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Research Article

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Investigation and inhibition of aluminium corrosion in methane sulphonic acid solution by organic compound

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ABSTRACT

Corrosion control of metals is an important activity of technical, economical, environmental and aesthetical importance. The continuous search for better corrosion inhibitors, due to vast differences in the media encountered in industry remains a focal point in corrosion control. The use of organic compounds to inhibit corrosion has assumed great significance due to their application in preventing corrosion under various corrosive environments. The corrosion inhibition of aluminium by thiourea in 1 M MSA has been investigated by weight loss measurements and temperature effect. The experimental data complied with Temkins Adsorption isotherm and the values of activation energy and heat of adsorption obtained suggested that inhibitor molecules have been spontaneously adsorbed on the aluminium surface by physical adsorption mechanism.

Keywords: Corrosion inhibition, Adsorption mechanism, Activation energy, Aluminium, Methane Sulphonic Acid.

INTRODUCTION

Corrosion is an electrochemical process by which metallic structures are destroyed gradually through anodic or cathodic reaction or both. Corrosion control can be achieved by the use of inhibitors [1]. This phenomenon necessitates the continuous search for better corrosion inhibitors due to vast differences in the media encountered in industry which remains a focal point in corrosion control as inhibitors slow down the corrosion process on metals. A number of organic compounds [2-10] are known to be applicable as corrosion inhibitors for aluminium in acidic environment. Such compounds typically contain nitrogen, oxygen or sulphur in a conjugated system and function via adsorption of the molecules on the metal surface creating a barrier to corrodent attack. The adsorption bond strength is dependent on the composition of the metal and corrodent inhibitor structure and concentration as well as temperature. Despite the broad spectrum of organic compounds, the choice of appropriate is restricted by several factors. Most of the acid inhibitors are organic compounds contain nitrogen [11-13], oxygen [14-17], phosphorous [18] and sulphur [19-20].

Attempts have been made to reduce surface film dissolution and hence protect the metal in aggressive acid and alkaline media. Aluminium is an important structural engineering material, its usage ranking only behind ferrous alloys. The growth in usage and protection of aluminium continues to increase. The extensive use of aluminium lies in its strength, density ratio, toughness and to some degree, its corrosion resistance. Aluminium is extensively used in industrial application such as automobiles, food handling, containers, electronic devices, building, aviations, etc. [21-23].

Usually acid solutions are often used in industry for cleaning, descaling and pickling of metallic structures which are normally accompanied by considerable dissolution of metal. Among the all mineral acids, methane sulphonic acid is far less corrosive employed in diverse industrial process [24]. MSA can replace fluoroboric acid and fluorosilicic acid (the only commercially successful acid for Pb electroplating), which have lachrymatory properties and evolve

HF, which is of great industrial concern [25]. It is also present in natural environment as a part of the bio geo chemical sulphur cycle, where atmospheric dimethyl sulphide arising from marine algae, cyanobacteria and salt marsh plants in photo chemically oxidized leading to MSA formation [26]. Highly corrosive and toxic HF can also be replaced by MSA in paracetamol production. [27].

There is several manufacturing process. In the chloro oxidation process (the conventional one, developed by Pennwalt Corporation in 1967[28]), methane thiol is oxidized by chlorine to form methane sulphonyl chloride, which is then hydrolysed to form MSA with HCl as a byproduct.
The overall reaction of this synthesis is given in Equation 1.

$$CH_3SH + 3Cl_2 + 3H_2O \longrightarrow CH_3SO_3H + 6\ HCl \quad (1)$$

Environmental compatibility is a prime requirement for reliable performance of metals. It is therefore essential to measure corrosion susceptibility in the media that bring used in real industrial applications.

The purpose of the present work is to study the inhibitive action of thiourea on aluminium in I M methane sulphonic acid using weight loss techniques and thermometric method. In addition adsorption isotherm will be investigated.

EXPERIMENTAL SECTION

2.1. Specimen Preparation

Aluminium metal with purity 98.5% was used in the present study. Each sheet was 0.1 cm in thickness and was mechanically press cut into 5cm X 2.5 cm coupons. Each specimens were ground manually under a stream of water starting with 400 grit SiC paper and continued and with 800, 1000, 1200 grit papers. Between each paper change, the sample was rinsed with distilled water to remove the particles arising during grinding. Each sample was ground in one direction until all imperfections were removed and the surface was covered with a uniform pattern of scratches. The polishing procedures were repeated until to achieve a mirror finish. After polishing, the samples were degreased by washing with ethanol, dried in acetone and preserved in a desiccator. Described procedure was used for the preparation of samples for the electrochemical and immersion tests as well as for the surface analysis. All reagents used for the study were analar grade and double distilled water was used for their preparation.

2.2. Electrolyte

An aqueous solution of 1M MSA was used as blank solution. Thiourea provided by Merck was used as inhibitor. The concentration range of employed inhibitor was 100 – 400 ppm in 1M MSA.

2.3. Weight loss method

The cleaned and dried aluminium coupons were weighed and suspended with the aid of glass hook in a beaker contain 100 ml of 1M MSA solution with and without different doses of thiourea concentration ranged from 100-400 ppm. The coupons were taken out of the test solution after 12 hours, washed in 70% nitric acid to remove the corrosive product using bristle brush, rinsed with distilled water, dried and reweighed. From the initial and final weight, the loss in weights was calculated. Corrosion rate was calculated by using the formula:

$$\text{Corrosion rate (mdd):} \quad \frac{\text{Weight loss X 1000}}{\text{Surface area (dm}^2\text{) X Time (days)}} \quad (2)$$

The loss in weight is expressed in milligram per square decimeter per day (mdd). This value can be converted into the equivalent corrosion current by using Faraday's laws. The conversion factor for the aluminium corroding to Al^{3+} [29] is 1mdd = 3.16×10^{-10} Amp cm^{-2}.

2.4. Temperature effect

Weight loss measurements were promoted at various temperatures of two hours in each case. The loss in weight was calculated. Weight loss measurement was performed in 1M MSA with and without the addition of inhibitor at their best inhibitory concentration percentage inhibitor at various temperature was calculated.

2.5. Adsorption isotherm

The adsorption isotherm can be determined by assuming that inhibition effect is due mainly to the adsorption of metal/solution interface. Basic in information as the adsorption of inhibitor on the metal surface can be provided by adsorption isotherm. In order to obtain the isotherm, the fractional surface area (θ) as a function of inhibitor concentration must be obtained. Surface coverage can be easily determined from the weight loss measurement by the ratio % I.E /100, where % I.E is Inhibition efficiency obtained by weight loss method. So it is necessary to determine empirically which isotherm fits best to the adsorption of inhibitor on the aluminium surface.

RESULTS AND DISCUSSION

3.1. Weight loss consideration

Different experimental techniques have been used to evaluate the inhibition efficiency of thio urea. Gravimetric method is one of the simplest method. Determination of the weight loss allows the calculation of inhibition efficiency and surface coverage. It was observed that thio urea inhibits the corrosion of aluminium in 1M MSA solution at all concentration used in study from 100 to 400 ppm. Maximum inhibition efficiency was shown at 300 ppm and it reached 78%. It is evident from Table 1, that the corrosion rate is decreased with increasing the concentration of thiourea.

Table 1 Corrosion parameters of aluminium in 1 M MSA in absence and presence of different concentration of thiourea from weight loss measurements

Concentration of thio urea (ppm)	Corrosion rate (mdd)	Corrosion Current X 10^{-7} Amp cm^{-2}	Percentage of Inhibition Efficiency (I %)	Degree of surface coverage (θ)
Blank	137.09	0.433	–	–
100	99.01	0.313	27.28	0.28
200	68.55	0.217	57.00	0.58
300	30.46	0.096	77.78	0.78
400	45.69	0.144	66.67	0.67

The results suggests that the increase the efficiency with increasing in inhibitor concentrations because of increase the number of molecules adsorbed on the aluminium surface and reduce the surface area that is available for the direct acid attack of the metal surface[30]. The percentage of inhibition efficiency (I %) and degree of surface coverage (θ) were calculated from the following relationship 3 and 4.

$$\text{\% of Inhibition Efficiency (I)} \longrightarrow W_B - W_i / W_B \text{ X } 100 \quad (3)$$

$$\text{Degree of surface coverage } (\theta) \longrightarrow 1 - W_i / W_B \quad (4)$$

where W_B and W_i are the weight loss data of the metal surface in the absence and presence of the inhibitor respectively.

3.2. Effect of Temperature

Two main types of interaction often describe adsorption of organic inhibitors corroding system are physical and chemical adsorption. It has been suggested [32-33] that physisorbed molecules are attached to the metal at the cathodes and essentially retard metal dissolution by stifling the cathodic reaction where as chemisorbed molecules protect anodic areas to reduce the inherent reactivity of the metal at the sites where they attacked. The apparent activation energy E_a for aluminium dissolution in 1 M MSA solution in the absence and presence of inhibitor thiourea was calculated from Arrhenius equation. [34]

$$\log r_2/r_1 \longrightarrow E_a / 2.303 \text{ R } [1/T_1 - 1/T_2] \quad (5)$$

Where r_1 and $r_{2\ are}$ the corrosion rates at temperatures T_1 and T_2 respectively.

The heat of adsorption (Q_{ads}) was obtained from the trend of surface coverage with temperature as follows: [35]

$$Q_{ads} \longrightarrow 2.303R \, [\log (\theta_2 /1- \theta_2) - \log (\theta_1 /1- \theta_1)] \text{ X } [T_1 \, T_2 / T_2 - T_1] \quad (6)$$

where θ_1 and θ_2 are degree of surface coverage at temperatures T_1 and T_2. R is the gas constant. The values obtained for the blank, inhibited system containing thiourea are presented in Table 2.

From the table 2 , it is evident that all cases, a decrease the inhibition efficiency with rise in temperature with analogous increase in corrosion activation energy in the presence of inhibitor compared to its absence is frequently interpreted that the formation of an adsorption film of physical nature. The effect corresponding to an increase in inhibition efficiency with rise in temperature and lower the activation energy in the presence of inhibitor suggest a chemisorptions mechanism [4, 7, 19]. From the foregoing, the trend for the thiourea inhibitor suggests a predominant effect physisorption of inhibiting species on aluminium in 1 M MSA.

Table 2 Calculated values of inhibition efficiency (I), activation energy (E_a) and heat of adsorption (Q_{ads}) for thiourea on aluminium in 1 M MSA at different temperature

Concentration of thiourea (ppm)	Inhibition efficiency (I %) at 30°C	Inhibition efficiency (I %) at 60°C	E_a ($KJmol^{-1}$)	Q_{ads} ($KJmol^{-1}$)
Blank	–	–	0.275	–
100	25.41	18.71	0.32	– 0.195
200	48.53	33.77	0.401	– 0.309
300	76.57	59.08	0.554	– 0.459
400	72.92	54.57	0.534	– 0.413

It is also evident that Q_{ads} values are negative ranged from – 0.195 to –0.413 $KJmol^{-1}$. The negative Q_{ads} values show that the physical adsorption and inhibition efficiency decreases with rise in temperature [34].

3.3. Adsorption consideration

To understand the mechanism of corrosion inhibition, the adsorption behavior of the inhibitor compound on the composite surface must be known. Values of degree of surface coverage (θ) were evaluated at different concentration of the thiourea in 1 M MSA solution from weight loss measurement. The surface coverage (θ) values were tested graphically by fitting a suitable adsorption isotherm. The plot of θ versus log C for different concentration of thio urea shows a straight line indicating that the adsorption of the compound on the composite surface follow Temkins adsorption isotherm.

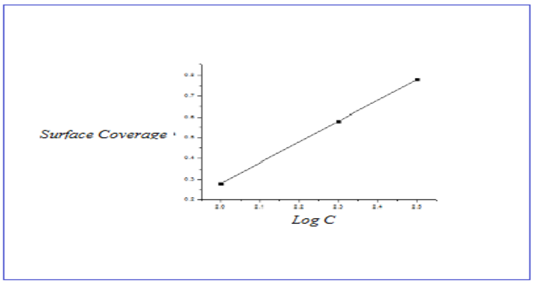

Figure 1 Temkins adsorption isotherm for thiourea on aluminium in 1 M MSA

The applicability of Temkins adsorption isotherm verifies the assumption of monolayer adsorption on the uniform homogeneous surface of aluminium with an interaction in the adsorption layer.

CONCLUSION

1. Thiourea was found to be effective inhibitor for aluminium surface in 1 M MSA solution.
2. Inhibition efficiency increase with increase inhibitor concentration but decrease with rise in temperature.
3. Activation energy increase as the concentration of inhibitor increases.
4. Negative values of Q_{ads} shows that the inhibition efficiency decreases with increase in temperature.
5. The data obtained from weight loss technique fit well with the Temkins adsorption isotherm.

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