

## Electrochemical Investigation of the Corrosion Inhibition of Aluminium in Koh by Urea with Ki As A Synergistic Agent

Okeke P. I., Odilora C. A., Chukwu P. I.

Department of Pure and Industrial Chemistry,  
Chukwuemeka Odumegwu Ojukwu University Uli, Anambra State, Nigeria.  
Corresponding Author: Okeke P. I.,

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**Abstract:** Electrochemical investigation of the corrosion inhibition of aluminium in KOH in the presence of 2.5 M and 4.0 M urea was carried out using weight loss and electrochemical techniques. The effects of the addition of KI and adsorption characteristics were also evaluated. The result for the weight loss measurements showed that weight loss of the aluminium was greatly reduced in the presence of the inhibitor. The addition of KI was seen to have synergistically reduced the weight loss further as concentration and time increased. Electrochemical result showed that the inhibitor reduced the cathodic and anodic current densities, and that urea functioned as a mixed type inhibitor. Inhibition efficiency increased also as concentration and time prolonged. Adsorption characteristic revealed that  $\Delta G_{ads}$  gave a negative value, showing that the adsorption process is spontaneous and feasible.

**Keywords:** Aluminium, Corrosion, Electrochemical, Inhibition efficiency, Adsorption.

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### I. Introduction

Metallic materials used for construction purposes are known to deteriorate and may eventually collapse completely when exposed to aggressive alkaline environments. Aluminium metal is widely put to use in most industrial and structural applications such as, tanks, aerospace aluminium parts etc. These and other aluminium based structures are often maintained by the use of alkaline cleaners in the etching and rinsing operations [1]. Due to the extensive usage and exposure of Aluminium, it becomes necessary to protect it from these aggressive environments. The use of inhibitors to protect this metal from such attacks have been reported over time [2-4]. The investigation of these corrosion inhibitors provides useful insight into the mechanism by which materials added into the aggressive environments impede the reaction between the corrodent and the metal surfaces. Such inhibitors have been reported to operate by adherence of the polar groups unto the metal surface through the metal ions present at the lattice structure of the metal. In most cases, adsorption occurs generally over a metal surface producing a layer that functions as a barrier between the metal and the corrodent, isolating it from aggressive attack [5-6]. This, usually leads to a structural modification in the double layer, giving rise to a reduction in the rates of the electrochemical half cell reactions; the cathodic reduction of hydrogen ions and the anodic reduction of metal dissolution [7-9]. The use of natural products of plant origin as inhibitors have been widely reported [10-13] Inorganic inhibitors like chromates are toxic and also cause pollution [7, 14-17] leading to the high demand for organic inhibitors that are eco-friendly, cheap and readily available. This study focuses on the electrochemical investigation of the corrosion inhibition of aluminium in KOH by urea with KI providing a synergistic effect.

### II. Experimental Section

#### 2.1 Aluminium Metal Preparation

The aluminium alloy AA1060 used for this experiment is 0.045cm in thickness and the composition in weight % is as follows: Si (0.35), Fe (0.7), Cu (0.15), Mn (0.05) while the balance is for Al. The specimen was mechanically pressed cut into 2 x 2 cm coupons. The two faces had a total geometric surface area of 8.0 cm<sup>2</sup>. The coupons were degreased in absolute ethanol, dried in warm air, and stored in moisture free desiccator before laboratory analysis

#### 2.2 Gravimetric measurements

Weight loss determination, also known as gravimetric experiment was carried out. Previously weighed aluminium metal coupons were completely immersed and suspended in 250 cm<sup>3</sup> of the test solution in an open beaker. The corrodent was 0.08 M KOH while the inhibitors were urea concentrations 2.5 M and 4.0 M. The aluminium coupons were suspended using polyethylene twines and wooden crossbars. The experiments were

carried out at room temperature. The coupons were drawn from the test solution at 3 hr intervals progressively for 15 hrs and washed in a solution containing 50% NaOH and 100 g/L zinc dust. The washed coupons were rinsed in ethanol, and dried with acetone before reweighing. The difference in weight for a period of 15 hrs was taken as the total weight loss from the mean value (mean of duplicate determination using 2 coupons for measurements). Inhibition efficiency was calculated using the formula,  $IE (\%) = ((W_1 - W_2) / W_1) \times 100$  in the different inhibitor/corroderent solutions for gravimetric test, where  $W_1$  and  $W_2$  are the corrosion rates in the uninhibited (blank) and inhibited system, respectively.

### 2.2.1 For the Synergistic Measurements

The coupons prepared for the gravimetric measurements were reproduced and 0.005 M KI was added to each beaker containing the blank and with the various concentrations of the inhibitors. The coupons were drawn from the test solution at 3 hr intervals progressively for 12 hrs and washed in a solution containing 50% NaOH and 100 g/L zinc dust. The washed coupons were rinsed in ethanol, and dried with acetone before reweighing.

The difference in weight for a period of 12 hrs was taken as the total weight loss from the mean value (mean of duplicate determination using 2 coupons for measurements). This has been described in our previous work [17]

### 2.3 Electrochemical Measurements

The metal used for constructing the working electrode was aluminium that had the same chemical composition with that used in gravimetric measurements. The aluminium was encapsulated in epoxy resin in such a way that only 1cm<sup>2</sup> surface was left uncovered. The exposed area (1cm<sup>2</sup>) was degreased in absolute ethanol and then dried in acetone.

The potentiodynamic polarization tests were carried out using a conventional three electrode electrochemical cell mainly: a saturated calomel electrode (SCE), which was used as the reference electrode, the working electrode which was aluminium, while a graphite rod was the counter electrode. The potentiodynamic polarization (pdp) measurements were done at  $\pm 0.25$  volts versus open circuit potential (OCP) at the step height of 1 mm, a step time of 3 s and at scan rate of  $\pm 0.333$  volts per second.

The working electrode was introduced into the test solution and allowed to run for 30 min at the open circuit potential to stabilize the system before the polarization measurement,

To test the reliability and reproducibility of the measurement, triplicate experiments were performed in each case of the same conditions.

For potentiodynamic polarization test (Pdp), inhibition efficiency was calculated from the relation,

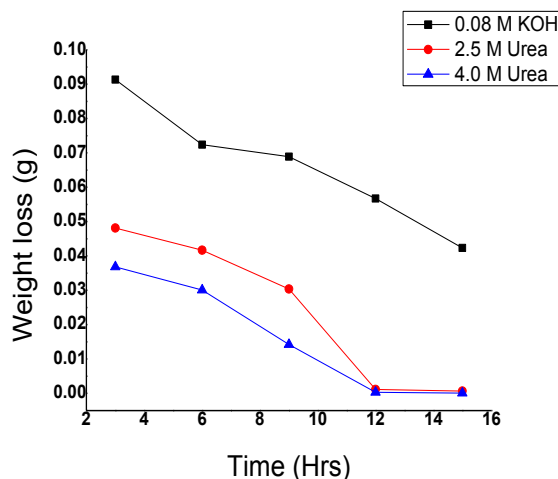
$$IE (\%) = ((i_{\text{corrb1}} - i_{\text{corrinh}}) / i_{\text{corrb1}}) \times 100$$

Where  $i_{\text{corrb1}}$  and  $i_{\text{corrinh}}$  are the corrosion current density in the absence and presence of the inhibitor.

## III. Result And Discussion

### 3.1 Gravimetric result

#### 3.1.1 Effect of Urea on Weight Loss of Aluminium



**Figure 1:** Graph of weight loss against time for aluminium in 0.08 M KOH blank and with 2.5 M and 4.0 M Urea.

Figure 1 presents weight loss of aluminium in 0.08 M KOH in the absence and presence of 2.5 M, and 4.0 M Urea for 15 hrs. Weight loss decreased appreciably in the presence of 2.5 M urea inhibitor from 0.0481 g at 3 hrs and sloped to 0.00065 g at 15 hrs as illustrated in Figure 1.

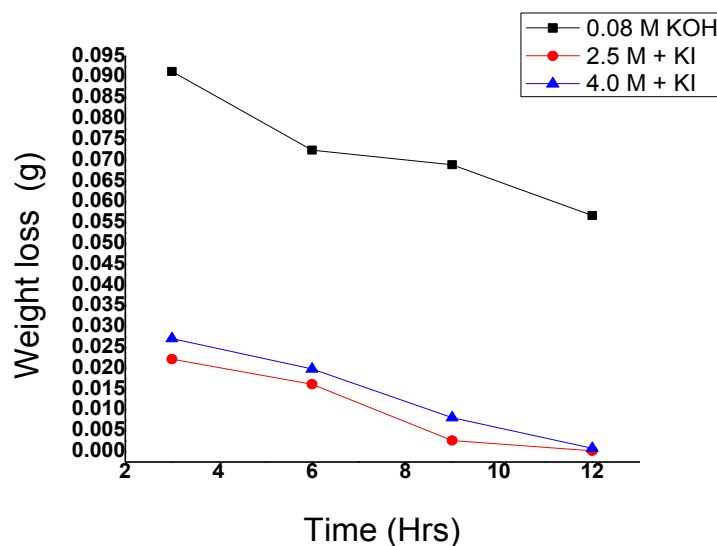
The effect of concentration of urea was evident as weight loss was lower in the 4.0 M urea concentration from 0.0368 g at 3 hrs and sloped to 0.0001 g at 15 hrs in comparison with the values obtained from the uninhibited system ranging from 0.0913 g at 3 hrs to 0.0423 g at 15 hrs. The deduction is that urea, protected aluminium from excessive weight loss. The weight loss decreased with increase in concentration and time as indicated from the Figure 1.

**Table 1:** Inhibition Efficiency (%) for Aluminium in 0.08 M KOH Blank and with 2.5 M and 4.0 M Urea.

Time (Hrs)	2.5 M	4.0 M
3	47.32	59.69
6	48.47	68.49
9	54.56	78.70
12	97.97	99.38
15	98.46	99.76

Table 1 shows Inhibition efficiency (%) for aluminium in 0.08 M KOH in the presence of 2.5 M and 4.0 M Urea. The inhibition efficiency in the presence of 2.5 M concentration of the inhibitor gave 47.32 % after 3 hrs, while 4.0 M gave 59.69 %. The efficiency increased continuously with time such that at 15 hrs, 2.5 M urea gave 98.46 %, while 4.0 M gave 99.76 %, exhibiting very high inhibition efficiency. The effect of concentration on the inhibition efficiency was evident as it also increased with increase in concentration as seen from the result.

### 3.1.2 Synergistic Effect of Urea /KI on Aluminium



**Figure 2:** Graph of Weight Loss Against Time for Aluminium in 0.08 M KOH Blank , 2.5 M Urea + 0.005 M KI and 4.0 M Urea + 0.005 M KI.

**Table 2:** Weight Loss of Aluminium in 0.08 M KOH in Absence (blank) and Presence of 2.5 M Urea + 0.005 M KI and 4.0 M Urea + 0.005 M KI.

Time(Hr)	BLANK	2.5 M Urea + 0.005 M KI	4.0 M Urea + 0.005 M KI
3	0.0913	0.02220	0.02715
6	0.0724	0.01620	0.01985
9	0.0689	0.00265	0.00815
12	0.0567	0.00020	0.00080

Figure 2 and Table 2 show the graph and data of weight loss of aluminium in 0.08 M KOH in absence (blank) and presence of 2.5 M Urea + 0.005 M KI and 4.0 M Urea + 0.005 M KI. The result revealed a further decrease in weight loss in the presence of 2.5 M urea inhibitor and 0.005 M KI from 0.0222 g instead of 0.0481 g for 2.5 M urea inhibitor without KI at 3 hrs to 0.0002 g instead of 0.00115 at 12 hrs under the same experimental conditions. However, the 4.0 M urea concentration revealed a different trend in Figure 2, showing that the synergistic effect was more significant in lower concentrations of urea.

**Table 3:** Inhibition Efficiency (%) for Aluminium in 0.08 M KOH with 2.5 M Urea + 0.005 M KI and 4.0 M Urea + 0.005 M KI.

Time (Hrs)	2.5 M + 0.005 M KI	4.0 M + 0.005 M KI
3	75.68	70.26
6	78.11	73.18
9	96.04	87.82
12	99.65	98.58

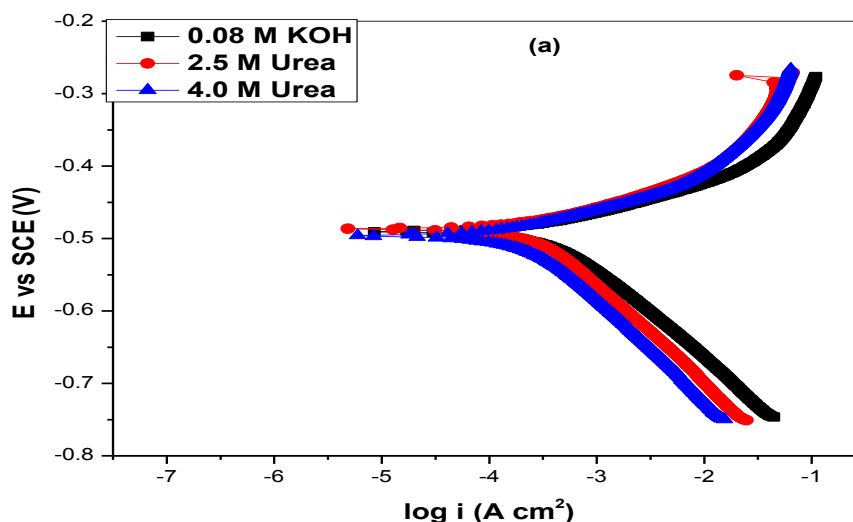
Table 3 is the result of the inhibition efficiency (%) for aluminium in 0.08 M KOH in presence of 2.5 M Urea + 0.005 M KI and 4.0 M Urea + 0.005 M KI. Inhibition efficiency in the presence of 2.5 M concentration of urea gave 47.32 % after 3 hrs and 75.68 % in the system with KI. 4.0 M urea gave 59.69 % and 70.26 % in the system with KI, showing very high inhibition efficiency.

As seen in Table 3, inhibition efficiency increased due to the synergistic effect of urea +KI. It is more pronounced at lower concentrations; but observed to have reduced slightly with increase in concentration.

### 3.2 Electrochemical Result

**Table 4:** Potentiodynamic Polarization Results for Aluminium in 0.08 M KOH Blank, with urea and 0.005 M KI.

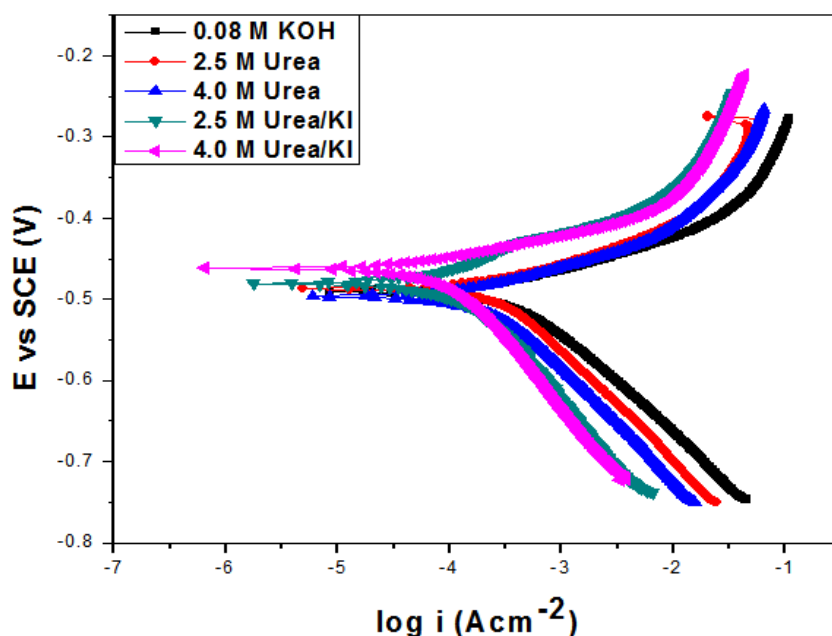
System	$E_{corr}$ (mV vs SCE)	$I_{corr}$ (mA/cm <sup>2</sup> )	IE%
0.08 M KOH	-485.1	649.5	—
2.5 M Urea	-482.3	295.3	54.5
4.0 M Urea	-452.4	231.7	64.3
2.5 M Urea/KI	-480.7	113.7	82.5
4.0 M Urea/KI	-453.8	142.5	78.1



**Figure 3:** Potentiodynamic Polarization Curves for Aluminium in 0.08 M KOH Blank and with 2.5 M and 4.0 M Urea.

Figure 3 shows potentiodynamic polarization curves for aluminium in 0.08 M KOH blank and in the presence of 2.5 M and 4.0 M urea. In 2.5 M and 4.0 M urea environment containing aluminium coupon, the corrosion potential,  $E_{corr}$ , are -482.3 mV and -452.4 mV respectively as shown in Figure 3 and in table 3. The corresponding  $i_{corr}$  values are 295.3 mA/cm<sup>2</sup> and 231.3 mA/cm<sup>2</sup> for the 2.5 M and 4.0 M concentrations. The result indicates that the presence of the inhibitor reduces both the cathodic and the anodic corrosion current densities. This is depicted in Figure 3. The inhibitor shifts both the anodic and cathodic curves to lower values of current densities when compared to the blank values where  $E_{corr}$  is -485.1 mV and  $I_{corr}$  is 649.4 mA/cm<sup>2</sup>, showing that the corrosion rate of aluminium was reduced. Also, the  $E_{corr}$  of the 4.0 M concentration of urea is more negative (cathodic) than that of the 2.5 M concentration.

Inhibition efficiency is higher in the 4.0 M concentration, giving 64.5 % while the 2.5 M concentration gave 54.5 %.



**Figure 4:** Potentiodynamic Polarization Curves for Aluminium in 0.08 M KOH Blank and in the Presence of 2.5 M Urea, 4.0 M Urea, 2.5 M Urea + 0.005 M KI and 4.0 M Urea+ 0.005 M KI.

Figure 4 is the Potentiodynamic polarization curves for aluminium in 0.08 M KOH blank and in the presence of 2.5 M urea, 4.0 M urea, 2.5 M urea + 0.005 M KI and 4.0 M urea+ 0.005 M KI. In the 2.5 M urea + 0.005 M KI and 4.0 M urea+ 0.005 M KI environment containing aluminium coupons, the corrosion potential,  $E_{\text{corr}}$ , are -480.7 mV and -453.8 mV respectively as can be seen in Figure 4 and in Table 4. The corresponding  $i_{\text{corr}}$  values are 113.7 mA/cm<sup>2</sup> and 142.5 mA/cm<sup>2</sup> which have been reduced compared to 295.3 mA/cm<sup>2</sup> and 231.3 mA/cm<sup>2</sup> for the 2.5 M and 4.0 M urea concentrations without 0.005 M KI.

This is attributed to the effect of synergy due to the reduction of both the cathodic and the anodic corrosion current densities significant in Figure 4. Urea + KI shifts both the anodic and cathodic curves to lower values of current densities when compared to the blank values where  $E_{\text{corr}}$  is -485.1 mV and  $I_{\text{corr}}$  is 649.4 mA/cm<sup>2</sup> showing that the corrosion rate of aluminum decreased. The  $E_{\text{corr}}$  of the 4.0 M urea+ 0.005 M KI concentration is more positive (anodic) followed by the other systems. Inhibition efficiency is higher in the 2.5 M + 0.005 M KI than in 4.0 M urea+ 0.005 M KI, giving 82.5 % and 78.1 % respectively, while inhibition efficiency of 4.0 M and 2.5 M concentrations without KI gave 64.5 % for the 4.0M and 54.5 % for the 2.5 M.

### 3.3 Adsorption Considerations:

Adsorption isotherm and surface coverage data are very useful in determining inhibitor adsorption characteristics. Such data are applied in determining adsorption mechanism and the mode of adsorption of inhibitor molecules on the metal surface. The data obtained from gravimetric measurements can be used to determine the adsorption characteristics of urea on aluminium in alkaline environment using the Langmuir equation:

$$C/\Theta = 1/K_{\text{ads}} + C, \quad \Theta = (\text{IE \%})/100 \quad \Delta G_{\text{ads}} = -RT \ln (55.5 K_{\text{ads}})$$

Where  $1/K_{\text{ads}}$  is the intercept,  $K_{\text{ads}}$  is the equilibrium constant of adsorption process,  $C$  is the inhibitor concentration,  $\Theta$  is the surface coverage,  $\Delta G_{\text{ads}}$  is the free energy of adsorption (KJmol<sup>-1</sup>), 55.5 is the concentration of water molecules in the solution in mol/L,  $T$  is the temperature (298 °K) and  $R$  is the universal gas constant (8.314JK<sup>-1</sup>mol<sup>-1</sup>).

**Table 5:** Adsorption Characteristics of Urea for Gravimetric Measurement at Room Temperature.

Urea at 3 Hrs		
Concentration, C (M)	2.5	4.0
Inhibition efficiency, IE (%)	47.32	59.69
Surface coverage, $\Theta$	0.4732	0.5969
C/ $\Theta$	5.28	6.70
$K_{ads}$	0.36	0.37
$\Delta G_{ads}$ (KJmol <sup>-1</sup> )	-7.4	-7.5
Urea at 15 Hrs		
Concentration, C (M)	2.5	4.0
Inhibition efficiency, IE (%)	98.46	99.76
Surface coverage, $\Theta$	0.9846	0.9976
C/ $\Theta$	2.54	4.01
$K_{ads}$	25	100
$\Delta G_{ads}$	-17.9	-21.4

At 3hrs immersion, 2.5 M urea gave  $K_{ads}$  of 0.36, while 4.0 M urea gave 0.37. At 15 hrs immersion, it increased to 25 and 100 respectively. Large values of  $K_a$  indicates efficient adsorption and hence better inhibition efficiency. This is evident in Table 5, and also in agreement with the gravimetric results. Surface coverage increased with increase in time and concentration, showing favourable adsorption. Value of  $\Delta G_{ads}$  of 0 KJmol<sup>-1</sup> up to -20 KJmol<sup>-1</sup> indicates physisorption due to interaction between the charged organic molecules and the charged metal surface while those more negative than -40 KJmol<sup>-1</sup> indicates chemisorption [18]. Free energy of adsorption,  $\Delta G_{ads}$  for 2.5 M urea at 15 hrs gave -17.9KJmol<sup>-1</sup> while 4.0 M urea gave -21.4KJmol<sup>-1</sup>, signifying the presence of physical adsorption. The negative value of  $\Delta G_{ads}$  reveals that the adsorption process is feasible and spontaneous.

#### IV. Conclusion

The findings from this research showed that urea protected aluminium from excessive weight loss; this ability increased with increase in concentration and time. Inhibition efficiency also increased due to the synergistic effect of KI. This is more pronounced at lower concentration. Potentiodynamic polarization curves revealed that urea inhibitor itself functioned as a mixed type inhibitor, reducing both the anodic and cathodic curves. Free energy of adsorption,  $\Delta G_{ads}$ , obtained for 2.5 M urea at 15 hrs gave -17.9KJmol<sup>-1</sup> while 4.0 M urea gave -21.4KJmol<sup>-1</sup>, indicating the presence of physical adsorption. The negative value of  $\Delta G_{ads}$  reveals that the adsorption process is feasible and spontaneous. This shows that urea being eco-friendly, cheap and readily available can effectively be used to protect aluminium from excessive corrosion in an alkaline system.

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