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**KN Rathod**  
 Department of Chemistry,  
 Navyug Science College,  
 Rander Road, Surat-395005,  
 Gujarat, India.

**RT Vashi**  
 Department of Chemistry,  
 Navyug Science College,  
 Rander Road, Surat-395005,  
 Gujarat, India.

## Inhibition effect of ammonium dichromate on the corrosion of aluminium in phosphoric acid

**KN Rathod, RT Vashi**

### Abstract

The inhibition effect of ammonium dichromate on the corrosion of aluminium in phosphoric acid was investigated by weight loss method, Potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) measurements. The study revealed that as the concentration of acid increases corrosion rate increases. Inhibition efficiency (I.E.) increases as the concentration of inhibitor increases. The investigation of adsorption isotherm indicate that the inhibitor fit Langmuir isotherm, fairly good. The phenomenon of physisorption is attributed to the values of  $E_a$ ,  $Q_{ads}$  and  $\Delta G^0_{ads}$ . The Potentiodynamic polarisation result reveals that the inhibitor act as mixed type inhibitor. Percentage I.E. of inhibitor was found almost similar by weight loss, polarisation and by EIS methods.

**Keywords:** Corrosion, Aluminium, Ammonium dichromate, Phosphoric acid.

### 1. Introduction

The mechanism of corrosion studies of aluminium (Al) and its alloy are still of considerable interest because of their technological importance and industrial application, especially in automobile, aviation, household appliances, containers and electronic device. Aluminium is remarkable for the metal's low density relatively soft, durable, lightweight and non-magnetic. Phosphoric acid is widely used for acid cleaning and electro polishing of aluminium<sup>[1]</sup>.

Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitor<sup>[2-4]</sup>. According to Heckerman *et al.*<sup>[5]</sup> studied the inhibitive properties of a series of secondary aliphatic and cyclic amines in acid media are controlled by the percentage of  $\pi$ -orbital of free electron on the nitrogen atom of these compounds. R. T. Vashi *et al.*<sup>[6]</sup> has studied the corrosion inhibition of zinc in phosphoric acid by 4-amino antipyrine. R. T. Vashi *et al.*<sup>[7]</sup> studied aniline as corrosion inhibitor for zinc in phosphoric acid. Mohammed *et al.*<sup>[8]</sup> studied the corrosion inhibition of aluminium in phosphoric acid by purine. Xianghong Li<sup>[9]</sup> *et al.* has studied effect of *Dendrocalamus brandisii* leaves extract on aluminium in HCl/H<sub>3</sub>PO<sub>4</sub> solution. Deepa prabhu<sup>[10]</sup> *et al.* has studied *coriandrum sativum L.* seed extract as novel eco-friendly inhibitor for aluminium in phosphoric acid. M. Abdulwahab<sup>[11]</sup> *et al.* studied inhibitive effect by *Ricinus Communis* on corrosion of aluminium alloy in HCl/H<sub>3</sub>PO<sub>4</sub> acid. Magda Ameer *et al.*<sup>[1]</sup> has studied electrochemical corrosion inhibitor of Al-alloy in phosphoric acid. In the present work, the corrosion of aluminium in phosphoric acid and its inhibition by ammonium dichromate has been reported.

### 2. Materials and methods

To study the corrosion of aluminium in phosphoric acid several methods like weight loss, temperature effect, potential, polarization measurements and electrochemical impedance spectroscopy (EIS) have been used.

Aluminium sheets of the 2S type Aluminium (Al=99.54%, Si=0.090%, Fe=0.320%, Cu=0.0012%, Mn=0.0034%, Mg= 0.0014%, Cr= 0.0042%, Ni = 0.0046%, Zn = 0.0020%, Ti = 0.0079%, Pb = 0.0005% and Sn = 0.0026%) were used in this study. Rectangular specimens of aluminium having an area of 0.2977 dm<sup>2</sup> were taken and cleaned by buffing and immersed in 1.0, 1.25, 1.50 and 1.75 M phosphoric acid concentration with and without inhibitor containing 230 ml test solution at 301± 1 K for 24 h immersion period. After the test, specimens were cleaned by chromic and nitric acid solution for a period of about 2 minutes. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier. The mean value of weight loss was reported as mg/dm<sup>2</sup> shown in Table 1. All chemicals used were of AR grade.

### Correspondence

**KN Rathod**  
 Department of Chemistry,  
 Navyug Science College,  
 Rander Road, Surat-395005,  
 Gujarat, India.

The corrosive solution was prepared in double distilled water. To study the effect of temperature on corrosion of aluminium in 1.0 M H<sub>3</sub>PO<sub>4</sub>, the specimens were immersed in 230 ml of corrosive solution and corrosion rate was determined at various temperatures like 313, 323 and 333 K for an immersion period of 2 h with and without inhibitor. From the data, I.E. (in %), energy of activation (Ea), heat of adsorption (Q<sub>ads</sub>) and Gibbs free energy (ΔGa) were calculated and were shown in Table 2.

For polarization study, metal specimens having an area of 1 cm<sup>2</sup> were immersed in 230 ml corrosive solution without and with 4 mM inhibitor concentration in 1.0 M H<sub>3</sub>PO<sub>4</sub>. The test cell includes the metal specimens as a working electrode, corrosive solution in which the specimen was to be tested and saturated calomel electrode (SCE) as a reference electrode as well as platinum electrode as an auxiliary electrode. The polarization study was made by using potenti-galvano-scan meter, polarization curves were plotted with potential against log current density (called Tafel plots). Cathodic and anodic polarization curves give cathodic and anodic Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines gives the corrosion current (I<sub>corr</sub>) and the corrosion potential (E<sub>corr</sub>)<sup>[12]</sup>.

EIS measurements were carried out in the frequency range of 10<sup>5</sup> Hz to 0.1 Hz. The open circuit potential was measured after 30 minutes of immersion of electrode in test solution by applying amplitude of 0.005 V sine wave ac signal. EIS data were analysed using frequency response analyzer electrochemical set up. The charge transfer resistance (R<sub>ct</sub>), was obtained from the diameter of the semicircle of the Nyquist plot<sup>[13]</sup>.

### 3. Results and discussion

The results were presented in Table 1 to 3 and in Figs. 1 to 3. To study the effect of corrosion of aluminium in phosphoric acid, ammonium dichromate was added as inhibitor.

I.E. has been calculated as follows:

$$\text{I.E.} = \frac{W_u - W_i}{W_u} \times 100 \dots \dots (1)$$

Where, W<sub>u</sub> is the weight loss of metal in uninhibited acid and W<sub>i</sub> is the weight loss of metal in inhibited acid.

Energy of activation (Ea) has been calculated from the slop of log ρ versus 1/T (ρ = corrosion rate, T = absolute temperature) and also with the help of the Arrhenius equation<sup>[14]</sup>.

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R} \left[ \left( \frac{1}{T_1} \right) - \left( \frac{1}{T_2} \right) \right] \dots \dots (2)$$

Where ρ<sub>1</sub> and ρ<sub>2</sub> are the corrosion rate at temperature T<sub>1</sub> and T<sub>2</sub> respectively.

The value of heat of adsorption (Q<sub>ads</sub>) were calculated by following equation<sup>[15]</sup>.

$$Q_{ads} = 2.303 R \left[ \log \left( \frac{\theta_2}{1 - \theta_2} \right) - \log \left( \frac{\theta_1}{1 - \theta_1} \right) \right] \times \left[ \frac{T_1 \times T_2}{T_2 - T_1} \right] (3)$$

Where, θ<sub>1</sub> and θ<sub>2</sub> are the fractions of the metal surface covered by the inhibitors at temperature T<sub>1</sub> and T<sub>2</sub> respectively.

The values of the free energy adsorption (ΔGa) were calculated with the help of following equation (4).

$$\log C = \log \left( \frac{\theta}{1 - \theta} \right) - \log B \dots \dots (4)$$

Where, log B = -1.74 -  $\left( \frac{\Delta G_a}{2.303 RT} \right)$  and C is the inhibitor concentration.

The enthalpy of adsorption (ΔH<sub>a</sub><sup>0</sup>) and entropy of adsorption (ΔS<sub>a</sub><sup>0</sup>) are calculated using the equations (5) & (6).

$$\Delta H_a^0 = E_a - RT \dots \dots (5)$$

$$\Delta S_a^0 = \frac{\Delta H - \Delta G}{T} \dots \dots (6)$$

**Corrosion in acid:** The rate of corrosion increases with increase in acid concentration. The corrosion rate was found 389.7, 454.0, 486.2 and 525.6 mg/dm<sup>2</sup> in 1.0, 1.25, 1.50 and 1.75 M H<sub>3</sub>PO<sub>4</sub> concentrations respectively for a exposure period of 24 h at 301 ± 1 K as shown in Table 1.

**Corrosion in presence of inhibitor:** To assess their protective value ammonium dichromate was added in 1, 2, 3 and 4 mM concentrations in a solution of 1.0, 1.25, 1.50 and 1.50 M H<sub>3</sub>PO<sub>4</sub> acid for 24 h duration period (Table 1).

**Effect of inhibitor concentration:** At constant acid concentration, the I.E. of the ammonium dichromate increases with the inhibitor concentration. In case of ammonium dichromate the I.E. was found to be 35.78, 92.66, 93.58 and 97.25% with respect to 1, 2, 3 and 4mM inhibitor concentration respectively in 1.0 M H<sub>3</sub>PO<sub>4</sub> (Table 1).

**Effect of acid concentration:** At constant inhibitor concentration, the I.E. decreases with the increase in acid concentration. At 4 mM inhibitor concentration, the I.E. of ammonium dichromate was found as 92.52, 93.38, 96.85 and 97.25% with correspond 1.0, 1.25, 1.50 and 1.75 M acid concentration respectively (Table 1).

**Effect of temperature:** As the temperature increases, corrosion rate increases while percentage of I.E. decreases (Table 2). Mean 'Ea' values were calculated by using equation- 2 for aluminium in 1.0 M H<sub>3</sub>PO<sub>4</sub> was 66.32 kJ mol<sup>-1</sup> while in acid containing inhibitor, the mean Ea values were found to be higher than that of uninhibited system (Table 2). The higher values of mean Ea indicate physical adsorption of the inhibitors on metal surface. The values of Ea calculated from the slop of Arrhenius plot (Fig 2) and using equation 2 are almost similar. From Table 2, it is evident that in all cases, the Q<sub>ads</sub> values are negative and ranging from -5.08 to -47.13 kJ mol<sup>-1</sup>. The mean ΔGa values are negative almost in all cases and lie in the range of -10.47 (1 mM) to -11.46 (4 mM). Thus suggest that they are strongly absorbed on the metal surface<sup>[16]</sup>. The enthalpy changes (ΔH<sub>a</sub><sup>0</sup>) are positive indicating the endothermic nature of the reaction and suggesting that higher temperature favours the corrosion process. The entropy (ΔS<sub>a</sub><sup>0</sup>) values are positive confirming that the corrosion process is entropically favourable.

**Polarization behaviour:** Anodic and cathodic galvanostatic polarization data were shown in Table 3, which shows polarisation of both anodes as well as cathodes (Fig 3). In almost all the cases, the I.E. from Tafel plots agree well with the values obtained from weight loss data.

The electrochemical corrosion current density *i<sub>corr</sub>* was evaluated using following equation.

$$i_{corr} = \frac{\beta_a \times \beta_c}{2.303(\beta_a + \beta_c)} \dots \dots (7)$$

**Electrochemical Impedance Spectroscopy Measurements:**

The interfacial double layer capacitance ( $C_{dl}$ ) values were obtained by determining the frequencies at which the imaginary component of the impedance is maximum  $f(-Z''_{max})$  using following equation:

$$C_{dl} = \frac{1}{2\pi f R_{ct}} \dots \dots \dots (8)$$

The percentage of I.E. was calculated by using this equation:

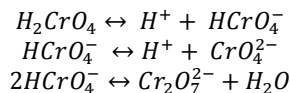
$$I.E. (\%) = \frac{C_{dl(uninh)} - C_{dl(inh)}}{C_{dl(uninh)}} \times 100 \dots \dots \dots (9)$$

Impedance plots were semicircles both in the absence and in the presence of the inhibitor. The diameter of the capacitive loop increased with increase in the concentration of the inhibitor [17]. This indicates that the impedance of the inhibited substrate increases with the inhibitor concentration. Nyquist plots recorded for Aluminium in 1M  $H_3PO_4$  solution without and with 4 mM concentration of aluminium dichromate (Fig 4).

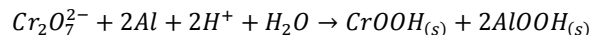
**Mechanism of corrosion inhibitor:** Corrosion protection by chromates has focused on number of specific working hypotheses regarding the mechanism of inhibition. They can be condensed to the following statements.

$Cr^{6+}$  oxoanions being highly soluble and very mobile in solution, are transported to sites of localized corrosion where are reduced to  $Cr^{3+}$  and irreversibly adsorbed at metal surface where they inhibit oxygen reduction [19].

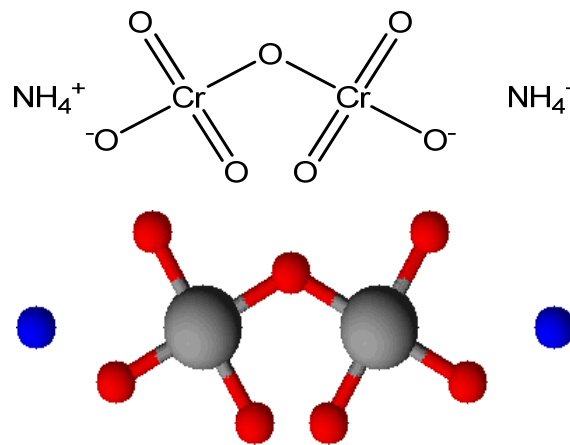
The speciation of  $Cr^{6+}$  oxoanions in aqueous solution involves the following equilibria:



The overall formation reaction for chromium on Al is typically given as.



$Cr^{6+}$  oxoanions modify the chemical composition of the surface of passive oxides and passivated intermetallic phases by adsorption.  $Cr^{6+}$  adsorb on aluminium oxides, lowering the zeta potential, there by discouraging adsorption of anions such as chloride, which promote dissolution and destabilization of protective oxides [18].



**Ammonium Dichromate [(NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>]**

The mechanism of inhibitor of corrosion is believed to be due to the formation and maintenance of a protective film on the metal surface. Further, when  $\log(\Theta/1-\Theta)$  is plotted against  $\log C$  straight lines are obtained (Fig 1) in the case of inhibitor used. This suggests that the inhibitor cover both the anodic as well as cathodic regions through general adsorption following Langmuir isotherm.

**Table 1:** Corrosion rate (CR) and inhibition efficiency (I.E.) of aluminium in 1.0, 1.25, 1.50 and 1.75 M  $H_3PO_4$  acid containing ammonium dichromate as an inhibitor for an immersion period of 24 h at 301±1K.

Inhibitor	Inhibitor Concentration mM	Acid Concentration							
		1.0M		1.25M		1.50M		1.75M	
		C L mg/dm <sup>2</sup>	I. E. %	C L mg/dm <sup>2</sup>	I. E. %	C L mg/dm <sup>2</sup>	I. E. %	C L mg/dm <sup>2</sup>	I. E. %
A	-	389.7	-	454.0	-	486.2	-	525.6	-
	1	250.3	35.78	307.5	32.28	400.4	17.65	439.7	16.33
B	2	28.6	92.66	39.3	91.34	89.4	81.62	235.9	55.10
	3	25.0	93.58	35.7	92.13	39.3	91.91	89.3	82.99
	4	10.7	97.25	14.3	96.85	32.1	93.38	39.3	92.52

A= $H_3PO_4$

B= $H_3PO_4$ +Ammonium Dichromate

**Table 2:** Effect of temperature on corrosion rate (CR), inhibitive efficiency (I.E.), energy of activation (Ea), heat of adsorption (Qads) and free energy of adsorption ( $\Delta G_a^0$ ) for Aluminium in 1.0 M  $H_3PO_4$  acid containing inhibitor.

Inhibitor Concentration: 4mM

Immersion period = 2h

Effective area of specimen = 0.2797 dm<sup>2</sup>

System	Temperature, K						Mean Ea From Eq(1) kJmol <sup>-1</sup>	Qads(kJ mol <sup>-1</sup> )	
	313		323		333			313-323	323-333
	CR mg/dm <sup>2</sup>	I.E. %	CR mg/dm <sup>2</sup>	I.E. %	CR mg/dm <sup>2</sup>	I.E. %			
A	92.95	-	175.18	-	425.45	-	66.32	-5.16	-80.73
B	3.58	96.15	7.15	95.92	28.6	93.28	91.13	-5.08	-74.13

A= $H_3PO_4$

B= $H_3PO_4$ +Ammonium Dichromate

**Table 3:** Polarization data and inhibition efficiency (I.E.) of ammonium dichromate for aluminium in 1.0 M H<sub>3</sub>PO<sub>4</sub> at 301 ± 1K.

Inhibitor concentration: 4 mM

System	E <sub>corr</sub> V	CD I <sub>corr</sub> μA/cm <sup>2</sup>	Tafel slope (V)		β (V)	I.E.(%) from methods	
			Anodic	Cathodic		By Weight loss	By Polarization
			β <sub>a</sub>	β <sub>c</sub>			
A	-0.815	0.0010	3.406	6.345	0.963	-	-
B	-0.750	0.0001	4.064	4.933	0.968	97.25	90.11

$$\beta = (\beta_a \times \beta_c) / [2.3(\beta_a + \beta_c)]$$

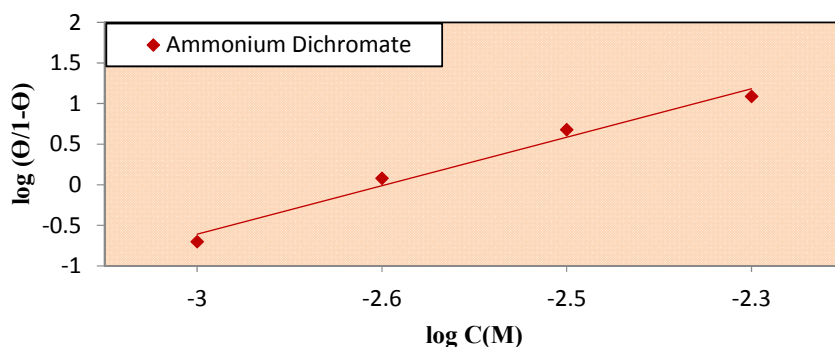
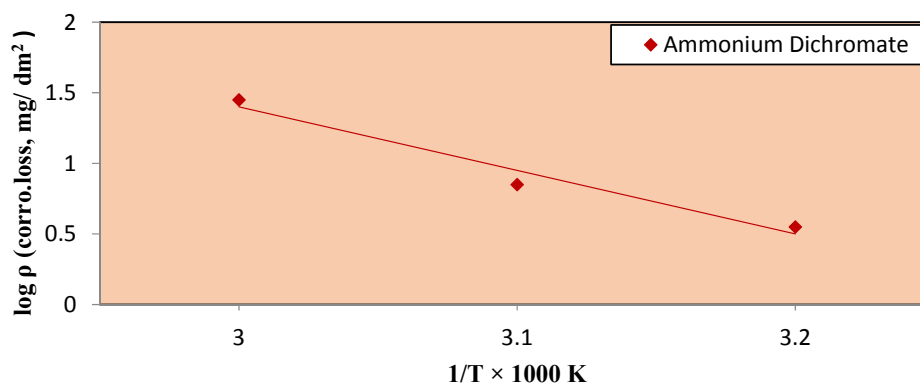
A=H<sub>3</sub>PO<sub>4</sub>B=H<sub>3</sub>PO<sub>4</sub>+Ammonium Dichromateβ<sub>a</sub>= Anodic Tafel constant, β<sub>c</sub> = Cathodic Tafel constant.

CD = Corrosion current density from interception of anodic and cathodic lines.

**Table 4:** Electrochemical impedance parameters and I.E. of aluminium in 1M H<sub>3</sub>PO<sub>4</sub> solution in the absence and presence of ammonium dichromate.

Inhibitor concentration: 4 mM

System	R <sub>ct</sub> (Ω cm <sup>2</sup> )	Cdl (μFcm <sup>2</sup> )	I.E.(%)
A	40	22.116	-
B	520	1.0936	95.05%

A=H<sub>3</sub>PO<sub>4</sub>B=H<sub>3</sub>PO<sub>4</sub>+Ammonium Dichromate**Figure 1 :** Plot of log (Θ/1-Θ) versus log C of aluminium in 1.75 M H<sub>3</sub>PO<sub>4</sub> concentration.**Figure 2 :** Arrhenius plot for corrosion of aluminium in 1 M H<sub>3</sub>PO<sub>4</sub> in presence of 4 mM inhibitor concentration.

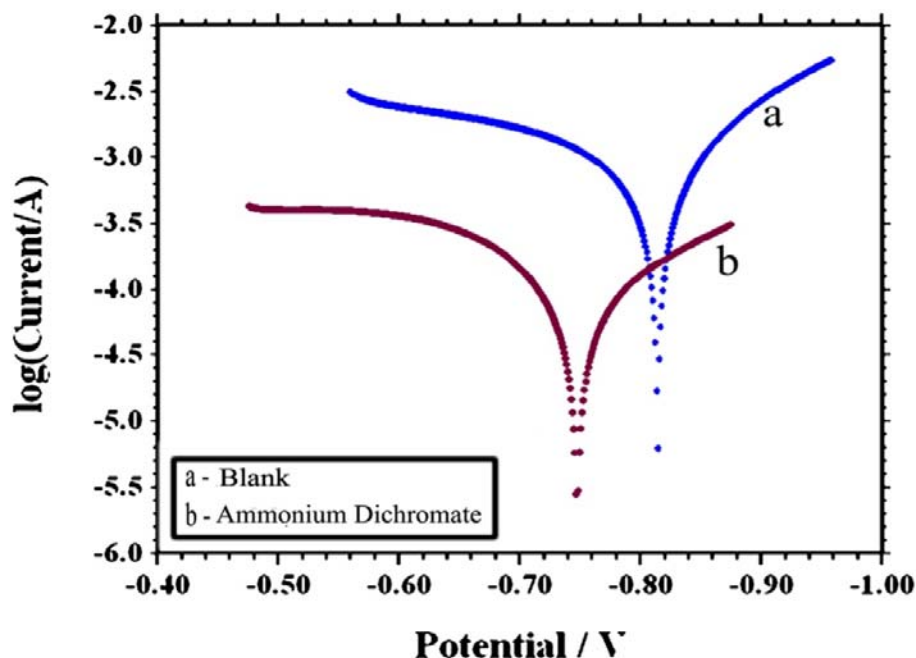


Fig 3: Polarization curves for corrosion of aluminium in 1 M  $H_3PO_4$  without and with 4 mM Inhibitor.

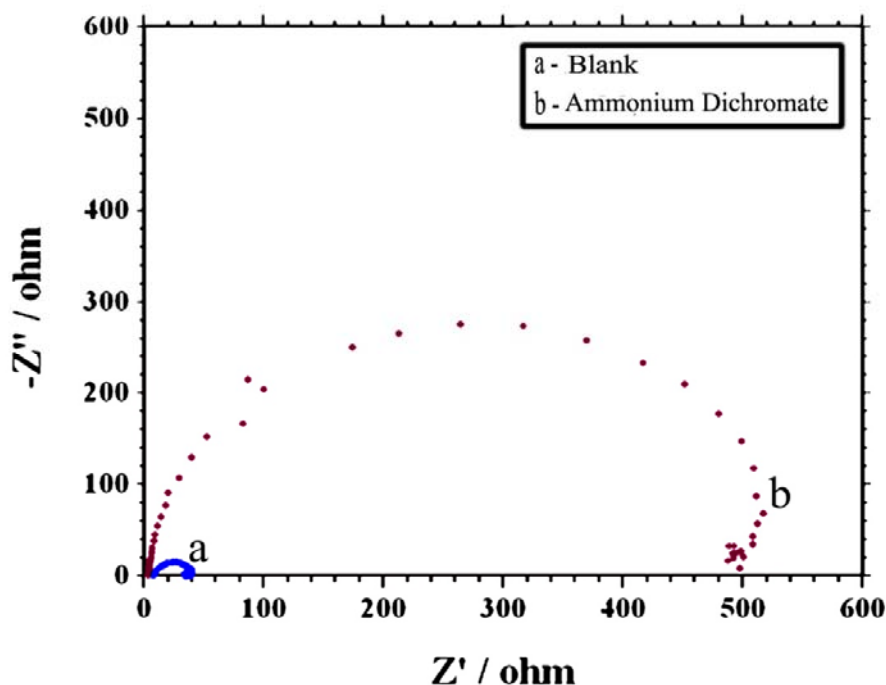


Fig 4: Nyquist plot of the corrosion of aluminium in 1.0 M  $H_3PO_4$  containing 4 mM Inhibitor.

#### 4. Conclusion

- ❖ As the acid concentration increases the corrosion rate increases.
- ❖ As the concentration of acid increases I.E. decreases at all concentration of inhibitor.
- ❖ As the inhibitor concentration increases I.E. increases and corrosion rate decreases.
- ❖ As the temperature increases corrosion rate increases while I.E. of inhibitor decreases.
- ❖ Polarization measurements indicates that the inhibitor behave as a mixed type inhibitor.

- ❖ EIS spectra exhibit one capacitive loop which indicates that the corrosion reaction is controlled by charge transfer process.

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