

DEVELOPMENT OF INHIBITION EFFICIENCY, THERMODYNAMICS AND KINETICS PROPERTIES OF NICOTINAMIDE ON ALUMINUM CORROSION IN HYDROCHLORIC ACID SOLUTION

T.LAKSHMIKANDHAN¹, V.L.CHANDRA BOSS²

^{1,2} Associate Professor, Department of Chemistry,

BIST, BIHER, Bharath University, Chennai-73

lakshmikandhan.che@bharathuniv.ac.in, Chandraboss.che@bharathuniv.ac.in,

1. INTRODUCTION

Corrosion is defined as the gradual destruction deterioration of metals or alloys by the chemical or electrochemical reaction with its environment

Aluminium is actually a very active metal, that its nature is to oxidize very quickly .while a weakness for most metals, this quality is actually the key to its ability to resist the corrosion. When oxygen is present (in the air , soil or water) aluminium instantly reacts to form aluminium oxide [1-6]. This aluminium oxide layer is chemically bound to the surface, and it seals the core aluminium from any further reaction. This is quite different from oxidation (corrosion) in steel, rust puffs up and flakes off, constantly exposing new metal to corrosion. Aluminium and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries because of their advantages. Hydrochloric Acid solutions are used for pickling [7-9], chemical and electrochemical etching of aluminium. It is very important to add corrosion inhibitors to prevent metal dissolution and minimize acid consumption. Aluminium is an important metal in many industries owing to its many excellent characteristics especially its good electrical and thermal conductivities, low density high ductility, low cost and availability for the fabrication and construction industries. It is widely used as a material for automobiles, aviation, house hold appliances, containers, electronic devices, good corrosion resistance [10-15].

3.1 OBJECTIVE AND THE SCOPE OF THE PRESENT WORK

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- ❖ The majority of cooking and storing utensils are made up of different metals alone or in combination. Evidences are available that constituent metals from utensils during cooking and storage of food. Intake of heavy metal is an important problem in human health[16-21].
- ❖ Aluminium is a widely used material in food preparations and in home and commercial cookware. Aluminium is readily attacked by organic acids, particularly at cooking temperatures. Iron and chromium are released from the aluminium materials in to the food[22-26].
- ❖ Chromium and iron are essential nutrients for which aluminium could be a useful source. However over dose of iron and chromium produced numerous health hazards. So it is essential to study the evaluation of aluminum by various organic compounds. The present study gives the evaluation of aluminium in the presence of L-Cystine[27-31].

3.1.2 Objective and scope of present study;

The studies are confined to commercially available aluminium of composition and the remaining aluminium.

COMPOUNDS	COMPOSITION
Chromium	0.10%
Nickel	3.8-4.9%
Carbon	0.30-0.9
Silicon	0.50
Iron	0.50
Sulphur	1.2-1.8

3.1.3 Chemical formula of inhibition:

Nicotine amide: $C_6H_6N_2O$

The present work is undertaken,

- 1) To evaluate the corrosion of aluminium in the presence of by Nicotine amide by weight method surface of the aluminium in 0.5M HCl acid by Langmuir adsorption isotherm
- 2) The adsorption of different concentrations of the Nicotine amide on the surface of the aluminium in 0.5 M HCl acid by Langmuir adsorption isotherm[32-36].

MATERIALS AND METHODS

4.1. Preparation of the Specimens

95% of pure commercial aluminum specimens of the dimensions 1.0 X 4.0 X 0.2 cm were polished to a mirror finish and degreased with Nicotine amide, and used for the weight-loss method and surface examination studies[37-41].

4.2. Weight-Loss Method

Aluminium specimens in triplicate were immersed in 100 mL aqueous solution containing 100 ppm of HCl at various concentrations of the inhibitor in the absence and presence of Nicotine amide for a period of one day. The weights of the specimens before and after immersion were determined using a Shimadzu AY62 model balance. The corrosion products were cleaned with Clarke's solution [1]. The inhibition efficiency (IE) was then calculated using the equation[42-45]

$$IE\% = (W_0 - W_T / W_0) * 100 \quad [1]$$

where W₁ and W₂ are the mass loss of aluminium coupons in the absence and presence of inhibitor, respectively. Inhibitor in the presence of various concentrations of nicotine amide were also determined.

4.3 Surface Examination Study

The aluminium specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was analyzed by surface analysis technique.

4.4 Electrochemical polarization studies

Electrochemical polarization measurements were carried out using Electrochemical analyzer (BioLogic, VSP, France) in a conventional three-electrode glass cell. A platinum foil of surface area $2 \times 2 \text{ cm}^2$ was used as the auxiliary electrode and a saturated calomel electrode as the reference electrode. Both anodic and cathodic polarization curves were recorded in the absence and presence of various concentrations of the *SL* extract from a cathodic potential of -1900 mV to an anodic potential of -1300 mV (vs SCE) at a sweep rate of 1 mV per second. From the polarization curves, Tafel slopes, corrosion potential and corrosion current were calculated. The inhibitor efficiency was calculated using the formula [2]

$$IE(\%) = \frac{I_{corr(blank)} - I_{corr(inhibitor)}}{I_{corr(blank)}} \times 100 \quad [2]$$

Where, I_{corr} and I^*_{corr} are corrosion current in the absence and presence of *SL* extract.

4.5 Electrochemical impedance studies

The electrochemical AC-impedance measurements were performed using Electrochemical analyzer (BioLogic, VSP, France) as described earlier. Experiments were carried out at the open circuit potential for the frequency range of 100 kHz to 1 mHz . A plot of Z' vs Z'' were made. From the plots, the charge transfer resistance (R_t) were calculated and the double layer capacitance (C_{dl}) were then calculated using the following equation [3]; Where, R_t is charge transfer resistance and C_{dl} is double layer capacitance. The experiments were carried out in the absence and presence of various concentrations of *SL* inhibitor. The percentage of inhibition efficiency was calculated using the equation [4]

$$IE (\%) = \frac{R_{ct}(\text{inhibitor}) - R_{ct}(\text{blank})}{R_{ct}(\text{inhibitor})} \times 100$$

Where, R_{ct}^* and R_t are the charge transfer resistance in the presence and absence of SL extract.

5.1 RESULTS AND DISCUSSION

5.1.1 Inhibitive action of Nicotinamide

5.1.1.1 Analysis of the results of the mass-loss method

Corrosion rates (CR) of the aluminium immersed in 0.5 M, HCL at various temperatures in the presence and absence of various concentrations of nicotinamide and the inhibition efficiencies (IE) using mass loss method are calculated as follows and the results are given in table

$$\text{Corrosion Rate} = \frac{\text{weight loss (g)}}{[\text{surface area of the specimen (cm}^2\text{)} \times \text{period of immersion (h)}]}$$

$$IE\% = \frac{CR_0 - CR_t}{CR_0} \times 100$$

Table 5.1 The percentage inhibition efficiency and corrosion rate of aluminium in 0.5M HCL by Nicotinamide at 303 k, 313 K and 323K by weight loss method.

Concentration	Corrosion Rate $\times 10^{-2}$ $g\text{cm}^{-2}\text{h}^{-1}$			Inhibition efficiency		
	303k	313k	323k	303k	313k	323k

Blank	0.316	0.986	1.213	-	-	-
100	0.202	0.689	0.941	36.07	30.12	22.42
200	0.177	0.614	0.949	43.98	37.72	21.76
300	0.133	0.581	0.841	57.91	41.07	30.66
400	0.126	0.513	0.761	60.12	47.97	37.26
500	0.092	0.488	0.669	70.88	50.50	44.84

The results show that the corrosion rate decreases on the addition of Nicotinamide. This may be due to the adsorption of Nicotinamide on the surface of the aluminium through the interaction of N, O and Br also electrons present in Nicotinamide with the aluminium surface. Corrosion inhibition is strengthened with increase in the concentration of inhibitors. This trend results from the increased adsorption of Nicotinamide on the surface of the metal. As a result the metal surface is effectively separated from the acid medium. Inhibition efficiency is found to decrease with increase in experimental temperature. This is an indication that at higher temperatures there might be desorption of Nicotinamide from aluminium surface. Decrease in inhibition efficiency with increase in temperature is an indication that the adsorption of Nicotinamide on aluminium surface is physical in nature ()

5.1.2 Study of Kinetics and Thermodynamic Parameters on the Corrosion process

The relation between the corrosion rates (CR) and temperature (T) is expressed by the Arrhenius equation (158).

$$\text{Log}(\text{CR}) = \frac{-E_a}{2.303RT} + \log \lambda \text{ -----(12)}$$

Where E_a is the apparent effective activation energy, R is the molar gas constant and λ is the Arrhenius pre exponential factor. A plot of $\log$ of corrosion rate versus $1/T$ gives a straight line and is shown in Figure 5.1.1 A plot of $\log (CR/T)$ versus $1/T$ gives straight line and is shown in Figure 5.1.2. The values of apparent activation energy ΔH^* , ΔS^* and ΔG^* obtained from Arrhenius plot and transition state theory plot are given in

Figure 5.1 Arrhenius plot for aluminium corrosion in 0.5 M HCL in the absence and presence of different concentrations of Nicotinamide.

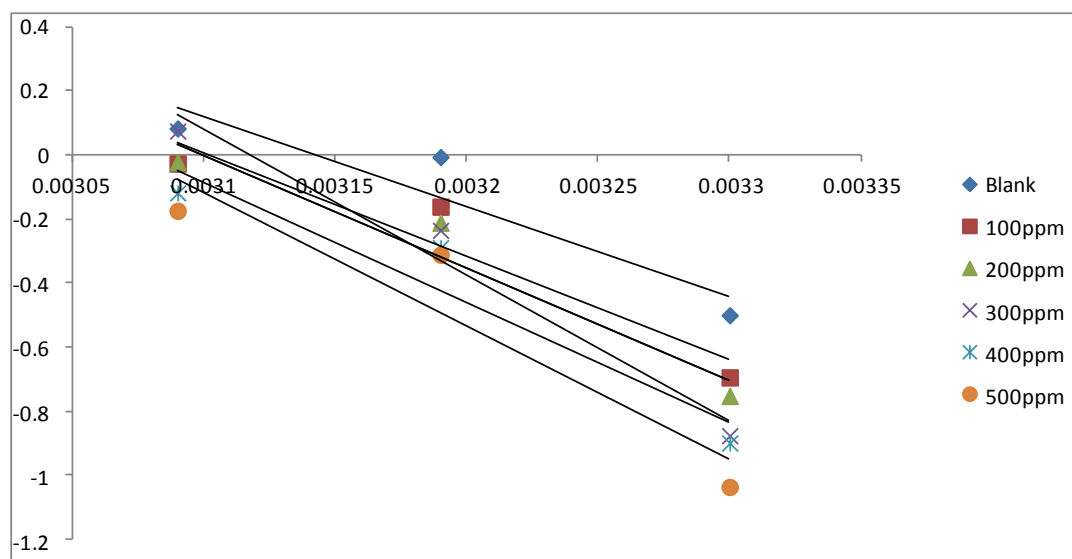


Figure 5.2 Transition state plot for aluminium corrosion in 0.5 M HCL in the absence and presence of different concentrations of Nicotinamide.

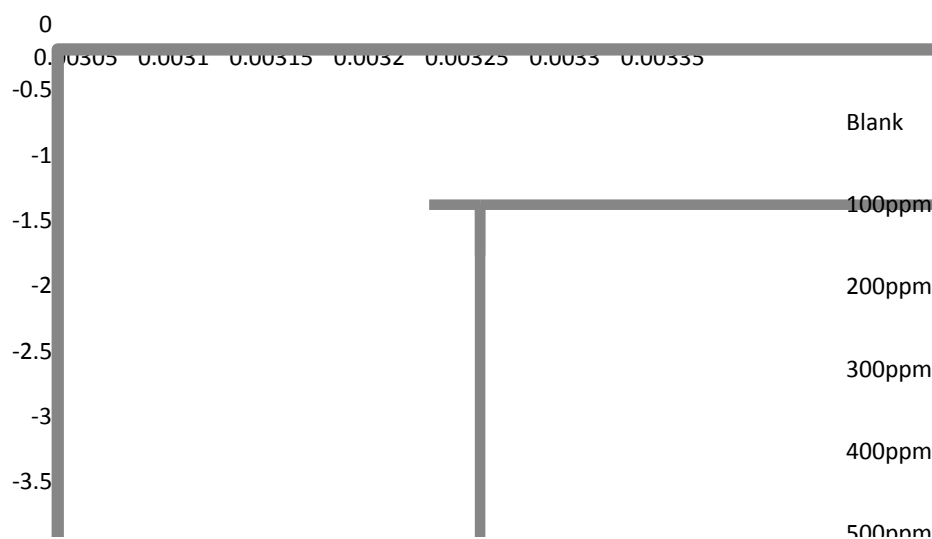


Table 5.2 Activation parameters of Nicotinamide in 0.5 M HCL.

Concentration	E_a (KJ mol ⁻¹)	ΔH^* (KJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)
Blank	53.168	512.75	-0.965
100	61.38	589.72	-0.943
200	67.01	644.48	-0.926
300	73.65	711.31	-0.906
400	71.78	693.12	-0.913
500	79.38	678.17	-0.890

Comparison of the activation energies at various concentrations show that the activation energy of the corrosion process increases on the addition of BBAF. The higher value of activation energy clearly reveals that the corrosion process is inhibited by the addition of inhibitor. Higher

Ea value leads to lower corrosion rate. Decrease in the corrosion rate with increase in the inhibitor concentration suggests that the Ea is the deciding factor which influences the corrosion rate. Experimental corrosion rate values evaluated from the weight loss data for aluminium in 0.5M HCL in the absence and presence of Nicotinamide are used to determine the enthalpy of activation (ΔH^*) and the apparent entropy of activation (ΔS^*) for the formation of the activated complex in the transition state using absolute reaction rate theory as (159,160)

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{\Delta H^*}{RT}\right) \text{ --- (4)}$$

Where h is the Planck 's constant, N is the Avogadro's ΔS^* is the apparent entropy of activation.

The positive value of enthalpy of activation (ΔH^*) in the absence and presence of various concentration of inhibitor reflects the endothermic Aluminium dissolution process. Increase in the ΔH^* value with respect to blank implies that the dissolution of Aluminium is difficult in the presence of inhibitor (161). The value ΔH^* is greater in the presence of the inhibitor than in the absence of inhibitor. This may be attributed to the higher energy barrier of the reaction, which leads to rise in enthalpy of the corrosion process.

Entropy of activation of the corrosion process in free acid solution shows a negative value. This implies that the transition state represents more orderly arrangement compared to the reactants. The addition of inhibitor shifts the ΔS^* value to less negative side. This shows that addition of inhibitor increases the randomness in the transition state. The change in activation free energy (ΔG^*) of the corrosion process can be calculated at each temperature by applying the equation

$$\Delta G^* = \Delta H^* - T\Delta S^* \text{ ----- (5)}$$

5.1.3 Results of potentiodynamic polarization studies

The potentiodynamic polarization of aluminium immersed 0.5M HCL in the presence and absence of Nicotinamide with KI are given in figure 5.2 the corrosion parameters of aluminium immersed in different concentration of HCl solution in the presence and absence of Nicotinamide with KI are given in

Figure 5.2 Blank of potention dynamic curve for corrosion of aluminium in 0.5 M HCl

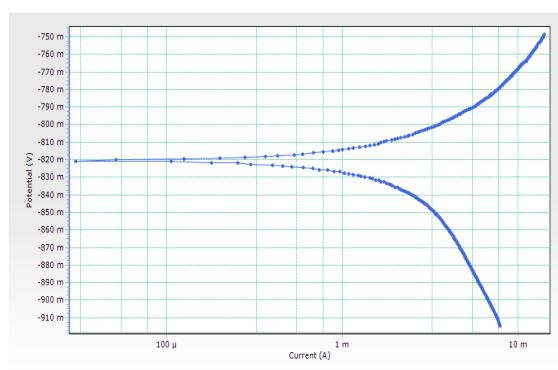


Figure 5.2 200ppm of potention dynamic curve for corrosion of aluminium in 0.5 M HCl

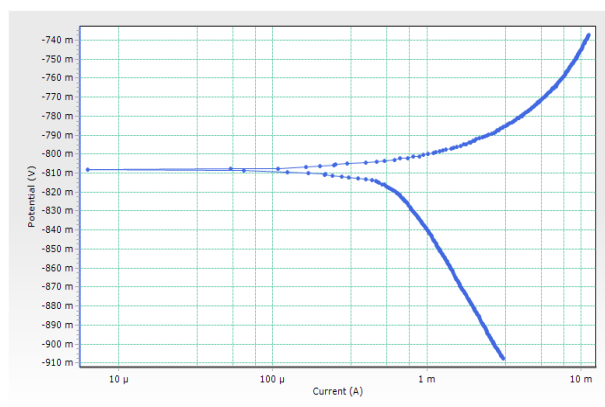
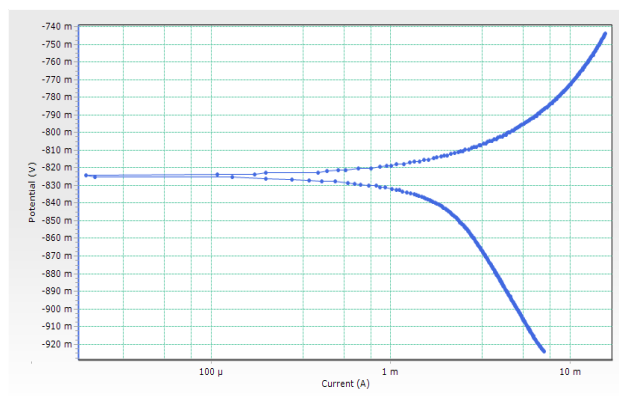


Figure 5.3 400ppm of potentiation dynamic curve for corrosion of aluminium in 0.5 M HCl**Table 5.3 potentiodynamic polarization parameters of aluminium immersed in 0.5M HCl in the presence and absence of inhibitor system at 303K**

Medium of 0.5M HCl in Nicotine amide

Concentration	-E _{corr} Mv	I _{corr} $\mu\text{A cm}^{-2}$	β_c Mv dec^{-1}	Ba Mv dec^{-1}
Blank	-820.497	-7.729	1.667	143.24
200	-808.256	-1.207	2.678	36.254
400	-824.706	-7.659	2.094	150.587

I_{corr} value is the measure of corrosion rate of metal in given medium. The decrease in the I_{corr} value on the addition of inhibitor system clearly shows the inhibiting effect of inhibitor system. The shift in the E_{corr} value towards more negative value when the concentration of the medium changes from -574.334 mV versus SCE to -591.957mV versus SCE shows that the chloride ion attacks the aluminium more vigorously and causes dissolution of iron and chromium. In 0.5M HCl the E_{corr} value is shifted from -574.33mV versus SCE to -498mV versus SCE on the

addition of inhibitor. In 0.5M HCl the E_{corr} value is shifted from -591.957m V versus SCE to -542.287m V versus SCE on the addition of inhibitor. The shift towards less negative value indicates that the inhibitor is an anodic inhibitor [].

6.1 CONCLUSION

- ✓ Inhibition efficiency value increases with the increasing inhibitor concentration.

- ✓ Effect of temperature results reveal that the inhibition efficiency decreases with rise in temperature.
- ✓ Thermodynamic and kinetic data reveals that it follows the physical adsorption mechanism.
- ✓ Impedance study explain the solution behavior of inhibitor like R_s , R_{ct} , C_{dl} .whenever increase the concentration increase the R_{ct} , C_{dl} , R_s value.
- ✓ Electrochemical polarization curves proved that Nicotinamide act as mixed type inhibitor by inhibiting both anodic and cathodic reactions to some extent. The inhibitor minimum concentration act as cathodic inhibitor maximum concentration act as anodic inhibitor.

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