

# Pitting Corrosion of Aluminum in Aqueous Solution with Low pH Containing Nitrate Ion and Its Inhibition Using Different Surfactants

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**Abstract** Localized or pitting corrosion of aluminum in acidic medium is a problem for some industries. Severe attack can lead to pinhole leaks and instrument breakdown. The results showed that pitting corrosion occurred in waters with low nitrate ion concentration. The effect of adding different types of surfactants on the inhibition of the pitting corrosion of aluminum in 0.1 M HNO<sub>3</sub> was studied using potentiodynamic polarization and electrochemical impedance (EIS) spectroscopy techniques. The electrochemical results proofed that both the anionic surfactant sodium lauryl sulfate and the cationic surfactant cetrimide can decrease the pitting corrosion of aluminum in aqueous solution containing nitrate ion to a great extent. The mechanism of adsorption of surfactants on metal surface was studied using the kinetic thermodynamic model. The free energy change of adsorption indicated that the adsorption of surfactants on metal surface is spontaneous in nature. The adsorption of both surfactants is comprehensive process (physical and chemical).

**Keywords** Pitting corrosion, Surfactant, Electrochemical, Physical Adsorption

## 1. Introduction

It is not surprising that aluminum and aluminum alloys are used through the world due to their high technological value and their use in industrial applications especially in household and aerospace industries [1-3]. Aluminum and its alloys are economically important due to their light weight, high electrical capacity and good corrosion resistance [4, 5]. Despite the fact that aluminum is a reactive metal, it is resistant to corrosion in solutions of moderate pH ranged from 4 to 9, only in absence of aggressive ions as chlorides and sulfates [6, 7]. The resistance of aluminum to corrosion is a result of the formation of a thin, well adhered and protective oxide layer [8, 9]. Far away from the pH range 4 to 9, the oxide film is soluble and promote uniform attack [6, 10].

The behavior of aluminum and its alloys in aggressive environments have been studied [10-14]. Acid pickling of aluminum is widely used in the chemical industries to remove the scales from the metallic surface [15]. Many chemical inhibitors are used to prevent the dissolution of

aluminum surfaces during its chemical etching [16, 17]. The organic compounds containing hetero atoms such as sulphur, nitrogen or oxygen in their structure are the most effective corrosion inhibitors [18-21]. Finding new inhibitors for corrosion of aluminum is still understudy.

The pitting corrosion of aluminum usually occurs in aqueous solutions in presence of aggressive ions such as Cl<sup>-</sup> [22-27], ClO<sub>3</sub><sup>-</sup> [28], ClO<sub>4</sub><sup>-</sup> [28-31] and SCN<sup>-</sup> [32] anions. It is said that pitting corrosion of aluminum can be described by the local break down of the passive oxide film. The pitting corrosion of aluminum in aluminum-electrolyte system is characterized by a critical break down potential E<sub>b</sub> resulting in break down of the oxide passive film [22].

Surfactants are commonly used chemicals in many industrial applications [33]. Nowadays, Surfactants play a new role in corrosion inhibition technology [34-38]. The advantages of surfactants over other chemical inhibitors are their cheapness, easy production and their low toxicity [39]. The mechanism of action of surfactants on the metal surface is its adsorption in such a way that the polar part (hydrophilic) attaches the metal surface. On the other hand, the non-polar part (hydrophobic) extends in the solution [40].

The adsorption of surfactant on the metal surface depends on the structure of the surfactant [35, 41, 42]. Li et al, [43] studied the effect of tetradecylpyridinium bromide (TDPB) as corrosion inhibitor for aluminum in 1.0 M HCl solution by using weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) techniques.

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The results showed that TDPB acts as cathodic-type inhibitor where its efficiency increases with increasing its concentration, and were found to be inversely proportional to the temperature. The adsorption of TDPB on aluminum surface is consistent with Langmuir adsorption isotherm. The inhibition effect of a 3-(10-sodium sulfonate decyloxy) aniline monomeric surfactant and the polymeric surfactant poly[3-(decyloxy sulfonic acid) aniline] (PC10) on the corrosion of aluminum in 0.5 M hydrochloric acid was studied by using weight loss and potentiodynamic polarization techniques [44]. The results showed that both surfactants acted as mixed-type inhibitors in which their inhibition efficiency increased with increasing surfactant concentration and decreased with increasing temperature. Mehdaoui et al, [45] synthesized some anionic surfactants [gasoil sulfonate (GOS), kerosene sulfonate (KES), heavy solvent sulfonate (HSS) and total gasoline sulfonate (TGS)] obtained from Algerian petroleum fractions and studied their effect on aluminum corrosion in hydrochloric solution (1 M HCl) using weight loss measurements, electrochemical polarization, and electrochemical impedance spectroscopy techniques. The results showed that the corrosion inhibition efficiency is in the order: TGS < HSS < KES < GOS which is in accordance with the number of carbon atoms in the hydrophobic chain of the inhibitor molecule. The electrochemical measurements showed that these surfactants act as cathodic inhibitors, and their adsorption on Al substrate is a physisorption-type, spontaneous and exothermic.

According to our knowledge, there is no previous studies narrated that aluminum and its alloys undergo pitting corrosion in  $\text{NO}_3^-$  ions containing solutions. The aim of this study is to focus on the pitting corrosion of aluminum in nitric acid and to evaluate the different types of surfactants as corrosion inhibitors for aluminum in this media. The present study will be extended to assess their role in controlling the localized form of corrosion of aluminum.

## 2. Experimental

### 2.1. Electrochemical Measurements

The electrochemical measurements were carried out by a frequency response analyzer potentiostat (ACM 604). The frequency range for impedance measurements (EIS) was 30 kHz to 0.01 Hz with applied potential signal amplitude of 10 mV around the rest potential. A three electrode mode cell was used, the cell contains an auxiliary graphite electrode and saturated calomel reference electrode. The working electrode was fabricated in cylindrical form. Aluminium was encapsulated in epoxy resin in such a way that only one surface was left uncovered. The working electrode has the chemical composition (% wt): Al 99.687; Mn 0.001; Zn 0.001; Ni 0.003; Fe 0.171; Si 0.135; Cu 0.001. The exposed area ( $0.5 \text{ cm}^2$ ) of the sample was wet hand-polished using emery papers of variable grades starting with a coarse one and proceeding in steps to the finest (1000) grade. The sample was then washed thoroughly with double-distilled water and finally dried by absolute ethanol just before immersion in the solution. Each experiment was carried out with freshly polished electrode.

Before polarization and EIS measurements, the working electrode was introduced into the test solution and left for 20 min at the open circuit potential. The polarization curve measurements were obtained at scan rate of 20 mV/min starting from cathodic potential ( $E_{\text{corr}} - 300 \text{ mV}$ ) going to anodic direction until 250 mV after the rest potential. All the measurements were done at  $30.0 \pm 0.1^\circ\text{C}$  in solutions open to the atmosphere under unstirred conditions. To test the reliability and reproducibility of the measurements, duplicate experiments were performed in each case of the same conditions.

### 2.2. Solution Preparation

**Table 1.** Chemical structure of Tween 80, Cetrimide and Sodium Lauryl Sulfate

Surfactant	Chemical Formula	Molecular Structure
Cetrimide	$\text{C}_{17}\text{H}_{38}\text{BrN}$	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_2-\text{N}^+(\text{CH}_3)_3 \text{Br}^-$
Sodium Lauryl Sulfate	$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{O}-\text{S}(=\text{O})_2\text{ONa}$
Tween 80	$\text{C}_{64}\text{H}_{124}\text{O}_{26}$	$\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_x-\text{CH}_2-\text{CH}(\text{O}(\text{CH}_2\text{CH}_2\text{O})_y\text{CH}_2\text{CH}_2\text{OH})-\text{CH}_2-\text{CH}(\text{O}(\text{CH}_2\text{CH}_2\text{O})_z\text{C}(=\text{O})\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}=\text{CH}_2)$

The test solutions were prepared from analytical grade reagents and distilled water. 70%  $\text{HNO}_3$  was purchased from Aldrich Chemicals Company. Stock solution, of 1 M of  $\text{HNO}_3$  and 0.02 M of surfactant were used to prepare the test solution. Prior to each experiment, 1.0 M  $\text{HNO}_3$  is added to an appropriate volume of 0.02 M surfactant solution and double distilled water to obtain a solution of 0.1 M  $\text{HNO}_3$  and the required concentration of the surfactant. Tween 80, Cetrimide and Sodium Lauryl Sulphate were obtained from Alpha Chemica Company. Their molecular structures are given in Table 1.

### 3. Results and Discussion

In this study we were aiming to study the effect of different types of surfactants; neutral surfactant (Tween 80), anionic surfactant (Sodium Lauryl Sulfate, SLS) and cationic surfactant (Cetyl trimethyl ammonium bromide, Cetrimide) on the pitting corrosion of aluminum in 0.1 M  $\text{HNO}_3$ , using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. In order to test this idea, the potentiodynamic polarization curves and the Nyquist impedance diagrams of aluminum in 0.1 M  $\text{HCl}$  were recorded in absence and presence of 0.05 M of each of the neutral surfactant (Tween 80), cationic surfactant

(Cetrimide) and the anionic one (SLS). Figure 1 shows the polarization curves of aluminum in 0.1 M  $\text{HNO}_3$  solution in absence and presence of 0.05 M Tween 80, Cetrimide or SLS surfactants.

The polarization curves show Tafel behavior both in absence and presence of the different types of surfactants. In both cases, the absence of surfactants and the presence of both TW 80 and SLS surfactants, the active regions are followed by a break down potential  $E_b$ , this behavior has been previously reported by several authors [46-48] and has been explained on the basis of pitting corrosion of aluminum in presence of nitrate anion. In the presence of Cetrimide surfactant the activation behavior is followed by passivation region in which the break down potential is not observed indicative that the presence of Cetrimide decreases the potential for aluminum to undergo pitting corrosion.

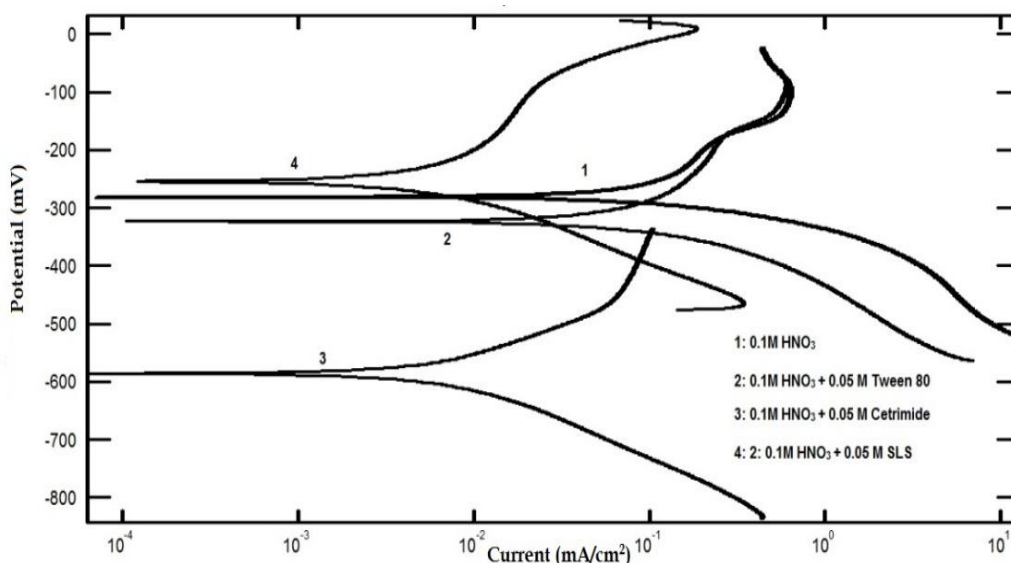
The potentiodynamic polarization parameters for aluminum in 0.1 M  $\text{HNO}_3$  in absence and presence of 0.05 M of Tween 80, Cetrimide or SLS surfactants and the protection efficiency, which can be calculated from the following equation, are presented in table 2.

$$\%P = [(i_0 - i) / i_0] \times 100 \quad (1)$$

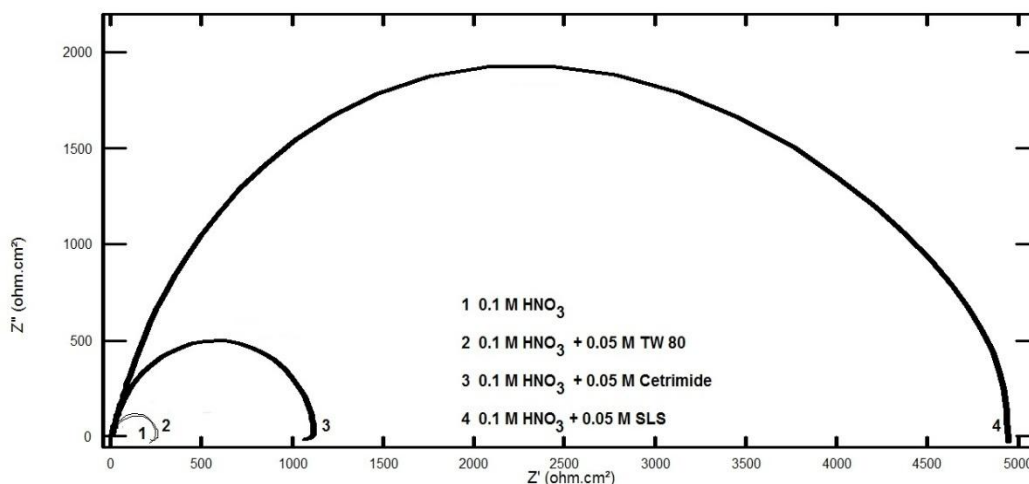
Where,  $i_0$  represents the corrosion current density of aluminum in  $\text{HNO}_3$  solution and  $i$  represents the corrosion current density in presence of the surfactant.

**Table 2.** Potentiodynamic polarization parameters for aluminum in 0.1 M  $\text{HNO}_3$  solution in absence and presence of 0.05 M Tween 80, Cetrimide or SLS surfactants

Concentration mol/L	$-E_{\text{corr}}$ (mv)	$i_{\text{corr}}$ ( $\text{mA} \cdot \text{cm}^{-2}$ )	$\beta_a$ (mv/decade)	$\beta_c$ (mv/decade)	I %
0.00	251.83	0.6690	317.57	96.973	-----
0.05 M Anionic	256.30	0.0130	192.45	94.571	98.05
0.05 M Neutral	309.86	0.6039	224.92	108.97	9.73
0.05 M Cationic	578.62	0.0996	100.13	117.53	85.11



**Figure 1.** Potentiodynamic polarization curves for aluminum in 0.1 M  $\text{HNO}_3$  solution in absence and presence of 0.05 M Tween 80, Cetrimide or SLS surfactants

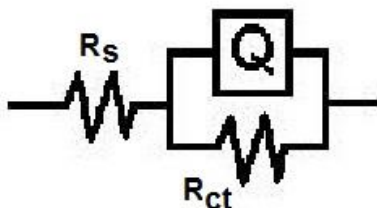


**Figure 2.** Nyquist plots for aluminum in 0.1 M HNO<sub>3</sub> solution in absence and presence of 0.05 M Tween 80, Cetrimide or SLS surfactants

Inspection of the data in table 2 indicating that the corrosion current density and hence the corrosion rate is decreased to a great extent only in the presence of either the anionic or the cationic surfactants while, in case of the neutral surfactant, a very small decrease in corrosion current density is obtained. Consequently the percentage inhibition is great in case of the presence of both the anionic and cationic surfactants and small in case of the neutral surfactant. This observation results in the conclusion that both the SLS and Cetrimide can be used as effective corrosion inhibitors for aluminum in nitric acid taking into consideration the potential of Cetrimide in controlling the pitting attack of nitrate ion on the aluminum surface. On the other hand, poor efficiency of the neutral surfactant Tween 80 towards inhibition of corrosion of aluminum in nitric acid solution is found.

Figure 2 represents the Nyquist plots for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of the different types of surfactants TW 80, Cetrimide and SLS.

These plots indicate that the impedance response consisted of only one depressed capacitive semicircle. The experimental data were analyzed by fitting the data to the equivalent circuit model given in figure 3 using Zsimpwin program.



**Figure 3.** Equivalent circuit

This equivalent circuit includes the solution resistance  $R_s$  shorted by the constant phase element  $Q_{dl}$  which is placed parallel to the charge transfer resistance  $R_{ct}$ . The impedance parameters obtained from analysis and the percentage

inhibition which is calculated by using equation 2 are given in table 3.

$$\% P. = [(R_{ct} - R_{ct0}) / R_{ct}] \times 100 \quad (2)$$

Where,  $R_{ct0}$  and  $R_{ct}$  are the charge transfer resistance in absence and in presence of surfactants respectively.

**Table 3.** Impedance parameters for aluminum in 0.1 M HNO<sub>3</sub> solution in absence and presence of 0.05 M Tween 80, Cetrimide or SLS surfactants

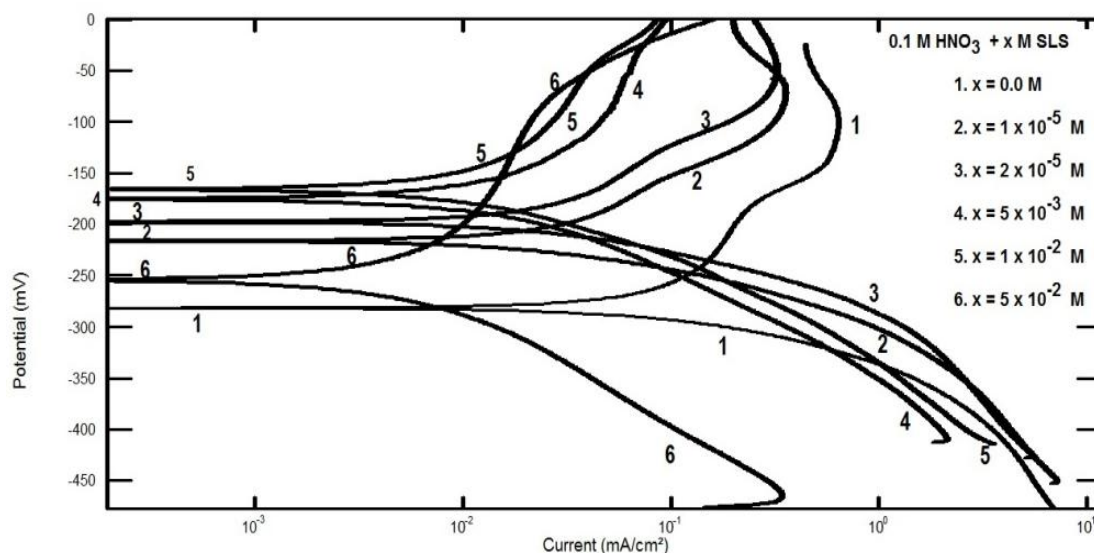
Concentration (mol/L)	$R_s$ (ohm.cm <sup>2</sup> )	$Q$ (μF)	$n$	$R_{ct}$ (ohm.cm <sup>2</sup> )	I %
0.0	5.70	45.9	0.89	265.1	----
0.05 M Anionic	7.80	20.5	0.86	5045	94.74
0.05 M Neutral	6.72	53.0	0.84	272.2	2.60
0.05 M Cationic	5.60	37.6	0.88	1183	77.59

The data in table 3 indicate that the charge transfer resistance is higher to a great extent only in the presence of both the anionic and the cationic surfactants while in case of the neutral surfactant it shows very small value and consequently the percentage inhibition is great in case of the presence of both the anionic and cationic surfactants and small in case of the neutral surfactant. This observation results in the conclusion that both the SLS and Cetrimide can be used as effective corrosion inhibitors for aluminum in nitric acid while the neutral surfactant Tween 80 cannot be used as corrosion inhibitor for aluminum in nitric acid solution. The results obtained by the impedance measurements are in good agreement with that obtained from the polarization measurements.

### 3.1. Inhibition of the Dissolution of Aluminum in 0.1 M HNO<sub>3</sub> by Sodium Lauryl Sulfate (SLS)

#### 3.1.1. Potentiodynamic Polarization Technique

Figure 4 represents the potentiodynamic polarization curves for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of SLS surfactant.



**Figure 4.** Potentiodynamic polarization curves for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of SLS surfactant

**Table 4.** Potentiodynamic polarization parameters for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of SLS surfactant

Concentration (mol/L)	- E <sub>corr</sub> (mv)	i <sub>corr</sub> (mA.cm <sup>-2</sup> )	β <sub>a</sub> (mv/decade)	β <sub>c</sub> (mv/decade)	I. %
0.0	249.80	0.6370	304.83	92.11	-
1 x 10 <sup>-5</sup>	215.38	0.2742	78.80	92.11	56.95
2 x 10 <sup>-5</sup>	172.54	0.1978	85.90	92.11	68.94
5 x 10 <sup>-3</sup>	189.82	0.1187	282.16	92.11	81.36
1 x 10 <sup>-2</sup>	154.11	0.0966	212.43	92.11	84.83
5 x 10 <sup>-2</sup>	257.31	0.0140	261.52	92.11	97.80

Inspection of the polarization curves showed that the anodic polarization curves in absence and presence of SLS exhibit active/passive transition regions, before the passivation region a break down potential appeared. In the active region, the dissolution current increases linearly with the applied potential. This is followed by a break down potential indicating the pitting corrosion of aluminum followed by the passive region. It also shows that the presence of SLS affect only the anodic polarization curves and has no effect on the cathodic curves this means that SLS suppress the anodic reaction. Increasing the concentration of the surfactant has no effect on the pitting corrosion as the break down potential still appear in presence of different concentrations of SLS. The potentiodynamic polarization parameters and the protection efficiency are given in table 4.

It is clear that the presence of SLS has no effect on the β<sub>c</sub> and affects β<sub>a</sub> only; this means that the presence of SLS affects only the anodic reaction. The corrosion current density decreased by the presence of SLS and further decrease by increasing the concentration of SLS. The protection efficiency increases by increasing the concentration of SLS reaching a value of 97 % at 0.05 M concentration. We can conclude that SLS acts as anodic

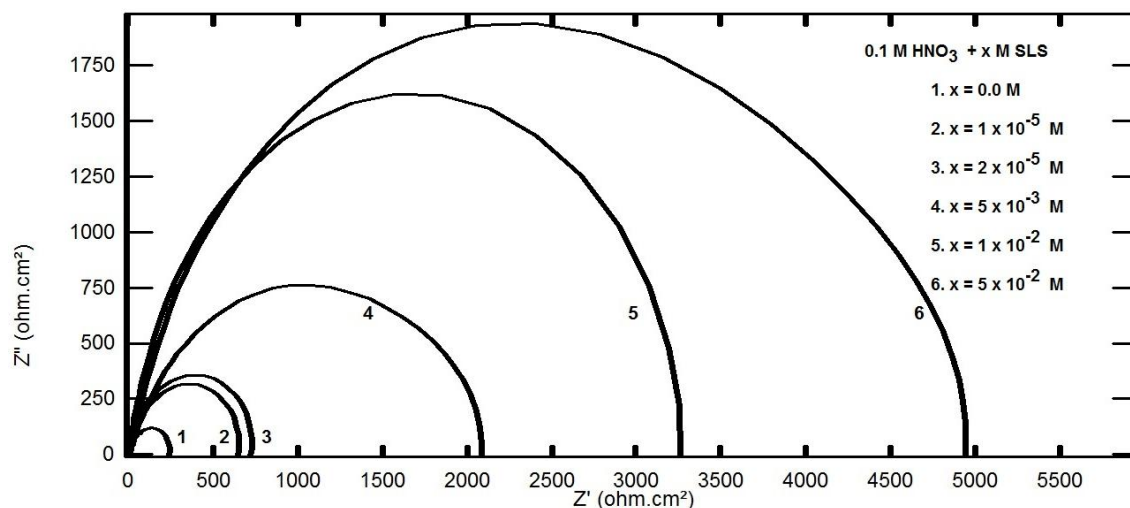
corrosion inhibitor for aluminum in nitric acid but it cannot hinder the pitting corrosion of aluminum in nitric acid.

### 3.1.2. Electrochemical Impedance Spectroscopy

Figure 5 represents Nyquist plots for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of SLS.

The Nyquist plots showed only one depressed capacitive semicircle in which its diameter increases with increasing the concentration of SLS. Analysis of the experimental data was done by using Zsimpwin program by fitting the data to the suitable equivalent circuit given in figure 3. The impedance parameters and the protection efficiency are given in table 5.

The results showed that the charge transfer resistance increase in presence of the surfactant and further increase with increasing the concentration of surfactant. The protection efficiency was found to increase with increasing the concentration of SLS reaching a value of 94% at concentration 0.05 M SLS. Also, the value of the capacitance of the double layer decreases with increasing the concentration of SLS confirming the adsorption of the surfactant on the metal surface and its interference in the electric double layer.



**Figure 5.** Nyquist plots for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of SLS

**Table 5.** Impedance parameters for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of SLS

Concentration (mol/L)	R <sub>s</sub> (ohm.cm <sup>2</sup> )	Q (μF)	N	R <sub>CT</sub> (ohm.cm <sup>2</sup> )	I %
0.0	5.70	45.9	0.89	265.1	-
1 x 10 <sup>-5</sup>	6.58	28.9	0.89	708.7	62.64
2 x 10 <sup>-5</sup>	6.33	25.2	0.93	796.8	66.72
5 x 10 <sup>-3</sup>	8.07	19.1	0.79	2195	87.92
1 x 10 <sup>-2</sup>	6.97	16.9	0.91	3699	92.83
5 x 10 <sup>-2</sup>	7.80	10.5	0.86	5045	94.74

### 3.2. Inhibition of Dissolution of Aluminum in 0.1 M HNO<sub>3</sub> by Cetrimide

#### 3.2.1. Potentiodynamic Polarization Technique

Figure 6 represents the potentiodynamic polarization curves for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of Cetrimide surfactant. Inspection of the figure shows that the presence of the cationic surfactant Cetrimide affect the equilibrium potential by shifting it to more negative potential. In the mean time, the presence of Cetrimide affects greatly the anodic polarization curves.

This is clear by the disappearance of the break down potential which is clear in the absence of Cetrimide. This means that Cetrimide not only act as corrosion inhibitor for aluminum in nitric acid but also decreases the potential of pitting corrosion of the metal. The potentiodynamic polarization parameters and the protection efficiency are given in table 6.

It is clear that the presence of Cetrimide has no effect on the  $\beta_c$  and affects only  $\beta_a$ . This means that Cetrimide affects the anodic reaction only. Also, the presence of Cetrimide decreases the corrosion current density and the corrosion current density decrease by increasing the concentration of Cetrimide. The protection efficiency increases by increasing

the concentration of Cetrimide reaching a value of 97% at 0.05 M concentration. We can conclude that Cetrimide acts as anodic corrosion inhibitor for aluminum in nitric acid with the advantage that it can hinder the pitting corrosion of aluminum in nitric acid.

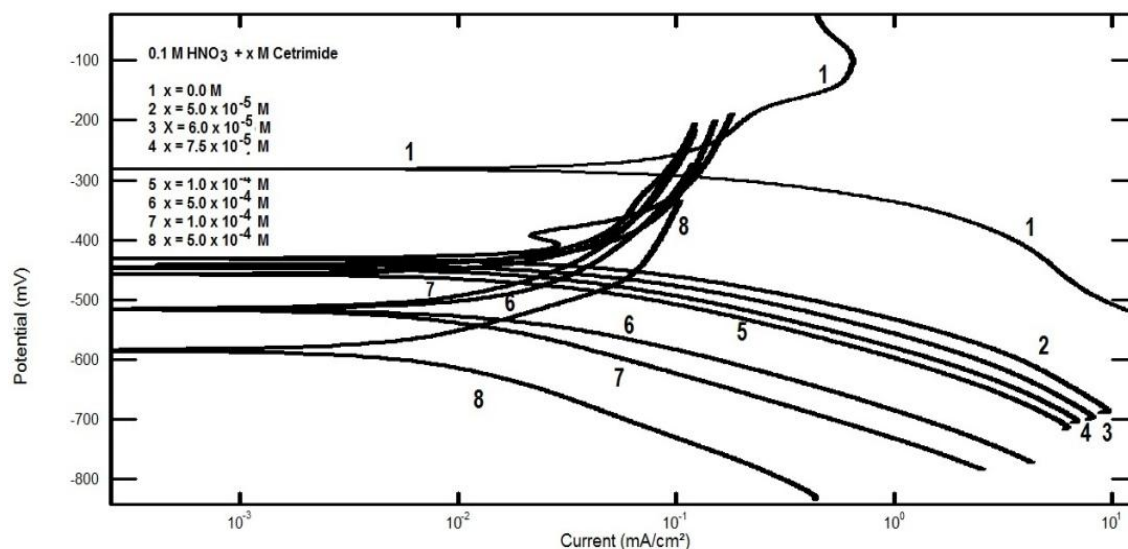
#### 3.2.2. Electrochemical Impedance Spectroscopy Technique

Figure 7 represents Nyquist plots for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of Cetrimide.

The Nyquist plots showed only one depressed capacitive semicircle in which its diameter increases with increasing the concentration of Cetrimide. Analysis of the experimental data was done by using Zsimpwin program by fitting the data to the suitable equivalent circuit given in figure 3. The impedance parameters and the protection efficiency are given in table 7.

The results showed that the charge transfer resistance increases in presence of the surfactant and further increase with increasing the concentration of surfactant. The protection efficiency was found to increase with increasing the concentration of Cetrimide. Also, it was found that the value of the capacitance of double layer decreases with increasing the concentration of Cetrimide confirming the adsorption of the surfactant on the metal surface and its interference in the electric double layer.

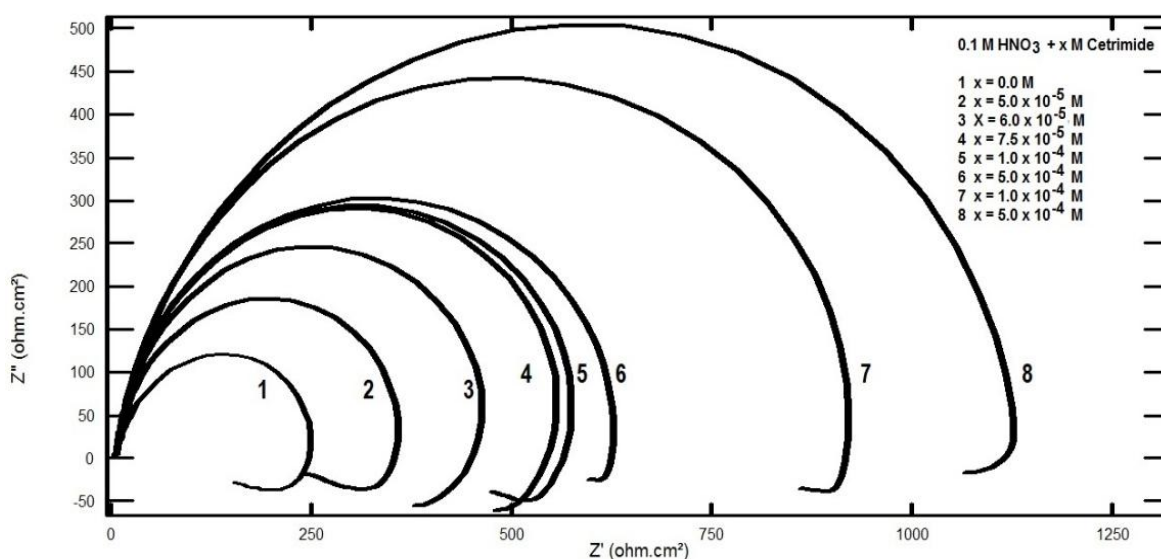




**Figure 6.** Potentiodynamic polarization curves for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of Cetrimide

**Table 6.** Potentiodynamic polarization parameters for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of Cetrimide

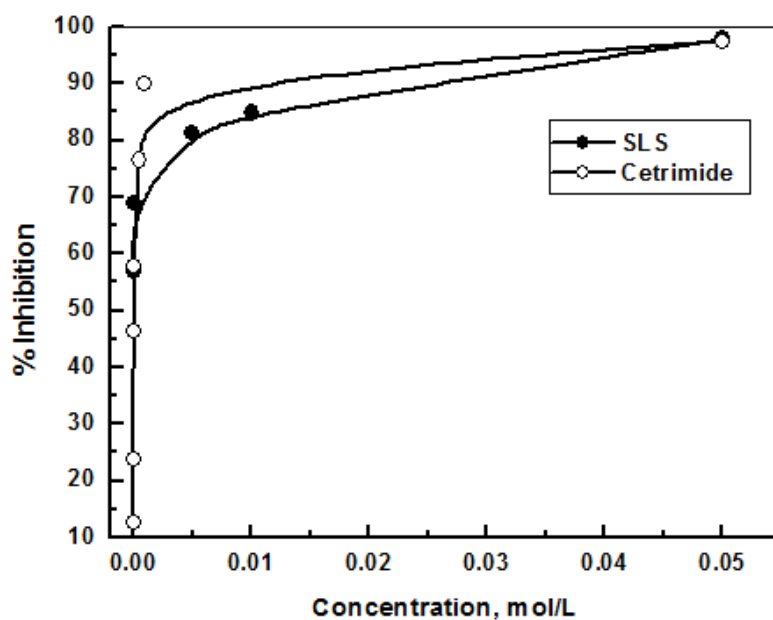
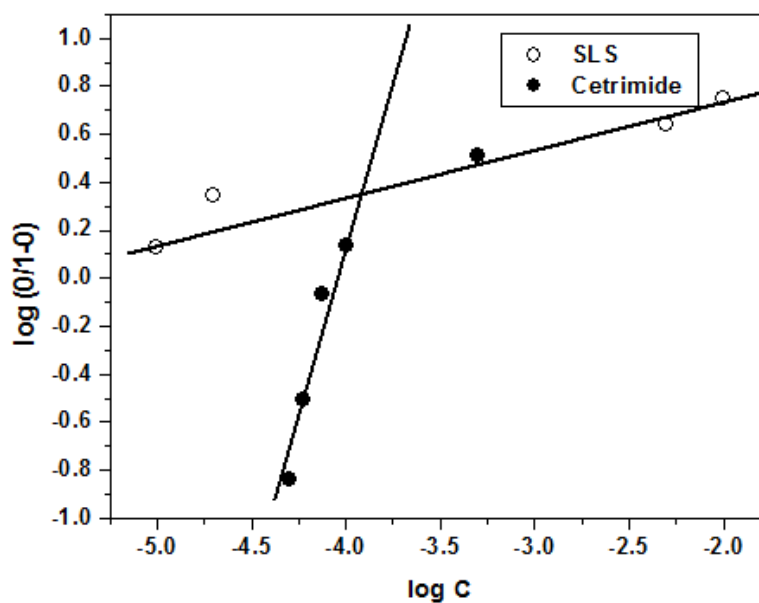
Concentration (mol/L)	- E <sub>corr</sub> (mv)	i <sub>corr</sub> (mA.cm <sup>-2</sup> )	Bc (mv/decade)	βa (mv/decade)	I %
0.0	253.86	0.6109	257.42	92.11	----
5.0 x 10 <sup>-5</sup>	401.83	0.5338	95.974	92.11	12.62
6.0 x 10 <sup>-5</sup>	449.44	0.4653	476.88	92.11	23.83
7.5 x 10 <sup>-5</sup>	447.58	0.3289	286.94	92.11	46.16
1.0 x 10 <sup>-4</sup>	454.80	0.2589	198.21	92.11	57.61
5.0 x 10 <sup>-4</sup>	512.10	0.1437	193.11	92.11	76.47
1.0 x 10 <sup>-3</sup>	519.25	0.0618	140.11	92.11	89.88
5.0 x 10 <sup>-2</sup>	583.70	0.0159	118.76	92.11	97.39



**Figure 7.** Nyquist plots for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of Cetrimide

**Table 7.** Impedance parameters for aluminum in 0.1 M HNO<sub>3</sub> in absence and presence of different concentrations of Cetrimide

Concentration (mol/L)	R <sub>s</sub> (ohm.cm <sup>2</sup> )	Q (μF)	n	R <sub>CT</sub> (ohm.cm <sup>2</sup> )	I %
0.0	5.70	45.9	0.89	265.1	-
5.0 x 10 <sup>-5</sup>	6.13	20.6	0.94	375.3	29.36
6.0 x 10 <sup>-5</sup>	6.28	6.7	0.94	486.8	45.54
7.5 x 10 <sup>-5</sup>	5.98	14.1	0.96	595.6	55.49
1.0 x 10 <sup>-4</sup>	6.01	13.2	0.93	606.1	56.26
5.0 x 10 <sup>-4</sup>	5.83	12.4	0.91	655.4	59.55
1.0 x 10 <sup>-3</sup>	5.84	11.2	0.91	960.0	72.38
5.0 x 10 <sup>-2</sup>	5.60	10.1	0.88	1183.0	77.59

**Figure 8.** Variation of the percentage inhibition of the corrosion of aluminum in 0.1 M HNO<sub>3</sub> with concentrations of SLS and Cetrimide**Figure 9.** Application of the Kinetic-Thermodynamic model to the results of adsorption of SLS and Cetrimide on steel surface in 0.1 M HNO<sub>3</sub>



### 3.3. Mechanism of Adsorption of Surfactants

It is known that surfactants have a tendency to associate at interfaces and in solution to form aggregates [49]. Adsorption of the surfactant molecules on to metal surface, which is the primary action of the surfactant functional group, was found to be responsible for the corrosion inhibition of the metal and is related to its capability to aggregate to form micelles [50-55]. The variation of the percentage inhibition, which was calculated from the polarization measurements, with different concentrations of both SLS and Cetrimide surfactants is plotted in figure 8.

The curve was characterized by steeply rising part initially with increasing the concentration followed by levelling off at high concentrations indicating the saturation of the surface of substrate with surfactant molecules. In order to identify the nature of the adsorption and calculating the free energy change of adsorption  $\Delta G_{ads}^0$ , the experimental data was fitted to the Kinetic-Thermodynamic model which is given by the following equation [56]:

$$\text{Log } [\theta / (1-\theta)] = \text{log } K' + y \text{ log } C \quad (3)$$

Where, K is the binding constant which represent the extent of interaction between the surfactant and the aluminum substrate, C is the concentration of surfactant in mol/L and  $\theta$  is the degree of surface coverage by the surfactant molecules.

It is clear from the graph that the data fit the Kinetic-Thermodynamic model. The values of K which is the slope of the relation and the values of the free energy change of adsorption  $\Delta G_{ads}^0$  which is calculated from the following relation [57], is given in table 8.

$$K = 1/C_{\text{solvent}} \exp (-\Delta G_{ads}^0/RT) \quad (4)$$

Where, R is the universal gas constant, T is the absolute temperature;  $C_{\text{solvent}}$  is the molar concentration of solvent which is in this case water and equal to 55.5 mol/L.

**Table 8.** The values of the binding constant K and the free energy change of adsorption  $\Delta G_{ads}^0$  for the adsorption of SLS and Cetrimide on aluminum surface in 0.1 M  $\text{HNO}_3$

Surfactant	K	$\Delta G_{ads}^0$ (kJ/mol)
SLS	$1.97 \times 10^4$	-35.02
Cetrimide	$1.71 \times 10^4$	-34.67

It is reported that values of  $\Delta G_{ads}^0$  approximately -20 kJ/mol or lower are consistent with an electronic interaction between the inhibitor molecule and the metal surface (physisorption). Values higher than - 40 kJ/mol are involved in charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate bond (chemisorption) [58-60]. The large values of K obtained in both cases indicate strong interaction between the surfactants and the aluminum surface. The negative values of  $\Delta G_{ads}^0$  obtained in both cases indicative that the adsorption of both SLS and Cetrimide on the aluminum surface is spontaneous process. Moreover, the higher values of  $\Delta G_{ads}^0$  in presence of both SLS and Cetrimide indicate that the adsorption of both surfactants is comprehensive process (physical and

chemical).

Adsorption of surfactants on the metal surface can change their interfacial properties such as hydrophobicity, surface charge and corrosion inhibition [61]. Generally, adsorption of the surfactant on the metal surface is controlled by covalent bonding, electrostatic interaction, hydrogen bonding, non-polar interaction between the adsorbed species, lateral association interaction, solvation and de-solvation [62]. The overall adsorption process is a mixture of all these forces [63].

It is reported that [64] the adsorption of ionic surfactants on oppositely charged metal surface can be explained by considering the mechanism of adsorption as follow, at low surfactant concentrations, the adsorption occur by electrostatic interaction between the charged ionic surfactant and the oppositely charged solid surface, after then, the surfactant molecules starts to aggregates on the metal surface due to lateral interactions between the hydrophobic chains which enhances the electrostatic interaction between the charged surfactant and the metal surface, when the solid surface is electrically neutralized by the adsorbed surfactant molecules, the electrostatic forces is no longer play the important role and adsorption takes place because of the lateral interaction only, when the concentration of surfactant reaches the critical micelle concentration, the surfactant activity becomes constant and any increase in concentration leads only to micellization in solution. In the last two steps the surfactant molecules adsorb with a reverse orientation in which the head ionic groups faced the solution resulting in a decrease in the hydrophobicity of the particles in this region.

The adsorption of surfactants at the solid-liquid interface is affected by a number of factors such as: i) the nature and the surface charge of the metal (whether it contains highly charged sites or essentially nonpolar groupings); ii) the chemical structure of the surfactant (whether it is ionic or nonionic, the hydrophobic group is long or short, aliphatic or aromatic, straight chain or branched); iii) the nature of the electrolyte (its pH, content of the electrolyte, presence of any additives such and its temperature) [65]. There are a number of mechanisms by which surfactants molecules may adsorb onto metal surface from aqueous solution [66-75].

In case of the adsorption of SLS on the metal surface, the mechanism of adsorption can be explained by considering the ion pairing which involves the negative (hydrophilic parts) ions of surfactant adsorption from solution onto oppositely charged sites (positive charge) on the metal surface unoccupied by counter ions resulting in strong interaction between the metal and the surfactant anions.

In case of the adsorption of the cationic surfactant Cetrimide, The counter ion which is bromide ion plays the important role in the adsorption process of surfactant on the metal surface. The driving force for the adsorption of organic cations onto the aluminum surface is the presence of bromide ion which forms an intermediate bridge between the metal surface and the cationic surfactant molecules, the negative ends of the bromide-aluminum dipoles oriented towards the solution setting up an additional potential difference between

the steel surface and the bulk solution. This will shift the potential of zero charge positively making the charge on the aluminum surface negative and enhances the adsorption of the positively charged surfactant molecules by formation of ionic bonds. The high hardness of bromide ions and cationic surfactant increase the tendency of electrostatic adsorption which in turn increase the inhibition efficiency [76, 77].

It was reported that Cetrimide has positive effect on the inhibition of the pitting corrosion of aluminum in aqueous solutions containing chloride ions. On the other hand, SLS has negative effect and acts as accelerator for the pitting corrosion of aluminum in aqueous solutions containing chloride ions [78].

## 4. Conclusions

- Both Cetrimide and SLS act as anodic corrosion inhibitors for aluminum in aqueous solutions containing nitrate ion.
- Cetrimide decreases the potential of aluminum to pitting corrosion in nitric acid while SLS couldn't hinder the pitting corrosion of aluminum in nitric acid.
- Tween 80 has very low efficiency toward decreasing the corrosion of aluminum in nitric acid solution.
- The adsorption of surfactants onto the aluminum surface is physical in nature.
- SLS and Cetrimide can solve the problems arises in the water treatment systems that caused by corrosion. Cetrimide can be used during the acid pickling process in presence of nitric acid to prevent the pitting attack that may occur.

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