4	0.085	90.0
0.6%	0.075	55.3	0.330	61.0	0.071	91.7
0.8%	0.072	57.1	0.304	64.1	0.057	93.3
SB_3						
0.2%	0.098	41.6	0.439	48.1	0.100	88.3
0.4%	0.092	45.2	0.382	54.8	0.092	89.2
0.6%	0.082	51.1	0.356	57.9	0.078	90.8
0.8%	0.080	52.3	0.313	63.0	0.064	92.5

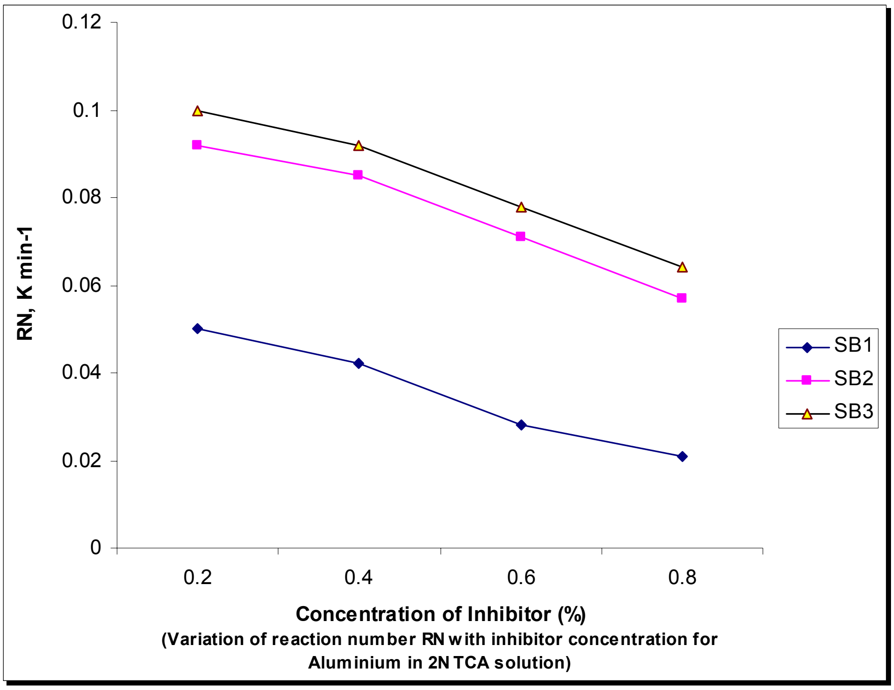


Fig. 1

Generally, the adsorption of organic molecules on a metallic surface involves oxygen, nitrogen and sulphur atoms and, in some cases, selenium and phosphorus. In the case of Schiff bases, oxygen and nitrogen atoms are responsible for the adsorption. This process may block active sites on metallic surface and hence, decreases the corrosion of the metal. The nitrogen atoms of the Schiff bases act as the reaction centre (polar function) because of its higher electron density resulting in the formation of a monolayer on the metal surface.

The $-OCH_3$ group present in 4-methoxyaniline exerts a positive mesomeric effect (+M > - I) which increase the electron density at the nitrogen atom. This explains the higher inhibitor efficiencies dislayed by *N*-(4-*N*,*N*-dimethylamino)benzylidene-4-methoxyaniline(SB_1). It has been observed that the inhibition efficiency increases as the acid concentration increases. This may be possibly due to more ionisation of Schiff base in presence of strong acid and thus causing more adsorption on metallic surface.

Adsorption plays an important role in the inhibition of metallic corrosion by organic inhibitors. Many investigators have used the Langmuir adsorption isotherm to study inhibitor characteristics.[16-17] Assuming that the inhibitors adsorbed on the metal surface decrease the surface area available for cathodic and anodic reaction to take place. Hoar and Holliday[16] have shown that the Langmuir isotherm.

$$\log [\theta/1-\theta] = \log A + \log C - (Q/2.303\ RT]$$

should give a straight line of unit gradient for the plot of log [θ/1-θ] *versus* logC, where A is a temperature independent constant, C is the bulk concentration of the inhibitor (percentage) and Q is the heat evolved during adsorption.

The corresponding plots, shown in Fig. 2 for 2N TCA are linear but the gradients are not equal to unity as would be expected for the ideal Langmuir adsorption isotherm equation. This deviation from unity may be explained on the basis of the interaction among the adsorbed species on the metal surface. It has been postulated in the derivation of the Langmuir isotherm equation that the adsorbed molecules do not interact with one another, but this is not true in the case of organic molecule having polar atoms or groups which are adsorbed on the anodic and cathodic sites of the metal surface. Such adsorbed species may interact by mutual repulsion or attraction. Thus, it is also possible for inhibitor molecules that are adsorbed on anodic and cathodic sites to interact with metallic surface as well as with each other.

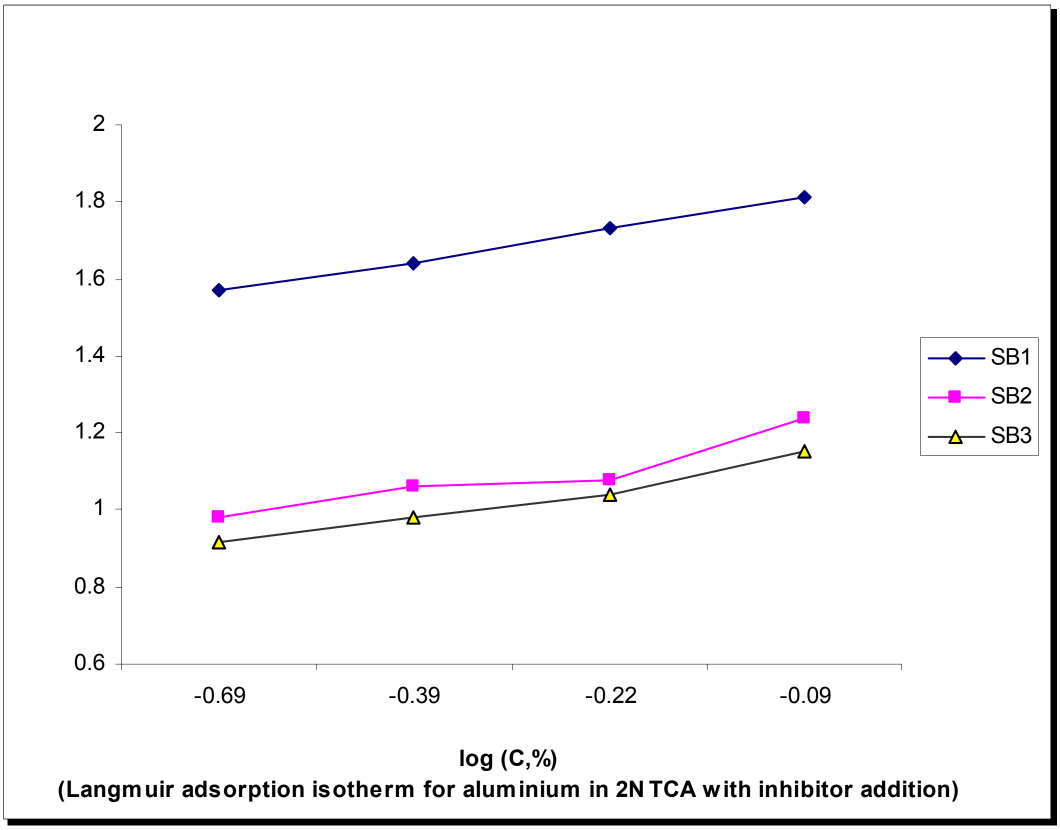


Fig. 2

CONCLUSION

A study of three newly synthesised Schiff bases (SB_1, SB_2 and SB_3) has shown them to be effective inhibitors for corrosion of aluminium in TCA solution.

Both weight loss and thermometric determinations have shown that the inhibition efficiency of Schiff bases increases with increasing concentration of acid and inhibitor.

Among the compound under investigation, the highest inhibition efficiencies (up to 98.5% in 2N

TCA) were shown by SB_1 at a concentration of 0.8%. Both methods show same trends in corrosion efficiency and results are in good agreement with each others.

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