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EFFECT OF INHIBITORS ON THE CORROSION BEHAVIOR OF ALUMINIUM AND ITS ALLOY IN ALKALINE ELECTROLYTE

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Abstract- The effect of thiosemicarbazone on hydrogen permeation and corrosion inhibition of aluminium alloys in alkaline medium has been studied using weight loss and various electrochemical corrosion monitoring techniques. Correlation of the structural changes with the protection efficiency of ApTSCN, SaTSCN, 2meTSCN with the parent TSC was reported. The compound brings down corrosion of aluminum alloys in alkaline medium. Electrochemical polarization measurements indicate that thiosemicarbazones perform as mixed-type inhibitor. The extent of hydrogen permeation current through aluminium alloys surfaces has been studied by the adoption of modified devanathan-stachurki's two component cell method.

Keywords: Aluminium alloys, Thiosemicarbazones, Alkaline corrosion, Inhibition efficiency, hydrogen permeation

I.INTRODUCTION

Earlier studies have revealed that the use of suitable aluminum alloy together with sodium hydroxide solution containing calcium oxide and sodium citrate to mitigate the problem to some extent. The use of inhibitors to combat corrosion in such situation is one of the well-known methods. The action of an inhibitor in aggressive media is presumed to be due to the control of the kinetics of the partial reactions of the corrosion process and/ or due to its adsorption at the metal solution interface. This phenomenon could take place via (i) electrostatic attraction between the charged metal and the charged inhibitor molecules, (ii) dipole type of interaction between uncharged parts in the inhibitor with the metal, (iii) π -interaction with the inhibitor metal surfaces (iv) a combination of all the above [1].

If the adsorption process involves charge sharing or charge transfer from the inhibitor molecules to the surface (meaning overlap of occupied ligand non — bonding orbitals with metal empty inner "d" or "f' orbitals) a co-ordinate type bond is formed and the process is termed as chemisorption [2]. This situation can arise if the inhibitor molecule contains lone pairs of electrons or multiple bonds of conjugate π - type system [3-7].

The use of thiosemicarbozones as inhibitors for the corrosion of aluminum in alkaline media has been discussed at length.

Following the clue from these papers, some thiosemicarbozone have been synthesized, characteriszed and evaluated as additives in the battery electrolyte for the corrosion inhibition of aluminum and its chosen alloy.

II.PREPARATION OF ALUMINIUM-ALLOY AND ITS CHARACTERIZATION

Aluminum-alloys of the following composition were prepared using graphite crucible by weighing the constituents.

Alloys:

- 1. A1+0.0% Pb +0.1% Ga+1%In
- 2. A1+0.5% Pb +0.1% Ga+1%In
- 3. A1+1.0% Pb +0.1% Ga+1%In
- 4. A1+1.5% Pb +0.1% Ga+1%In
- 5. A1+2.0% Pb +0.1% Ga+1%In

Of the various compositions (expected based on the weights mixed) given above, it is found that the aluminium - alloy of Al + 1.5% Pb + 0.1% Ga+ l% In composition to be the best showing minimum self-corrosion. Hence this alloy was characterized by AAS studies for its precise composition.

A. PREPARATION OF THE BATTERY ELECTROLYTES

The battery electrolyte used was prepared using 160gm of NaOH, 200gmof sodium citrate and 4gm of CaO per litre in distilled water. The chemicals used were of high purity.

B. SYNTHESIS OF CORROSION INHIBITORS

The thiosemicarbazones prepared were the condensation product of the respective carbonyl compounds with thiosemicarbazide in presence of 10% HCl as the catalyst [8]. Equimolar ratio of the two compounds were mixed together and the reaction mixture was refluxed with stirring for about three hours. Upon cooling, the precipitated products were filtered off, washed with ethanol and ether and dried in vacuum. The products obtained were re-crystallized from ethanol twice [9].

C. U.V STUDIES

The peak corresponding to λ_{mzx} at 304nm obtained for the electrolyte may be correlated with the weak Ca²⁺-citrate complex that exists in the solution. The absorption of > C =S appears only as a shoulder or inflection and its diagnostic value is questionable and the λ_{mzx} corresponding to 336nm may indicate this [10].

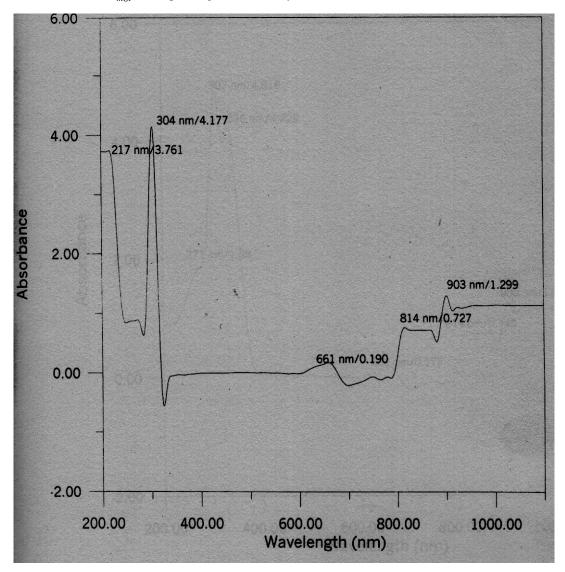


Figure (i). UV-Visible spectrum of battery electrolyte

Name of the Compound	Structure	Short Name
Thiosemicarbazide	S ⊒ 2HN — NH — C — NH ₂	TSC
Accetophenonethio semicarbazone	$ \begin{array}{c} C_6H_5 \\ CH_3 \end{array} C=N-NH-C-NH_2 $	ApTSCN
Salicylaldehydethio semicarbazone	OH S C—N—NH—C—NH ₂	SaTSCN
2- methylbezaldehyde thiosemicarbazone	C=N-NH-C-NH ₂ CH ₃	2meTSCN

D. ATOMIC ABSORPTION SPECTROSCOPY

The atomic absorption spectroscopy is an effective tool used to find the composition of the alloying materials In the present investigation among the aluminium alloys, the alloy of made out composition 97.4% Al, 0.1% Ga, 1% In. 1.5% Pb was found to be the best and hence it is analysed through AAS for its exact composition The composition of pure aluminium and the alloy specified are presented below The exact composition of the alloys more or less match with that of the expected composition prepared by weight percentage of the constituent.

E. METHODS OF EVALUATION OF SELF CORROSION OF ALUMINIUM / ITS ALLOY

WEIGHT LOSS MEASUREMENT

Aluminium specimens of size (4 x 1 x 0.2cm) were used for weight loss measurements. A small hole was punched near the upper edge of the specimen for hanging them through glass hooks into the experimental solutions. They were given necessary pretreatments such as polishing, pickling in suitable bath [11] and degreasing with trichloroethylene. The volume of the solution used in each experiment was 100ml. The initial weights of the specimens were noted. The specimens were completely immersed into the experimental solution. The duration of the experiment was three hours. At the end of three hours the specimens were taken out pickled, washed with distilled water, dried and their final weights were recorded. The loss in weights were calculated. Weight loss measurements were performed for pure aluminium as well as for its alloy in 4N NaOH and in battery electrolytes without and with the presence of the inhibitors.

F. GASOMETRIC STUDIES

The gasometric technique has been adopted by Nathan [12] Hakerman [13] and Hassan Shawky [14] for the study of iron and aluminium largely for inhibition effects. Mathur [15] et al have designed a gasometric unit using which corrosion rates can be monitored under controlled conditions of temperature and pressure without the need for any aqueous tension correction. The same type of setup was used in the present study. The size of the metal specimen was the same as that utilized for weight loss studies. The volume of the electrolyte used in each experiment was l00ml. The temperature and pressure were maintained constant throughout the experiments at 30°C and 1 atmospheric pressure. The experiment was carried out for two hours. The volume of the gas evolved was measured at time intervals of 15 minutes.

Gasometric studies were made for pure aluminium as well as aluminium — alloy in 4N NaOH and in battery electrolyte without and with addition of the inhibitors at their best protecting concentration. The inhibitor efficiency was calculated using the formulae.

I.E (%) =
$$\frac{V_0 - V_1}{V_0}$$
 x 100

Where V_0 and V_1 are the volumes of hydrogen liberated in the absence and presence of the inhibitor respectively.

G. SPECTROPHOTOMETRIC ANALYSIS

The solutions after weight loss studies in the case of control and best inhibiting case have been analysed through colorimetric methods to reinforce the results of the other studies. The colorimetric determination of aluminium present in solution was determined using Erio-chrome cyanine- R dye. This dye gives colored complex at λ_{max} 535nm [16].

H. ELECTROCHEMICAL POLARIZATION MEASUREMENTS

The polarization studies were carried out for a1minium - alloy specimens without and with the addition of inhibitors in 4N NaOH as well as in battery electrolyte.

The measurements were carried using corrosion measurements system (EG & G Electrochemical Impedance Analyzer Model 6310). A three electrode cell assembly was used. The working electrode used was a rectangular specimen of aluminium, with one face of the electrode of constant 1cm² area exposed and the rest being shielded with red acquer. A rectangular platinum foil was used as the counter electrode. The area of the counter electrode was much larger compared to the area of the working electrode. This can exert a uniform potential field on the working electrode and minimize the polarization effect on the counter.

The reference electrode used was Hg/ HgO/ 4N NaOH. The reference electrode was placed close to the working electrode to minimize IR contribution. A time interval of about 5 to 10min was given for the working electrode to attain a steady state open circuit potential. Polarization was carried out from a cathodic potential of -1700mV to an anodic potential of -1000mV at constant scan rate 1mV/sec. The results such as inhibition efficiency, Tafel slopes, E_{cor} and i_{corr} values are presented.

I. HYDROGEN PERMEATION MEASUREMENTS

Thin aluminium foil was used for the study. The specimens were mechanically polished and degreased with trichloroethylene AR grade sodium hydroxide and BDH grade palladium chloride was used Conductivity water was used for solution preparations.

One side on the membrane was electroplated with a thin layer of palladium by the following procedure.

Lacquer was applied on to one side of the membrane and the specimen was cathodically cleaned The membrane was electroplated with a thin layer of palladium from a solution of palladium chloride (0.8g/l) at a current density of $100~\mu$ A cm⁻² for 90 minutes with stainless steel anode. The specimens after repeated washings with distilled water were dried and kept in desiccators after removing the lacquer coatings on the other side. The purpose of palladium coating is to catalyse the hydrogen ionization, which is accounted as the permeation current.

The cell used for electro permeation study was similar to the one used earlier by Devananthan[17].

The cell has two compartments and they were connected through Teflon bushings, clamped between two stainless steel sheets suitably held intact The teflon stoppers were provided with a hole of inner area approximately equal to 1cm2 Both the compartments have provisions for inserting platinum auxiliary electrode and Hg/HgO/4N NaOH reference electrode.

J. MEASUREMENT OF PERMEATION CURRENT

The palladised aluminium membrane was fixed in between teflon bushings and clamped tightly The compartment facing the palladium plated side was filled with 0.2N NaOH solution which was pre-electrolyzed for a period of 24 hours at a constant current of $100~\mu$ A. The Hg/HgO/0.2 NaOH reference electrode and platinum auxiliary electrode were introduced to complete the circuit The cell was connected to a potentiostat and a constant potential of-300mV (vs Hg / HgO, OH $^-$) was applied to the specimen It has been shown by Srinivasan et al [11] that —300mV is the most suitable potential for ionizing the diffused hydrogen rapidly and efficiently at Pd /0.2N NaOH interface When the initial current had gradually decreased and reached a steady value, the other compartment facing non-plated side was filled with the test solution (electrolyte or

inhibitor solution) and the non- plated side was allowed to corrode and the permeation current was simultaneously recorded Finally the steady state permeation current was noted. The permeation current was measured for electrolyte solutions with and without the inhibitors.

III.RESULTS AND DISCUSSION

A. STUDIES ON THE CORROSION BEHAVIOUR OF ALUMINIUM AND SOME OF ITS ALLOYS

A.1. WEIGHT LOSS AND GASOMETRIC STUDIES

In alkaline medium the Al³⁺ formed is readily complexed with OH, ions resulting in the formation of A1O₂ [18]

$$AI^{3} + 4OH^{-}$$
 $AI(OH)_{4}^{-}$ ----- (1)
 $AI(OH)_{4}^{-}$ $AIO_{2}^{-} + 2H_{2}O$ ----- (2)

The reduction of water occurs simultaneously on the metal surface.

$$H_2O + e^ H + OH^-$$
(3) $H_2 + H_2$ $H_2 -----$ (4)

Due to low hydrogen over potential on aluminium substrate there is profuse evolution of hydrogen as aluminium corrodes in NaOH In another scheme the formation of Al^+ initially which converts into Al^{3+} subsequently is also predicted [19].

AI
$$A1^{3+}3e^{-}$$
 E=0-1.7V ------ (5)
AI AI^{+} e^{-} -----(6)
AI³⁺ + 2H₂O AI^{3+} + H₂ + 2OH² -----(7)

The corrosion results of pure aluminium in 4N NaOH and battery electrolyte (4N NaOH + 20% Sodium citrate + 0 1% CaO) are presented as weight loss results in Table 1. It is noted that the corrosion rate of aluminium is reduced by nearly 16% in the battery electrolyte This is due to the Ca²⁺ and citrate ion probably forming a complex and the complex compound getting physically adsorbed with the calcium disposed towards the aluminium surface having high negative potential in the alkaline medium Such types of reduction in the corrosion behaviour of aluminium in alkaline medium with the presence of Ca²⁺ and salicylate ion or phthalate ions also reported [20] Further it is reported that some zinc based aluminium alloys having gallium, indium, thallium and bismuth in small proportions perform as good galvanic anodes in alkaline medium [21-23] suitable for cathodic protection and for aluminium-air batteries. Hence in the present investigation instead of zinc a lead based aluminium alloy having indium and gallium in small proportions have been tried in the battery electrolyte and the results are presented in the following table. It is noted that as the concentration of lead in the aluminium alloy increases from 0% to 1.5% the corrosion inhibition efficiency of the alloy electrode in the battery electrolyte is increased. This may be due to the high hydrogen over potential of lead in the alloy. However with further increase to 2% there is fall in the efficiency. At relatively higher concentration of lead, there may be phase segregation of lead dominated intermetallic region forming a noble phase, making aluminium vulnerable to enhanced corrosion.

Gasometric studies under controlled conditions of temperature and pressure are possible, as there is quantitative hydrogen evolution governed by defined stoichiometry mentioned earlier. The results are presented in Table 2 These results are in conformity with weight loss results. From the studies it is identified that aluminium alloy of composition 97.4% Al +1.5% Pb +0.1% Ga +1% In) in 4N NaOH blended with 20% citric acid and 0.4% CaO results in minimum self-corrosion.

Table 1. Corrosion parameters of pure aluminium and its alloys in 4N NaOH and electrolyte by weight loss method

Metal Composition	Electrolyte	Corrosion Rate (mdd) x10 ³	% of inhibition (I.E)
Pure Aluminium	4N NaOH	228	
Pure Aluminium	Battery Electrolyte	192	15.17
Al+ X +0% Pb	"	182	20.79
Al+ X +0.5% Pb	"	144	24.84
Al+ X +1.0% Pb	"	140	27.03
Al+ X +1.5% Pb	"	136	29.00
Al+ X +2.0% Pb	"	144	24.95

X=0.1% Ga + 1% In

Table 2. Inhibition Efficiency (IE) for aluminium and its alloys in 4N NaOH and electrolyte by gasometric method

			Time in minutes						IE	
Metal Composition	Electrolyte	5	10	15	30	45	60	75	90	(%)
			Volume of gas collected in ml					(70)		
Pure Al	4N NaOH	12.4	21.0	29.0	61.0	82.5	94.7	102.6	119.6	
Pure A1	Battery	7.2	12.6	18.5	37.4	55.7	70.2	88.4	104.8	24
Al+ X +0% Pb	Electrolyte	4.9	10.2	15.1	25.4	40.7	55.7	69.7	94.8	19
Al+ X +0.5% Pb		4.7	10.0	15.0	25.2	39.8	48.5	60.5	88.5	25
Al+ X +1.0% Pb		4.5	9.7	14.7	23.4	37.4	44.7	59.9	79.6	30
Al+ X +1.5% Pb		4.3	9.5	13.6	19.2	36.7	40.3	37.5	67.8	42
Al+ X +2.0% Pb		5.2	9.9	14.7	22.6	39.5	43.5	61.7	72.8	31

X=0.1% Ga + 1% In

Table 3. Corrosion parameters of Al+X+1.5 Pb in electrolyte at best protecting concentration by weight loss method

Inhibitors	Corrosion rate mdd x 10 ³	Equivalent corrosion current mA/cm ²	I.E%
Control	136	169	
ApTSCN	71	89	47
SaTSCN	73	90	46
2meTSCN	75	92	45

B. ELECTROCHEMICAL POLARISATION STUDIES

The cathodic and anodic polarization curves in 4N NaOH and battery electrolyte with pure aluminium and its alloys are presented in Fig. 1 and in Table 4 The i_{corr} values indicate that when 4N NaOH is blended with CaO and citrate ions, there is marked beneficial effect as far as the self corrosion of aluminium/aluminium- alloys are concerned. As in the weight loss and gasometric studies, aluminium with 1. 5 Pb + 0.1% Ga + 1% In is found to be the most corrosion resistant. However, the high open circuit potential values obtained with pure aluminium in 4N NaOH is lost to some extent, when the electrolyte is blended with the additives mentioned earlier. This is also the case with all the aluminium alloys. The potential values in the range of -1.3 to -1.36V (Vs Hg / HgO) have been reported for 2S electrolytic grade aluminium in similar battery electrolyte [24,25] Also the open circuit potential for 3S aluminium in 4N NaOH containing 0.6M ZnO is reported to be-l.369V (Vs Hg / HgO). [26] In all the cases the values of b_a and b_c are more or less equal indicating mixed control of the corrosion reaction. Further the alloying has not basically altered the dissolution mechanism of aluminium in the electrolytes The inhibitive effect of Ca-citrate complex in 4N NaOH is accounted through a buffer solution layer close to the metal surface showing a constant pH suitable for the formation of a physically adsorbed layer containing a Ca- citrate inhibitive complex [27] The mixed control of the corrosion of aluminium as well as its alloys in the battery electrolytes has been brought out by the results presented in Table 5. In this table the reduction in partial currents (I_a and I_c) taken at a common potential of Ecor ± 100 mV are presented. Still there are considerable difficulties in getting reproducible results in corrosion studies as it involves highly

heterogeneous metal surface with number of variables affecting the kinetics of the reaction to a greater extent Hence the estimation of the Tafel slopes is found to be naturally subjective in most cases. The reduction in partial currents under inhibited conditions with respect to the control taken at the common reference potential of $E_{corr} \pm 100 \text{mV}$ can be used to predict the nature of control of the corrosion reaction This procedure is well known [28-30] and it is nothing but the estimation of the Tafel slope at a reference potential in the Tafel region.

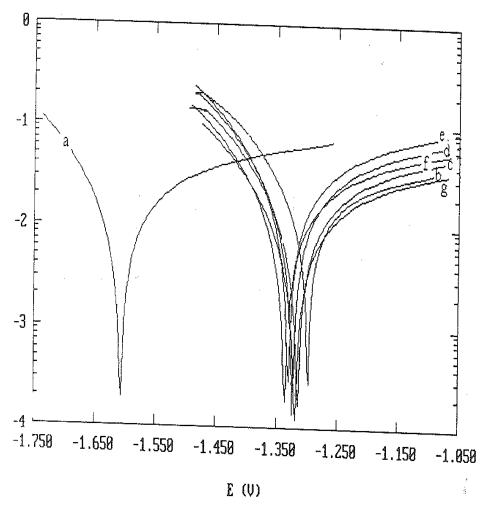


Figure.1 Electrochemical polarization curves of aluminium and its alloys in 4N NaOH and electrolyte.

a) Al-in 4N NaOH, b) Al 99.99%, c) Al+X+0%Pb, d) Al+X+0.5%Pb, e) Al+X+1% Pb, f) Al+X+1.5% Pb, g)
Al+X+2.0%Pb, (X-0.1% Ga+1% In) (b to g studies in battery electrolyte)

Table 4. Electrochemical polarization measurements of aluminium and its alloys in 4N NaOH and electrolyte

Metal Composition	Electrolyte	OCP (V)	F (V)	$i_{corr} (mA/cm^2)$	Tafel slope (1	mV/dec)	IE%
Wietai Composition	Electrolyte	OCF (V)	$\mathbf{E}_{\mathbf{corr}}(\mathbf{V})$		b_a	b_c	
Pure Al	4N NaOH	-1.500	-1.598	47.76	200	180	
Pure Al	Battery	-1.301	-1.297	40.59	185	165	15
	Electrolyte						
Al+ X +0% Pb	"	-1.325	-1.319	42.50	140	130	11
Al+ X +0.5% Pb	"	-1.324	-1.322	41.55	130	120	13
Al+ X +1.0% Pb	"	-1.316	-1.324	37.73	120	110	21
Al+ X +1.5% Pb	"	-1.318	-1.326	36.74	100	90	23
Al+ X +2.0% Pb	"	-1.320	-1.323	39.16	120	80	18

X=0.1% Ga + 1% In

Table 5. Reduction in partial currents at $E_{corr} \pm l00mV$ for aluminium and its alloys in 4N NaOH and electrolyte

Metal Composition	Electrolyte	E _{corr} (V)	Current at $E_{corr} \pm 100 \text{mV}$ (A)		% Reduction in partia Currents	
			Anodic Cathodic		Anodic	Cathodic
Pure Al	4N NaOH	-1.598	0.04950	0.02400		
Pure A1	Battery	-1.297	0.04090	0.01902	17	20
Al+ X +0% Pb	Electrolyte	-1.319	0.02944	0.01521	28	29
Al+ X +0.5% Pb		-1.322	0.02985	0.01350	27	28
Al+ X +1.0% Pb		-1.324	0.02903	0.01369	29	28
Al+ X +1.5% Pb		-1.326	0.02658	0.01255	35	34
Al+ X +2.0% Pb	1	-1.323	0.03067	0.01407	25	26

X=0.1% Ga + 1% In

Table 6. Inhibition efficiency (I.E) for Al + X + 15 Pb in electrolyte at best protecting concentration by gasometric method

	TIME in minute								
Inhibitors	5	10	15	30	45	60	75	90	I.E (%)
	Volume of gas collected in ml								
Control	6.1	10.9	15.9	32.8	52.7	67.2	84.2	99.0	
ApTSCN	3.3	5.9	9.0	16.8	28.1	35.5	44.5	52.4	46
SaTSCN	3.3	5.9	8.9	16.8	28.0	35.6	44.8	52.5	46
2meTSCN	3.3	6.0	9.1	17.1	28.4	36.1	45.4	53.4	45

C. STUDIES WITH AI — ALLOY

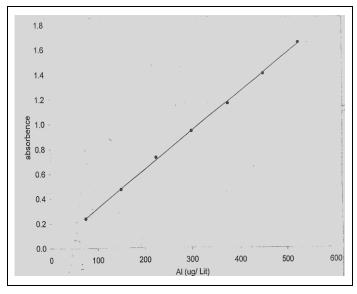


Figure.2 Calibration curve for aluminium in electrolyte

Aluminium-alloy of composition Al + X + 1.5% Pb has been evaluated for its dissolution behavior in the battery electrolyte with and without the inhibitors at the best protective concentration through weight loss and gasometric studies. The results are presented in Tables 3 and 6 respectively. Both the studies reveal the same trend as for pure aluminium except for a marginal increase of about 4-5% in the corrosion inhibition performance.

D. WITH ALUMINIUM - ALLOY ELECTRODE

The polarization results with aluminium — alloy of composition mentioned earlier in battery electrolyte are presented in Table 7 and in Fig 2. The same trend of results as for pure aluminium is revealed From the Table 8 where partial currents at the common reference potential are presented, the mixed-type control of the inhibitors with this electrode gets confirmed.

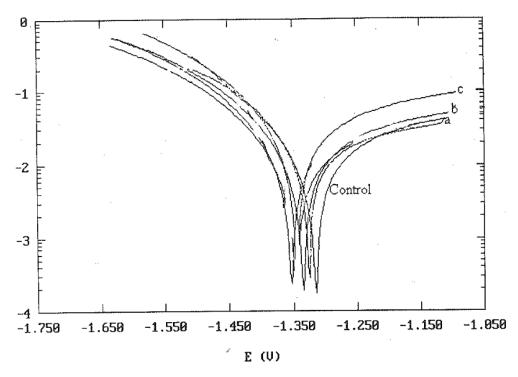


Figure 2. Electrochemical polarization curves of AI + X+ 1.5% Pb in electrolyte containing best protecting concentrations of inhibitors (a) ApTSCN (b) SaTSCN (c) 2meTSCN.

Table 7. Electrochemical polarization of AI +X+1.5% Pb in electrolyte using inhibitor at their best protecting concentration

Inhibitor	OCP (V)	E (W)	i _{corr} (mA/cm ²)	Tafel slope (mV/dec)		IE%
Innibitor	OCP (V)	E _{corr} (V)		b_a	b_{c}	
Control	-1.318	-1.326	36.74	100	90	
ApTSCN	-1.356	-1347	20.57	120	110	44
SaTSCN	-1.355	-1.353	20.94	100	90	43
2meTSCN	-1.350	-1.360	22.04	160	140	40

Table 8. Reduction in partial currents at $E_{corr} \pm 100 \text{mV}$ for best protecting concentration of inhibitors: Al + X + 1.5% Pb in electrolyte (Polarization results)

Inhibitor	E _{corr} (V)	Current (A) at E _{corr} ± 100mV			% Reduction in Partial currents		
		Anodic i _a	Cathodic i _c	Anodic	Cathodic		
Control	-1.326	0.02658	0.01255				
ApTSCN	-1.347	0.014661	0.00727	45	42		
SaTSCN	-1.353	0.01515	0.00740	43	41		
2meTSCN	-1.360	0.01568	0.00665	41	47		

E. HYDROGEN PERMEATION STUDIES

The hydrogen uptake by metals during the corrosion process in aqueous electrolytes has been a subject of great interest as it is related to the structural defects of the metal and / or dependent on the mechanism of hydrogen evolution reaction over the metal substrate. Devanathan and Stachurski's were the first to introduce an elegant method to study the electro permeation and this has been improved recently. This technique has been widely used for hydrogen uptake studies using palladium, steel and other transition metals. Little work has been reported on permeation studies using aluminium Chu Young Chan et al [31] have studied hydrogen permeation through pure aluminium using the hydrogen permeation method. Ono Chu Kwu and Trasatti [32] have studied the permeation of hydrogen through the aluminium alloy AA1060 in alkaline medium. Ono Chu Kewu et al [33] have also studied the influence of different anions and temperature on the extent of hydrogen permeation through aluminium in alkaline medium. In the present investigation, the influence of inhibitors (only for the best protecting concentration) on the extent to which hydrogen has permeated through pure aluminium sheets in battery electrolytes, have been monitored and the results are presented in Table 9 and in Fig 3. It is noted that all the compounds are able to reduce the permeation current. This can be explained as follows. The overall chemical reaction of aluminium dissolution can be written as [40].

Al (s) + 2 OH⁻(aq)
$$A1O_2^- + H_2$$
 ------ (8)

During hydrogen evolution it is adsorbed as atomic hydrogen on the metal surface, which is subsequently, discharged as gaseous hydrogen molecule or surface diffused atomic hydrogen that permeates into metal vacancies. The decreased permeation currents in presence of the inhibitors indicate that the cathodic process consists of a slow electrodic discharge of hydrogen followed by fast desortion of the adsorbed hydrogen from the metal surface.

Table 9. Permeation current measurement of aluminium in electrolyte using inhibitors at their best protecting concentration

Inhibitor	Permeation current μ a	I.E %
Control	13.3	
ApTSCN	8.97	32
SaTSCN	9.54	28
2meTSCN	9.77	26

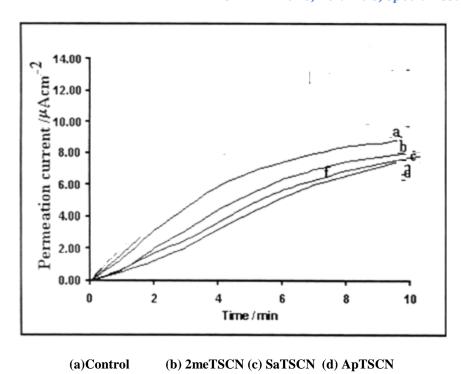


Figure. 3 Hydrogen permeation curve for aluminium in electrolyte containing various inhibitors

IV. CONCLUSION

Derivatives of thiosemicarbazones were synthesized characterized and studied as inhibitors for corrosion inhibition of aluminium alloys in alkaline electrolyte from the studies the following conclusions have been drawn. Weight loss, gasometric studies, electrochemical polarization and hydrogen permeation studies have been carried out to evaluate the performance of aluminium/aluminium- alloys in 4n naoh as well as in the electrolyte containing ca²⁺-citrate complex. Alkaline citrate ca²⁺ electrolyte offers better corrosion resistance than pure 4n naoh for the dissolution of aluminium. However there in reduction in the open circuit potential by about 200mv. The performance rating of the thiosemicarbazones with regard to their corrosion inhibition in as follows aptscn >satscn >2metscn. All the inhibitors are found to reduce the hydrogen uptake by the metal, which in evident from the reduced permeation currents for the corrosion of pure aluminium in the battery electrolyte. The steady permeation current values reflect the order of performance of the inhibitions as well.

REFERENCES

- [1] D.Schweinsgberg, G.George, A.Nanayakkawa, D.Steinert, Corros.Sci., 28 (1988) 33.
- [2] F.Mansfeld, Corrosion Mechanism, N.Y.Marcel Dekker., 1987.
- [3] K.Nobe, N.El-Dakar, Corrosion, 33 (1981) 271.
- [4] B.Abd El Nabey, N.Khanl., M.Shaban, M.Nasr, E.Khamis, G.Pomson, Proc. 6th Eur.Symp. On Corros. Of Inhibitors, Ferrara, Italy, 205, 1985.
- [5] B.Abd El Nabey, E.Khamis, M.Shaban, G.Thomson, J.Dawson, Surface and Coating Technology, 28 (1986) 67.
- [6] E.Khamis,B.Abd El Nabey, M.Shaban, A.El-Sharhoby, G.Thomposn, Proc. 7th Eur.Symp.on Corros. of Inhibitors, Fersara, Italy, 1173, 1990.
- [7] E.Khamis, Mat.Wiss. A.Werkstofftech., 28 (1997) 548.
- [8] M.NDesai, S.M Desai, C.B.Shah, Y.B.Desai, M.H.Gandhi, Corros, J.6 (1971) 269.
- [9] E.Khamis, M.A.Ameer, N.M.Alandis, G.Al Semam, Corrosion, 56, (2) (2000) 127.
- [10] Silversten, Bassler and Morrill, Textbook of spectrometric identification of organic compounds (1991) 296.
- [11] Venkatachari, Corrosion Bulletin 8th issue Jan (1982).
- [12] C.C.Nathan, Corrosion, 9 (1953) 199.
- [13] N.Hakerman and K.Aramaki, Corrosion Inhibitors, J.Electrochem, So.115 (1968) 1006.
- [14] M.Hasan Shawky, Y.A.Elawady, A.L. Ahemed and A.O.Baghlaf, Corroision Sci, 19, (1979) 951-959.
- [15] P.B. Mathur, T. Vasudevan, Corrosion, 38 (1982) 171.

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- [16] L.Vogel, Textbook of Quantitative Analysis (1964) 1056.
- [17] M.A.V.Devanathan and Stachurski, 2nd Proc.Roy.Soc. London, A270, (1962) 90.
- [18] E.Raijola and A.Davidson, J.Am. Chem. Soc., 78(1956) 556.
- [19] U.R.Evans, The Corrosion and Oxidation of Metals, 2nd sapple mentary Vol., Edward Arnold Press, London (1976) 100.
- [20] T.Jeyaraj, c.Raja, M.Senthilkuma rand J.Samu Solomon, Trans. SAEST, 36 (3&4) (2001) 69.
- [21] K.B.Sarangapani, V.Balaramachandran, V.Kapai, S.Venkatakrishna Iyer, Proc.Ann.Tech. Meeting Electrochem. Soc.India (1985).
- [22] Warner Bohn Streadt, J. Power Sources, 5 (1980) 245.
- [23] V.Kapali, N.Subramanian, Proc. 14th Seminar on Electrochem, CECRI, Karaikudi (1973) 59.
- [24] K.B.Sarangapani, V.Balaramachandran, V.Kapali, S.Venkatakrishna Iyer, M.G.Potdar, Surface Technology, 26 (1985) 67.
- [25] K.b.Sarangapani, V.Balaramachandran, V.Kapali, S.Venatakrishna Iyer, Bulletin of Electrochemistry, 1(3) (1985) 231.
- [26] D.D.MacDonald C.English, M.Urguidi-macdonald, Lawrenece Berkeley Laboratory, Califoria (March -1989).
- [27] U.R.Evans, Z. Electrochem., 62(1958) 619.
- [28] R.Shivkumar, G.Paruthinmal Kalaignan, T.Vasudevan, J.Surface Sci. Tech. 13 (1977) 49.
- [29] R.Shivkumar, G.Paruthinal Kalaignan, T.Vasudevan., J.Power Sources, 55 (1995) 53.
- [30] T.Vasudevan, S.Muraidharan, S.Alwarappan, S.Venkatakrishna Iyer, Corrosion Science, 37 (8) (1995) 1235.
- [31] Chu Young Chang, Yin Aeyun, R.M.Catanision, Proc. 10 Internat. Cong. Metallic Corro., organized by CECRI, Karaikudi, India, Nov. 1997, p. 2379.
- [32] A.I.Onochukwu, S.Transatti, Electrochim. Acta, 10 (1988) 1425.
- [33] A.I.Onochukwu, S.P.Transatti, S.Transatti, Corros. Sci., 36 (1994) 1815.