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Corrosion Inhibition of Aluminium by Some Thiocyanate Compounds

Abstract: Corrosion protection of metals and alloys in many industrial products is increasingly important from an economic and environmental point of view. Numerous chemical compounds have long been known as substances that influence the kinetics of electrode processes on which corrosion depends. Some of these compounds are found to retard electrode reactions and are termed inhibitors. The ability of the selected thiocyanate compounds as corrosion inhibitors for aluminium metal have been measured. The rate of corrosion was measured using weight loss, gas evolution and electrochemical techniques.

Keywords: Metals, Alloys, Protection, Chemial compounds, Substances, inhibitions.

تثبيط تآكل الألومنيوم بواسطة بعض مركبات الثيوسيانيت

رضا بن محمد خليل و فوزية محمد النويصر

المستخلص: تزداد أهمية حماية الفلزات والسبائك من التآكل خاصة من الناحية الاقتصادية والبيئية . والعديد من المركبات الكيميائية معروفة منذ زمن طويل كمثبطات لعمليات التآكل المختلفة . بعض من هذه المركبات تقوم بإعاقة التفاعلات القطبية التي تسبب التآكل وبالتالي تعد كمثبطات للتآكل. تم في هذا البحث دراسة إمكانية قيام بعض مركبات الثيوسيانيت كمثبطات لمنع تآكل فلز الألومنيوم وتم قياس معدل التآكل باستخدام طرق الفقد الوزني ، وقياس حجم الهيدروجين المتصاعد ، والطرق الكهروكيميائية.

كلمات مدخلية: فلزات، ألومنيوم، سبائك، حماية مركبات كيميائية، مثبطات، تفاعلات قطبية، إعاقة، ثيوسيانيت.

Introduction

No matter how homogeneous a piece of metal may appear, it has on its surface areas of different reactivities; that is, parts of its surface behave as anodes, and other parts of the surface behave as cathodes. This surface differentiation into anodic and cathodic areas is initiated by one or more of the following factors (El-Naggar 1994): impurities, concentration differences, phase heterogeneity, structural differences, different stress levels and surface defects.

Data of electrochemical reduction potentials of metals reveal that aluminium is a very active metal (E = -1.8 V), and that, in the absence of other factors, the corrosion of the metal in aggressive acid media should proceed at a fast rate. It is, however, well known that aluminium possesses excellent corrosion resistance characteristics. This is

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attributed to the rapid formation of a coherent inert oxide layer which renders the metal inactive in the pH range 4-9. Aluminium, however, is readily soluble in hydrochloric acid solutions or in other acid solutions containing chloride ions. The initiation of aluminium corrosion by chloride ions arises from the damage of the protective oxide layer. The process of partial or local oxide layer removal or dissolution leads to localized corrosion known as pitting.

Different methods can be applied for preventing or reducing corrosion. Altering the environment by changing the medium or adding inhibitors, however, provides a versatile means of reducing corrosion (Fontana and Greene 1984). Typical changes in the medium include: lowering temperature, removing oxygen or oxidizers and changing concentration. The effects produced by these changes vary depending on the particular system. Inhibitors can be regarded as retardants to corrosion and are classified in the following categories:

- Adsorption-type inhibitors
- Hydrogen evolution poisons
- Scavengers and oxidizers

Hydrochloric acid solutions are used for pickling of aluminium or for electrochemical etching of aluminium foils and lithographic plates. The dissolution rate of the metal in such solutions is very high and it is therefore desirable to inhibit these reactions by adding various additives which would help in controlling the degree of etching.

The inhibition of aluminium corrosion in hydrochloric acid has been the subject of many investigations. Various inhibitors have been studied, particularly organic compounds which are cheap and easy to use. Many assessment techniques have also been devised. The resistance of aluminium to corrosion in humid atmospheres is attributed to the property of passivation. Certain metals and alloys can be turned passive by special treatments, for example by dipping in a passivating solution of chromate or nitric acid. Passivity can develop whenever the metal is subjected to anodic polarization of the correct value. This requires an external power supply to polarize the metal. There are numerous inhibitor types and compositions. Most inhibitors have been developed by empirical experimentation, and many inhibitors are protected by patents and their composition is not disclosed. Inhibition is not completely understood because of these reasons, but it is possible to classify inhibitors according to their mode of action and composition. Aluminium corrosion has been studied under constant potential in electrolytes of different anionic and cationic compositions. The most intensive dissolution occurred with chloride anions, and it was of a pitting nature. In the presence of iodide or nitrate ions corrosion was also of a pitting nature, while in the presence of other anions, (HCO_3^-, SO_4^{--}, S^-, CO_3^{--}, PO_4^{---}), anodic dissolution was uniform.

Potassium thiocyanates were studied as corrosion inhibitors of aluminium-based alloys (Savov and Simeonov 1981). They proved to be effective in strongly alkaline media at elevated temperatures. Potassium thiocyanate was also included in formulations to study the inhibitive effect of aryl carboxylates. A low solubility film of metal-inhibitor-aggressive anion is formed. In the presence of thiocyanate, the protective complex did not include the aggressive anion. Therefore, the present study was carried out to investigate the ability of some selected thiocyanate salts as corrosion inhibitors for aluminium metal.

Experimental

Corrosion materials and solutions

The chemical composition of the commercial aluminium sheet used in the experiments was as follows:

Si	Fe	Mn	Mg	Cu	Al
0.15%	0.19%	0.005%	0.1%	0.02%	Rest

The sheet was cut into samples of average dimensions O.1mm x 0.01mm x 0.0062mm. Each aluminium test sample was first polished with a series of emery papers of increasing fineness so as to obtain a smooth surface. The samples were then immersed in a degreasing solution for 30 seconds, rinsed with distilled water, dried between filter papers and finally dried for 30 minutes in a desiccator over dry silica gel. Each sample was then accurately weighed.

The degreasing solution was prepared by dissolving 15g of sodium carbonate and 15g of trisodium phosphate in one litre of distilled water. The solution was heated to 85°C and immediately used for degreasing the aluminium samples.

About 2.0m hydrochloric acid solution was prepared by diluting concentrated hydrochloric acid with distilled water. The concentration of the acid was adjusted to exactly 2.0m after titration against a standard (0.1M) sodium carbonate solution.

Inhibitor solutions of different concentrations (0.2, 0.1, 0.05, 0.025mol/l) from thiocyanate salts (sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate) were prepared by dissolving the required amount of inhibitor in hydrochloric acid solution (2M).

Methods and procedures

The following methods were used to measure the corrosion rates of aluminium in acid solutions in the presence or absence of inhibitors. All the experiments were carried out in hydrochloric acid solution (2M) at 25°C.

Hydrogen evolution method

Seventy five ml of acid solution was placed in the flask and a degreased and weighed aluminum sample was introduced into the solution of the appropriate apparatus. The time was recorded and

the hydrogen evolved was collected in calibrated tubes by the downward displacement of water. The volume of hydrogen was then converted to STP values. The rates of aluminium corrosion were then measured by plotting the volume of hydrogen evolved against time (Samarkandy, A A, Alyoubi and Khalil 2001).

The inhibition efficiency of an additive is calculated from the equation:

$$\% RR = 100 \times (R_o - R) R_o$$

where R_o and R are the reaction rates in the absence and presence of additive, respectively.

Weight loss method

The apparatus for this method consists of a calibrated glass vessel, 45mm diameter and having a total volume of 350ml. 300ml of acid solution were used in each experiment. Degreased and weighed aluminium samples were suspended by glass hooks at the edge of the vessel and immersed under the surface of the acid solution by about 1 cm. After 10min intervals, the samples were taken out of the acid solution, rinsed with distilled water, dried between filter papers, and then dried in a desiccator for 30min, weighed and replaced in the acid solution. Two experiments were run simultaneously and the average aluminium weight loss per experiment for a set of three samples was calculated in mg per cm² of the sample area. The weight loss versus time curves were constructed (Subramanyam *et al.* 1993) and the inhibition efficiency (% Inh) of the studied inhibitors was calculated using the weight loss data as follows :

$$\% Inh = (1 - W_o - W/W_o) \, 100$$

where W and W_o are the weight losses in the absence and presence of inhibitor.

Electrochemical method

This method was used to determine the polarization curves of aluminium in 0.1m hydrochloric acid solutions that contained different concentrations of inhibitors. The polarizations were determined as potentio scans using EG and G model 273 A potentiostat/galvanostat for accurate measurement of potential and current density. All experiments were carried out at 25°C with a scan

rate of 1mV per second between -1.8V and + 0.2V.

The working electrode was made of aluminium (10 x 100 x 0.6mm) sealed to glass tubes with araldite. Electrical contact was made by a small mercury pool on the closed end of the metal electrode. The electrode was polished with fine grade emery paper, then immersed in the degreasing solution, rinsed with distilled water and dried between filter papers. A preselected area (10 x 10mm) was exposed to the electrolyte by covering the sample with teflon tape. The surface area of the electrode was calculated from its geometrical dimensions and the current densities were then determined.

The reference electrode was a saturated calomel electrode (SCE) and the auxiliary electrode was sealed to the end of a glass tube and fitted into a compartment, separated from the main bulk of the electrolyte by means of G4 sintered glass disc to ensure separation of anodic and cathodic reaction products. The working electrode was left at open circuit until a steady potential was attained. The electrode was first cathodically polarized and the polarization curves recorded. Then, the potential was left to decay to open circuit value and anodic potential was subsequently imposed on the electrode and anodic curves recorded. These measurements were carried out in the absence and presence of different concentrations of inhibitors. Each experiment was repeated using a freshly prepared aluminium sample and a fresh acid solution, and then the mean value was calculated.

Corrosion current densities were determined by extrapolation of anodic and cathodic Tafel lines to a point which gives log i(corr) and the corresponding corrosion potential E(corr) at each concentration of inhibitor and inhibitor-free acid solutions; i(corr) can then be obtained. The inhibition efficiency of a given inhibitor was evaluated using corrosion current as follows:

$$IE = (1-i/i_o) \, 100$$

where (i) and (i_o) are the corrosion current densities in the absence and presence of inhibitor, respectively.

Results and discussion

The results of the three different techniques used to evaluate the inhibition efficiency of the tested compounds are:

1. Hydrogen evolution method

Hydrogen is produced by the attack of hydrochloric acid on aluminum metal. To assess the effect of certain additives as inhibitors of this reaction, the rate of hydrogen evolution was followed in additive-free acid and in solutions containing additives at different concentrations The rates of hydrogen evolution for thiocyanate salts additives are shown in Figures 1-3.
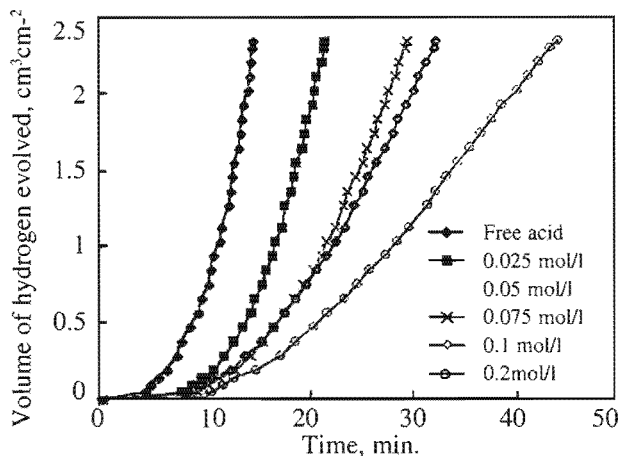

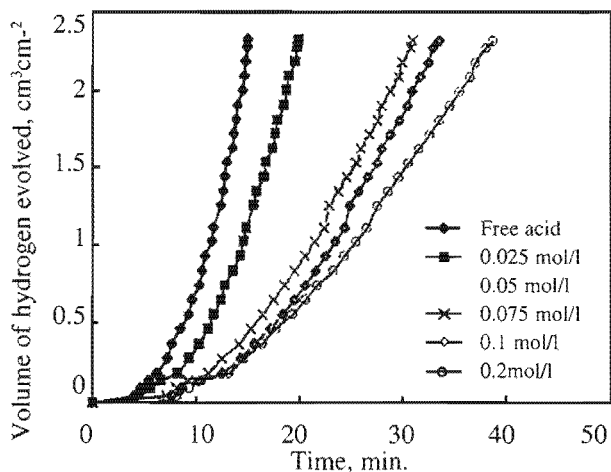**Fig. 1.** Volume of hydrogen-time curves at different concentrations of ammonium thiocyanate

Fig. 2. Volume of hydrogen-time curves at different concentrations of potassium thiocyanate
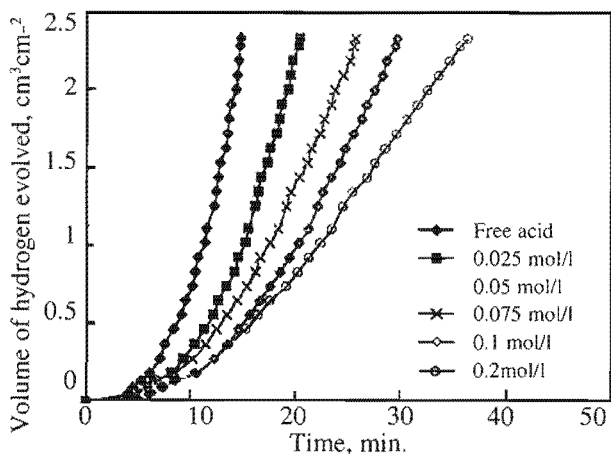

Fig. 3. Volume of hydrogen-time curves at different concentrations of sodium thiocyanate

From the graphs of hydrogen evolution with time, it is observed that these reactions follow a similar pattern. There is an initial slow reaction rate followed by a sharp increase in reaction rate as reflected by a large increase in hydrogen evolution. It is also noticeable that the rate of aluminium reaction with acid is slowed down by the addition of additives to varying extents and this effect is directly proportional to additive concentration: the initial slow reaction rate may be due to the dissolution of the aluminium oxide layer protecting the metal from acid attack. Once the metal has been exposed, the acid attack proceeds quickly leading to rapid evolution of hydrogen. The aluminium oxide layer is dissolved when chloride anions adsorb to its surface under the influence of the electric field at the oxide/solution interface, which leads to the formation of a basic soluble salt that readily goes in solution.

The results of inhibition efficiency are shown in Table 1. The differences in inhibition efficiencies of thiocyanate salts group inhibitors are not large and the inhibitive effect can be attributed mainly to the thiocyanate anion. The thiocyanate anion adsorbs onto the oxide surface in competition with the aggressive chloride anions. The thiocyanate is bulkier than chloride and has centers of concentrated negative charge (S and N) and it is therefore more adsorptive. The thiocyanate adsorption leads to the formation of a complex of lower solubility than the one formed by chloride anions and therefore less aluminium goes into solution.

Table 1: Effect of inhibitor concentrations on the inhibition efficiency as evaluated from hydrogen evolved using thiocyanate salts

Concentration of additive, mol l^{-1}	*% Inhibition efficiency		
	NH$_4$SCN	NaSCN	KSCN
0.025	36.43	30.36	30.71
0.050	37.86	43.2	43.57
0.075	52.86	52.86	60.71
0.100	61.79	60.0	63.93
0.200	73.57	69.64	70.71

* Each % inhibition efficiency is a mean of two experiments.

2. The weight loss method

Aluminium dissolves and loses weight by hydrochloric acid attack. This weight loss can be used as a measure of aluminium corrosion. The weight losses in mg/cm^2 of the surface area of aluminium samples were measured at different

intervals of time in 2M hydrochloric acid in the absence and presence of different inhibitor concentrations. The results of plotting weight losses with time for different concentrations of thiocyanate salts group additives are shown in Figures 4-6. From the graphs of the thiocyanate salts group it can be observed that there is an initial slow increase in weight loss followed by a sharp rise with time. It can also be observed that the weight loss is reduced by the presence of additives in comparison to free acid and this reduction in weight loss increases with additive concentration. The induction period may be attributed to the gradual dissolution of the protective aluminium oxide layer which exposes the metal to acid attack.
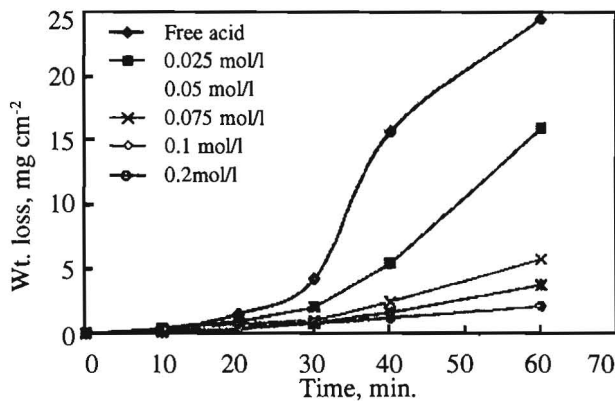

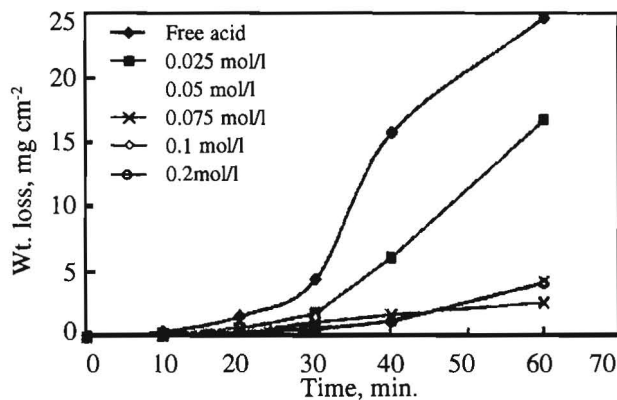**Fig. 4.** Weight loss-time curves at different concentrations of potassium thiocyanate

Fig. 5. Weight loss-time curves at different concentrations of ammonium thiocyanate
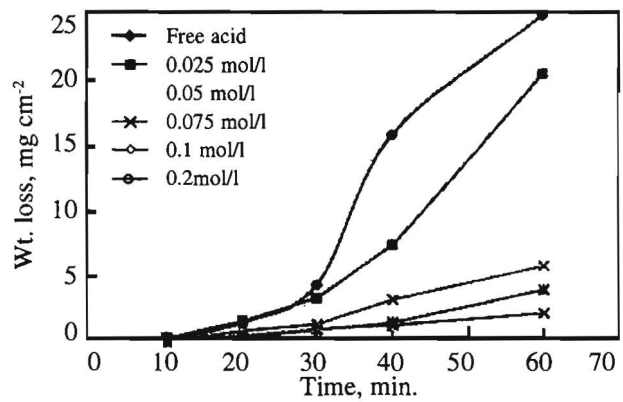

Fig. 6. Weight loss-time curves at different concentrations of sodium thiocyanate

The percentage inhibition (%Inh) of an additive, which is a measure of its inhibitive effect, is calculated and the corrosion resistance (C. R) which is a measure of inhibition effect too, is calculated from the equation :

$$C. R = 1 - (W_o-W)/W_o$$

Results for thiocyanate salts group additives are shown in Tables 2-5. From these results it can be observed that the percentage of inhibition increases with the increase of inhibitor concentration. An increase in inhibitor concentration leads to an increase in aluminium surface area covered by the inhibitor and hence leads to reduction in aluminium dissolution. It can also be observed that the percentage of inhibition of all the additives in this group are similar, at the highest concentrations suggesting that inhibition is mainly attributed to the thiocyanate anions which are adsorbed on to the surface of aluminium in competition with the aggressive chloride anions, thus inhibiting corrosion. This also suggests that these thiocyanates are dissociated to similar degrees in acid solution, and that the ammonium, potassium and sodium cations play insignificant roles in inhibition. Unlike divalent cations such as Zn, Ca, Mg, these monovalent cations do not suppress the solubility of the aluminium compounds or interfere with cathodic reduction of oxygen at the metal surface by blocking oxygen diffusion to the cathode because of the formation of calcarious scale.

Table 2: Efficiency of corrosion inhibition as determined by Weight - loss method

Concentration of additive, mol 1^{-1}	*% Inhibition efficiency		
	NH_4SCN	NaSCN	KSCN
0.025	32.29	37.73	35.15
0.050	46.04	47.84	46.74
0.075	76.42	83.57	77.36
0.100	84.13	84.91	84.69
0.200	90.18	92.05	91.54

Table 3: Corrosion resistance - time data for ammonium thiocyanate at different concentrations

Time, min	Corrosion resistance, C - R				
	0.025, mol l⁻¹	0.05, mol l⁻¹	0.75, mol l⁻¹	0.1, mol l⁻¹	0.2, mol l⁻¹
10	0.439	0.568	0.608	0.800	0.777
20	0.522	0.589	0.698	0.815	0.794
30	0.613	0.718	0.848	0.900	0.811
40	0.614	0.750	0.923	0.934	0.899
60	0.686	0.825	0.924	0.927	0.954

Table 4: Corrosion resistance - time data for potassium thiocyanate at different concentrations

Time, min	Corrosion resistance, C - R				
	0.025, mol l⁻¹	0.05, mol l⁻¹	0.75, mol l⁻¹	0.1, mol l⁻¹	0.2, mol l⁻¹
10	0.041	0.601	0.395	0.608	0.608
20	0.397	0.707	0.486	0.684	0.688
30	0.511	0.798	0.770	0.816	0.839
40	0.643	0.828	0.839	0.897	0.923
60	0.699	0.898	0.890	0.929	0.961

Table 5: Corrosion resistance - time data for sodium thiocyanate at different concentrations

Time, min	Corrosion resistance, C - R				
	0.025, mol l⁻¹	0.05, mol l⁻¹	0.75, mol l⁻¹	0.1, mol l⁻¹	0.2, mol l⁻¹
10	0.014	0.194	0.244	0.338	0.385
20	0.139	0.547	0.520	0.685	0.583
30	0.237	0.730	0.690	0.792	0.791
40	0.527	0.744	0.799	0.910	0.924
60	0.619	0.794	0.891	0.930	0.963

3. Electrochemical method

Polarisation measurements were conducted as potentiodynamic scans to find the values of corrosion current density by applying the Tafel equation (Payne 1995):

$$E = a + b \log i$$

Plots of electrode potential against corrosion current density for thiocyanate salts group additives are shown in Figures 7-9. The values of inhibition efficiency with corresponding E_{corr} in mV, i_{corr} in μA and b values are shown in Table 6.
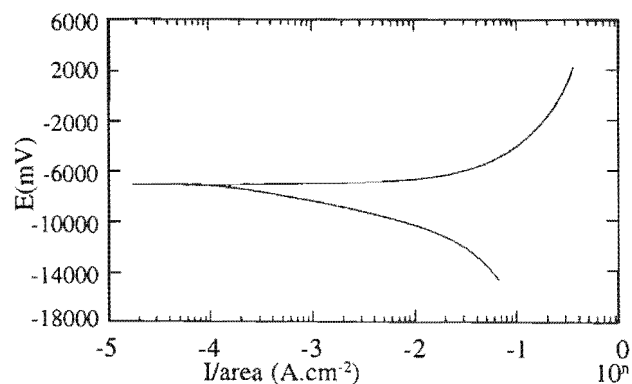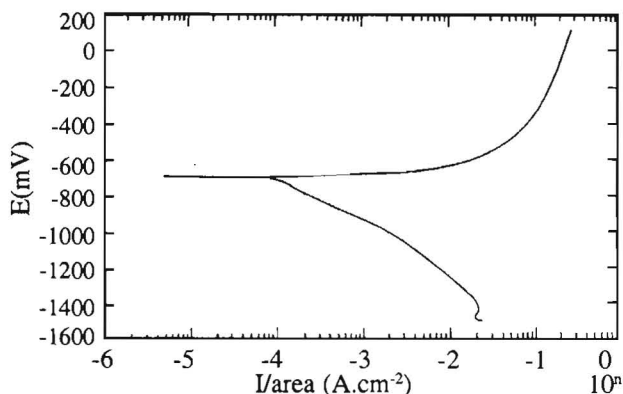

Fig. 7. Galvanostatic polarization curve of aluminium in presence of 0.1 mol.l⁻¹ KSCN

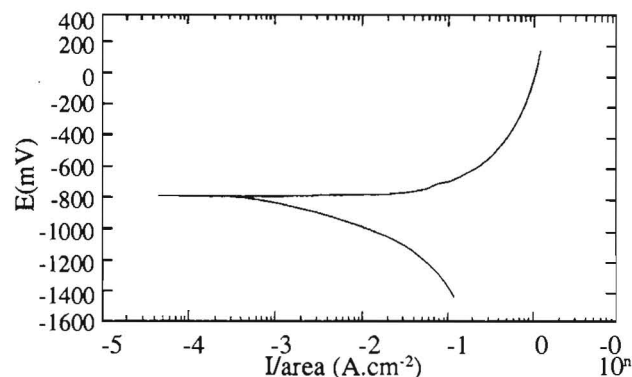**Fig. 8.** Galvanostatic polarization curve of aluminium in presence of 0.1 mol.l^{-1} NaSCN

Fig. 9. Galvanostatic polarization curve of aluminium in presence of 0.1 mol.l^{-1} NH$_4$SCN

Table (6): The effect of inhibitor concentrations on parameters calculated from electrochemical measurements for aluminum in the presence of NaSCN in 0.1 M HCI

Inhibitor Conc, mol 1^{-1}	E_{corr} mV	i_{corr} μAcm^{-2}	b x 10^{-3}	IE %
0.00	-821.0	1505.0	303.3	0.0
0.05	-770.5	1111.0	215.2	26.2
0.10	-717.3	309.2	397.5	79.5
0.20	-694.4	77.25	299.3	94.9
0.30	-660.9	67.0	230.6	95.6

From the scans it can be observed that the added inhibitor caused parallel displacement of both cathodic and anodic Tafel lines to more negative or positive potential values relative to those produced in the absence of the inhibitor. This suggests that the thiocyanates act as mixed-type inhibitors, and inhibition takes place by adsorption of thiocyanate anions on the electrode surface, hence blocking the sites for cathodic and anodic reactions. The overall results will be a reduction in the inhibitive effect of the thiocyanate ions produced from ammonium thiocyanate due to this increased anodic reaction.

From Tables 7 & 8, the values of corrosion current density and hence corrosion rate are noticed to decrease with addition of inhibitor and increase of

inhibitor concentration. Being increased with addition of an inhibitor as the increase in inhibitor concentration is commensurate with an adsorption mechanism for inhibition.

Table (7): The effect of inhibitor concentrations on parameters calculated from electrochemical measurements for aluminum in the presence of NH$_4$SCN in 0.1 M HCI

| Inhibitor Conc, mol 1^{-1}	E_{corr} mV	i_{corr} μAcm^{-2}	b x 10^{-3}	IE %
0.00	-821.0	1505.0	303.3	0.0
0.05	-780.9	1200.0	197.1	20.3
0.10	-758.2	871.3	190.9	42.1
0.20	-746.7	653.5	389.0	56.6
0.30	-738.1	378.2	309.4	74.9

Table (8): The effect of inhibitor concentrations on parameters calculated from electrochemical measurements for aluminum in the presence of KSCN in 0.1 M HCI

Inhibitor Conc, mol 1^{-1}	E_{corr} mV	i_{corr} μAcm^{-2}	b x 10^{-3}	IE %
0.00	-821.0	1505.0	158.5	0.0
0.05	-800.6	969.9	274.6	35.6
0.10	-709.5	170.8	344.5	88.7
0.20	-702.2	76.37	490.9	94.9
0.30	-687.1	49.70	361.8	96.7

The values of inhibition efficiency show that potassium and sodium thiocyanates have similar values to those obtained by the hydrogen evolution method and the weight loss method. Ammonium thiocyanate, however, gave comparatively lower inhibition values by the electrochemical method than potassium and sodium thiocyanates than it did through the inhibition values obtained by the hydrogen evolution method and the weight loss method. This could be attributed to the conditions of the reaction. The ammonium cation may be discharging under the relatively low acid conditions, 0.1M compared to 2.0M in previous experiments, and imposing polarization according to the following reaction:

$$NH4^+ + e = NH3 + 1/2\ H_2$$
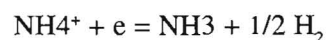
The ammonium cation, in this case, is acting like a sink for the anodic reaction by removing electrons, thus favoring the forward anodic reaction, aluminium corrosion:

$$Al = al^{+++} + 3\ e$$
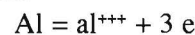
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