Research Article

Non-Ionic Surfactant as Corrosion Inhibitor for Aluminium in 1 M HCl and Synergistic Influence of Gemini Surfactant

Sheerin Masroor∗, Mohammad Mobin

Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh, India-202 002 (India)

Abstract

The corrosion characteristic of nonionic surfactant Triton X-100 on aluminium in 1 M HCl was studied in the temperature range of 30-60°C, by weight loss measurements, potentiodynamic polarization, EIS and SEM. The maximum inhibition efficiency was found to be 75.99% at surfactant concentration 1×10^{-3} (M) on temperature 30°C. Further, synergistic effect was also seen by addition of gemini surfactant 1,4-bis(N-tetradecyl-N,N dimethyl ammonium) butane dibromide (GS) (10^{-7} M) leading to enhancement of inhibition efficiency upto 94.62% at same nonionic surfactant concentration. The adsorption of inhibitors on aluminium surface obeyed Langmuir's adsorption isotherm. Thermodynamic parameters were also calculated.

Keywords: Aluminium, Nonionic surfactant, Gemini surfactant, Corrosion inhibitor, Synergism.
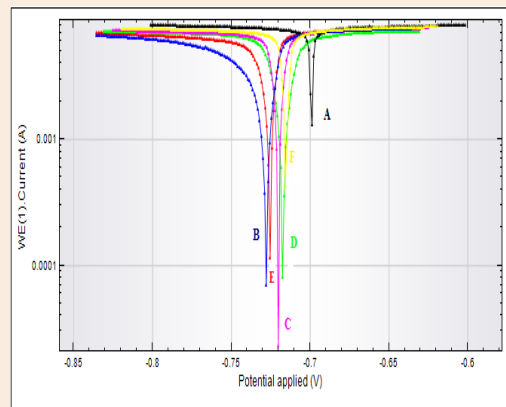
∗Correspondence
Sheerin Masroor,
Email: masroor.sheerin@gmail.com

Introduction

Aluminium is the most abundant (8.3% by weight) metallic element and the third most abundant of all elements (after oxygen and silicon) [1]. Aluminium is the most widely used non-ferrous metal [2]. It has good economic and industrial applications such as, transportation, packaging, construction, household items, watches, street lighting poles because of its low cost, light weight and high thermal and electrical conductivity. Aluminium is widely used because of its corrosion resistance property by forming thin surface layer of aluminium oxide that forms when the metal is exposed to air or aqueous solution, effectively preventing further oxidation [3-5].

Aluminium is not able to corrode in every corrosive medium. Mostly resistant in organic acids but in mineral acids corrosion varies with pH, i.e., in neutral solution (4 < pH < 9) aluminium becomes passive by forming a 50 Å thick oxide film on itself. In acidic solution aluminium corroded homogeneously by forming Al^{3+} and in alkaline solution with formation of aluminates (AlO_2^-). But mainly corrosion of aluminium takes place due to sulphuric and hydrochloric acid solutions as these are used for pickling of aluminium or for its chemical or electrochemical etching. So, provisions are done to save aluminium from corrosion by adding inhibitors also. Nonionic surfactants are mostly used to inhibit corrosion of mild steel [6-8]. Much literature is not found on aluminium by Triton X-100 in HCl, and synergistic effect with gemini surfactant (GS).

Experimental Details
Material preparation

Aluminium strips of size 2cm × 2cm × 0.025cm were used for weight loss measurements. For potentiodynamic and EIS measurements aluminium strips with exposed area 1 cm^2 were used. Strips were polished with different grades of emery papers and degreased with acetone. HCl (Merck) was used for preparing solutions. Double distill water was

used. Triton X-100 (Sigma-Aldrich) was used as nonionic surfactant. Gemini surfactant was synthesized following the earlier procedure discussed earlier [9, 10].

Weight loss measurements

An experiment was performed with taking different concentrations of Triton X-100, and seeing synergistic effect with GS for weight loss measurements as per ASTM designation G1-90 [11]. The freshly prepared aluminium specimens were suspended in 250 ml beakers containing 200 ml of test solutions maintained at 30-60°C in a temperature controlled water bath. The specimens were immersed in triplicate and the average corrosion rate was calculated. The uncertainty or RSD for three replicate measurements was less than 5%.The corrosion rate (CR) was determined using the equation:

$$Corrosion\ rate\ (mpy)\ =\ \frac{534\ W}{\rho\ A\ t}...............(1)$$

where, W is weight loss in mg; ρ is the density of specimen in g/cm^3; A is the area of specimen in square inch and t is exposure time in hrs. The inhibition efficiency (%IE) of the inhibitor was evaluated using the following equation:

$$\%\ IE = \frac{CR_o - CR_i}{CR_o} \times 100...............(2)$$

where, CR_o and CR_i are the corrosion rates of aluminium in absence and presence of inhibitor, respectively.

Potentiodynamic polarization measurements

The potentiodynamic polarization studies were carried out on Micro Autolab type III Potentiostat/Galvanostat (Model: μ3AVT 70762, Netherlands) with Ag/AgCl electrode (saturated KCl) as reference and Pt wire as counter electrode. The experiments were performed by keeping the potential between -0.25 and 0.25 V from open circuit potential at a scan rate of 0.0005 V/s. The specimen was allowed to stabilize in the electrolyte for 30 min prior to the experiment. All the experiments were done at room temperature (30$\pm$1°C).

Electrochemical impedance spectroscopy

Electrochemical impedance (EIS) measurements were carried out using using Ivium potentiostat/galvanostat (Model: IviumStat)/Autolab Potentiostat/Galvanostat, model 128N with inbuilt impedance analyzer FRA2. All electrochemical experiments were performed in a conventional three electrode cell at 30°C, with platinum as counter electrode, Ag/AgCl as reference electrode, and aluminium as working electrode, with exposed surface of 1 cm^2, was placed into the aggressive solution. EIS measurements were implemented at open circuit potential within frequency range of 10^{-2} Hz to 10^4 Hz with 10mV perturbation.

Surface morphological studies
Scanning electron microscopy (SEM) and Energy dispersive x-ray (EDAX) analysis

The surface morphology of aluminium specimens immersed in uninhibited and inhibited HCl solution was evaluated using SEM (Model: JEOL JSM- 6510LV) with an EDAX (INCA, Oxford) attachment. To study the surface morphology of the corroded aluminium, freshly polished specimens were immersed in uninhibited and inhibited acid solutions for 6 h. After completion of immersion the specimens were taken out, thoroughly washed with double distilled water, dried and then subjected to SEM and EDAX analysis.

Results and Discussion
Weight loss measurements

The corrosion of aluminium in 1 M HCl in absence and presence of varying concentrations of Triton X-100 was studied at four different temperatures namely, 30, 40, 50 and 60°C using weight loss technique. The concentration of

Triton X-100 was varied between $1 \times 10^{-5} - 1 \times 10^{-3}$ M. Table 1 shows the calculated values of corrosion rate and % IE at different concentrations of Triton X-100 under different temperatures obtained after 6 h of immersion.

The results are graphically presented in Figure 1. Considering the effect of surfactant concentration and solution temperature on the corrosion rate of aluminium in 1 M HCl, the corrosion rate of aluminium is reduced in presence of Triton X-100 as compared to free acid solution and depends upon both surfactant concentration and temperature. The IE increases with increasing surfactant concentration showing a maximum increase in IE of 76% at 1×10^{-3} M at 30°C. The increased IE with increasing inhibitor concentration indicates that more surfactant molecules are adsorbed on the aluminium surface at concentration near CMC, leading to greater surface coverage and hence formation of a protective film. The CMC of Triton X-100 in 1 M HCl is reported to be 18.9×10^{-2} M [12]. Considering the effect of temperature on the corrosion rate of aluminium in 1 M HCl, a decrease in IE is with increasing temperature at all the concentrations studied suggests physical adsorption as the weak van der Waal's forces responsible for such type of interaction tends to disappear at elevated temperatures.

Table 1 Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for aluminium in 1M HCl in absence and presence of Triton X-100 from weight loss measurements at different temperatures

| Surfactant concentration (M)	Corrosion rate (mpy)				Inhibition Efficiency (%IE)			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Blank	3511.62	8253.21	11267.52	15649.87	-	-	-	-
Triton X-100								
1×10^{-5}	1789.52	4405.56	6555.44	9629.37	49.04	46.62	41.82	38.47
7×10^{-5}	1629.39	4006.93	5726.15	8558.91	53.60	51.45	49.18	45.31
1×10^{-4}	1309.13	3144.47	4413.49	6527.56	62.72	61.90	60.83	58.29
7×10^{-4}	1161.90	2828.38	4223.07	6103.45	66.91	65.73	62.52	61.00
1×10^{-3}	842.79	2195.35	3358.85	5278.70	76.00	73.40	70.19	66.27
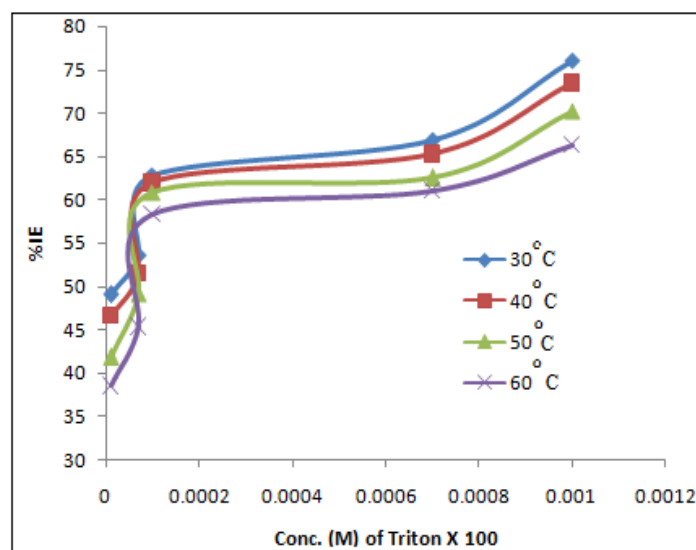
Figure 1 Plot of inhibition efficiency (% IE) vs. Triton X-100 for aluminium in 1 M HCl at different temperature. Along with steel, metal like Al is also susceptible to acid corrosion [13, 14] in many industries, specially to pickling processes [15]. Al has great industrial application owing to its low cost, low weight and high electrical and thermal conductivity. The corrosion inhibition of Al and its alloys in different acidic medium has been reported using surfactant [16]. Non ionic surfactants are known to have many applications in industry including application as corrosion inhibitor. They are not so expensive and can be mixed with other types of surfactants to enhance their properties and reduce surfactant precipitation. Non ionic surfactants have substantially lower CMC than

corresponding ionic surfactants. In the absence of charged head groups, the driving force for micellization is the hydrophobic force and van der waals attraction. Due to lower CMC they have greater tendency to adsorb at solid surfaces. The molecules of Triton X-100 are composed of a fairly polar hydrophilic head made of $(OCH_2CH_2)x$ OH, and a hydrophobic part from C_8H_{17}-C_6H_4-(the t-octyl-ph group). The corrosion inhibition behavior of Triton X-100 on aluminium in 1M HCl can be explained in terms of the adsorption of its molecules on the surface of aluminium. It may interact with the corroding aluminium and affect the corrosion reaction in more than one way. In the acidic medium the Triton X-100 can be easily protonated at the OH group and could interact with the corroding aluminium surface via protonated OH, which can be adsorbed at the cathodic sites and hinder the hydrogen evolution reaction. The oxygen atom carrying two lone pair of electrons could also be adsorbed on the anodic sites of the aluminium surface and retard the dissolution. Therefore, Triton X-100 is expected to involve both physical and chemical adsorption. However, the variation in the values of %IE with temperature in presence of Triton X-100 compared to blank suggested dominant role of physisorption in the adsorption process.
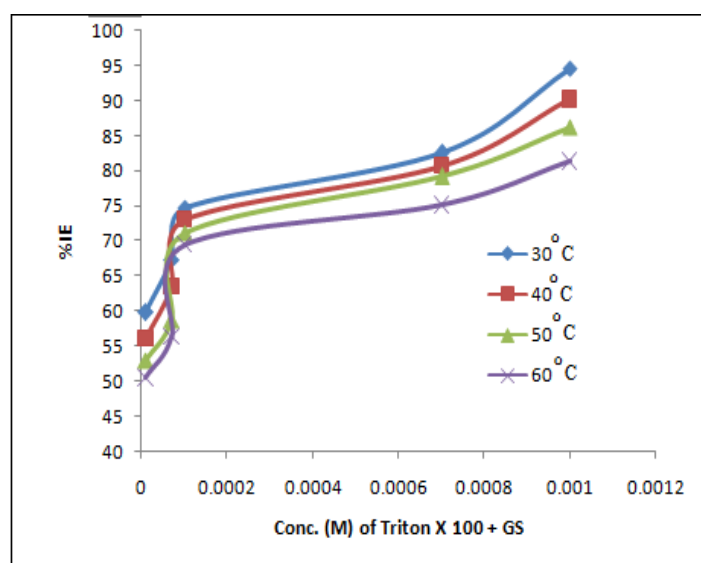

Figure 2 Plot of inhibition efficiency (% IE) vs. Triton X-100 in combination with GS for aluminium in 1 M HCl at different temperatures

To observe the effect of cationic gemini surfactant (GS), 1,4-bis(N-tetradecyl-N,N dimethyl ammonium) butane dibromide on the corrosion inhibition behavior of nonionic surfactant Triton X-100, the corrosion of aluminium in 1 M HCl in absence and presence of different concentrations of Triton X-100, in combination with 1×10^{-7} M GS, was separately studied in the temperature range of 30-60°C by weight loss technique. The results are shown in Table 2. Figure 2 shows the plots of % IE as a function of the concentration of Triton X-100 in combination with 1×10^{-7} M of GS at 30-60°C. The corrosion rates of aluminium in 1M HCl in presence of Triton X-100 in combination with GS are further reduced in comparison to Triton X-100 alone possibly due to hydrophobic interaction between them.

Determination of synergism parameter

The synergism parameter, S_1 for the interaction of Triton X-100 and GS was estimated from the weightloss data at 30-60°C using the equation 3. The values are given in Table 2. The values are all greater than unity. This is an indication that the enhanced IE resulting from the addition of GS to Triton X-100 is synergistic in nature and proved that addition of a very small concentration of GS can significantly improve the adsorption of Triton X-100 on the aluminium surface. The observed synergistic effect is due to the interaction of Triton X-100 and GS molecules [17].

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \ldots\ldots\ldots\ldots(3)$$

where, $I_{1+2} = (I_1 + I_2)$; I_1 is IE of Triton X-100; I_2 is IE of GS, and I'_{1+2} being the IE of surfactants taken together. Here $S_1 > 1$ which indicates a synergistic effect between Triton X-100 and GS.

Table 2 Calculated values of corrosion rate (mpy) ,inhibition efficiency (%IE) and synergism parameter (S_1) for aluminium in 1M HCl in the absence and presence of different concentrations of Triton X-100 with GS at 30-60°C from weight loss measurements

Triton X 100 (M)	GS (M)	Corrosion Rate (mpy)				Inhibition Efficiency (%IE)				Synergism parameter (S_1)			
		30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Blank		3511.62	8253.21	11267.52	15649.87	_	_	_	_	_	_	_	_
-	1×10^{-7}	1189.74	3047.91	4581.37	7006.45	66.12	63.07	59.34	55.23	_	_	_	_
1×10^{-5}	1×10^{-7}	1413.08	3621.51	5297.99	7757.64	59.76	56.12	52.98	50.43	1.94	1.97	1.93	1.88
7×10^{-5}	1×10^{-7}	1146.54	3011.60	4646.73	6832.73	67.35	63.51	58.76	56.34	1.79	1.82	1.86	1.82
1×10^{-4}	1×10^{-7}	889.14	2219.29	3258.57	4779.47	74.68	73.11	71.08	69.46	1.74	1.72	1.70	1.64
7×10^{-4}	1×10^{-7}	613.13	1588.74	2351.53	3904.64	82.54	80.75	79.13	75.05	1.63	1.60	1.55	1.56
1×10^{-3}	1×10^{-7}	188.93	812.94	1547.03	2928.09	94.62	90.15	86.27	81.29	1.51	1.52	1.50	1.51

Adsorption isotherm

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reaction. The inhibition of metallic corrosion in presence of various organic compounds has been attributed to their adsorption on the metal surface and is generally confirmed from the fit of the experimental data to various adsorption isotherms. The degree of surface coverage (θ) for various concentrations of Triton X-100, and Triton X-100 in combination with GS have been used to explain the best isotherm to determine the adsorption process. The data were tested graphically by fitting to various isotherms and the best result was obtained for Langmuir adsorption isotherm. The plots of C/θ against C are drawn which is characteristics of Langmuir adsorption isotherm given by equation 4. The plots of C/θ versus C for corrosion of aluminium in 1M HCl for Triton X-100 alone and in combination with GS, at 30–60°C are shown in Figure 3 (A and B). The plots gave a straight line. A linear correlation of slope close to unity suggests that adsorption of Triton X-100 alone and Triton X-100 in combination with GS follows Langmuir adsorption isotherm at all the temperatures studied.

$$\frac{C}{\theta} = \frac{1}{K} + C ....(4)$$

where, θ is the degree of surface coverage, K is the adsorptive equilibrium constant of the adsorption process and C is the inhibitor concentration.

Effect of temperature

The corrosion of aluminium in 1M HCl was studied in the temperature range of 30-60°C in absence and presence of Triton X-100, GS and Triton X-100 in combination of GS. A graph is plotted for logarithm of corrosion rate (log CR) vs. reciprocal of absolute temperature (1/T), which is shown in Figure 4 for 1 M HCl, Trition X-100, GS and combination of Triton X-100 with GS. By applying Arrhenius equation linear plot was obtained as given by equation 5 [18]. The values of E_a obtained from the graph are given in Table 3. A change in the value of E_a in presence of additives may be due to the modification of the mechanism of the corrosion process in presence of adsorbed inhibitor. The increases in E_a values in presence of the additives compared to the blank indicate the decrease in adsorption

process of the inhibitor on the aluminium surface with rise in temperature and corresponding increase in reaction rate. This indicates physical adsorption.
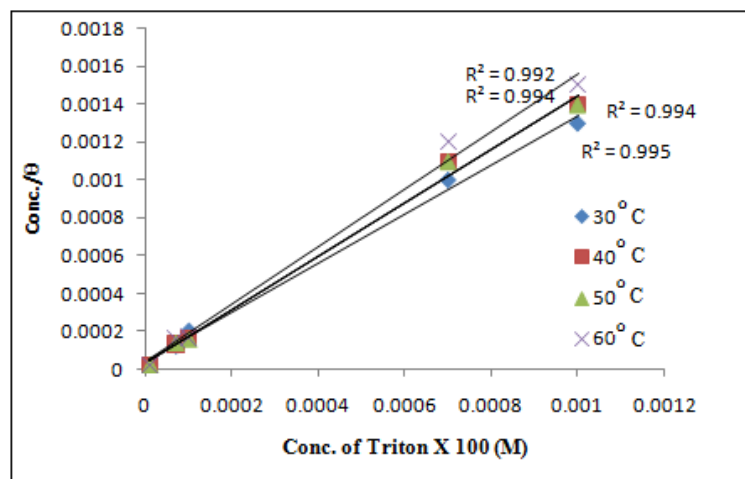
(A)
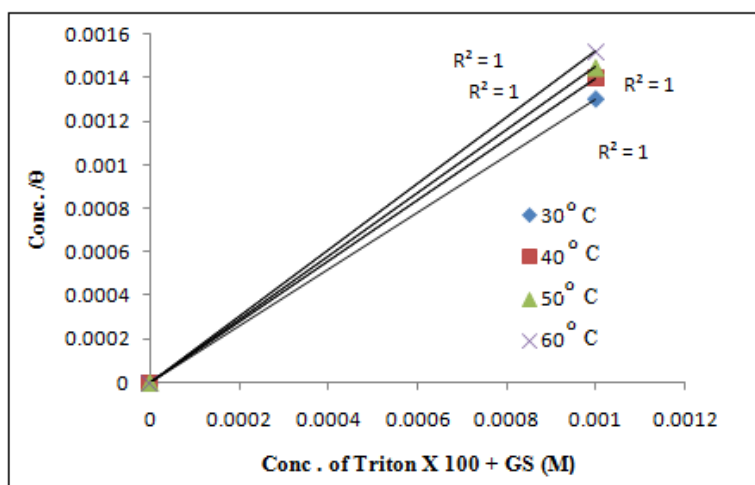
(B)

Figure 3 Langmuir adsorption isotherm plots for (A) Triton X-100 alone, (B) Triton X-100+ GS adsorbed on aluminium surface in 1 M HCl

$$Log\ CR = log\ A - \frac{E_a}{2.303\,RT}\ ....(5)$$

where, CR is the corrosion rate, A is the Arrhenius constant, E_a is the apparent activation energy, R is the molar gas constant and T is the absolute temperature.

The enthalpy of adsorption, ΔH and entropy of adsorption, ΔS for corrosion of aluminium in 1M HCl in presence of inhibitors was obtained by equation 6.

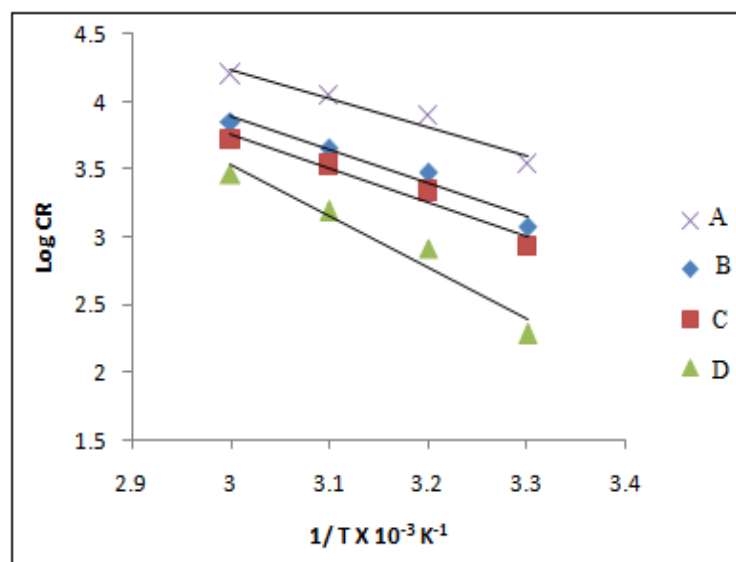$$CR = \frac{RT}{Nh}\,exp\left(\frac{\Delta S}{R}\right)exp\left(-\frac{\Delta H}{RT}\right)..............(6)$$

Figure 4 Adsorption isotherm plot of Log CR vs. 1/T for the adsorption of surfactants, (A) Blank, (B) GS, (C)Triton X-100, (D)Triton X-100+GS

The plot of log (CR/T) vs 1/T for blank, Triton X 100, and Triton X 100 in combination with GS is shown in Figure 5. The slope $\left(-\dfrac{\Delta H}{2.303RT}\right)$ and intercept $\left[\log\left(\dfrac{R}{Nh}\right)+\left(\dfrac{\Delta S}{2.303R}\right)\right]$ of the linear plot, gives the values of ΔH and ΔS, respectively. The values of ΔH and ΔS are presented in Table 3. From the given data it is observed that enthalpy of adsorption (ΔH) increases in presence of inhibited solution compared to uninhibited solution, this shows physical adsorption. The shift in the value of ΔS from negative to positive for uninhibited to inhibited system indicates decrease in the system order in the presence of additives. This suggests an increase in the disordering of the inhibited system which took place while going from reactants to activated complex. The more positive values of ΔS in presence of Triton X-100 - GS mixtures is again due to more disordering in the inhibited system due to presence of additional surfactant.

Another plot of log $\left(\dfrac{\theta}{1-\theta}\right)$ versus 1/T for the inhibitor was made (Figure 6). From the slope $\left[\dfrac{-Q}{2.303R}\right]$ of the plot, heat of adsorption, Q_{ads} was obtained and the values are given in Table 3. The calculated values of Q_{ads} are negative predicting the adsorption of inhibitor on aluminium to be exothermic. The free energy of adsorption, (ΔG_{ads}) at different temperatures was calculated from the following equation:

$$\Delta G_{ads} = -RT\ ln\ (55.5\ K)\ldots\ldots\ldots\ldots (7)$$

where, R is the universal gas constant, T the absolute temperature and the value of 55.5 is the concentration of water in mol L^{-1} in the solution . The equilibrium of adsorption, K is given by the following equation:

$$K= \theta/C\ (1-\theta)\ldots\ldots\ldots\ldots (8)$$

where, θ is the degree of coverage on the aluminium surface, C is the concentration of inhibitor in mol L^{-1}. The values of ΔG_{ads} are negative indicating spontaneous adsorption of inhibitor on the aluminium surface

Potentiodynamic polarization measurements

The potentiodynamic polarization curves for the corrosion of aluminum in 1M HCl in absence and presence of different concentration of Triton X-100 and Triton X-100 in combination with 1×10^{-7} M GS are presented in Figure 7

(A and B). Potentiodynamic parameter as deduced from these curves, e.g., corrosion potential (E_{corr}), corrosion current density (i_{corr}), the anodic Tafel slope (β_a), the cathodic Tafel slope (β_c), corrosion rate and % IE are shown in
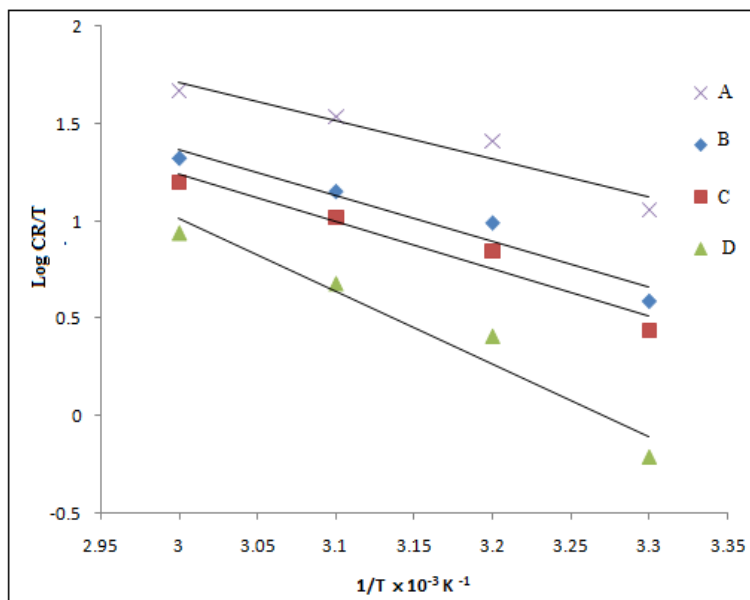

Figure 5 Adsorption isotherm plot of Log CR/T vs. 1/T for the adsorption of surfactants, (A) Blank, (B) GS, (C)Triton X-100, (D)Triton X-100+GS
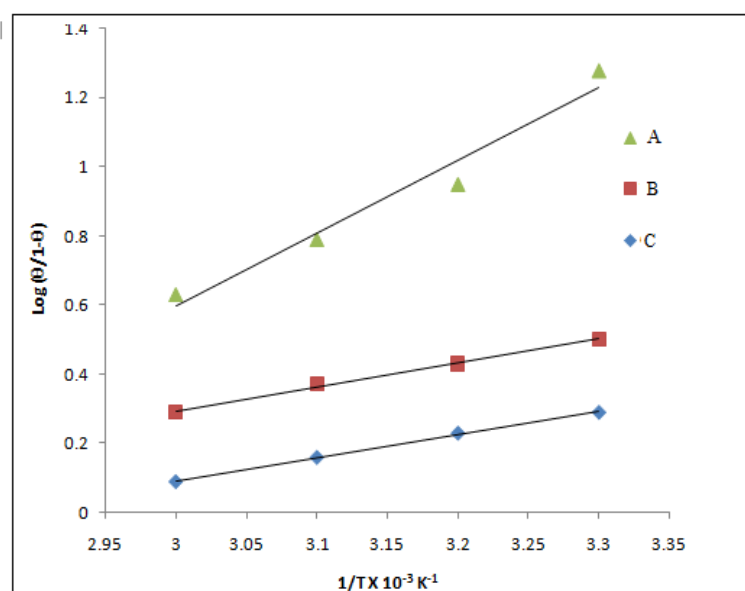

Figure 6 Adsorption isotherm plot of Log (θ/1-θ) for the adsorption of (A) Triton X-100+GS, (B) Triton X-100, (C) GS

Table 4. In presence of Triton X-100 and Triton X-100 in combination with GS the value of corrosion current density is lowered indicating that corrosion of aluminium is inhibited by Triton X-100 and GS. The value of i_{corr} continuously decreases in presence of Triton X-100. The IE was obtained by equation 9. The maximum IE of 76.00% was observed at a concentration of 1×10^{-3} M of Triton X-100 indicating that a higher coverage of Triton X-100 on aluminium surface is obtained in the solution with highest concentration of inhibitor. The addition of 1×10^{-7} M of GS to varying

concentration of Triton X-100 improved the IE of Triton X-100 considerably. The IE calculated from corrosion current density for the mixture reaches a considerably high value of 91.21%. There is a change in the values of both β_a and β_c indicating that the corrosion of aluminium in presence of inhibitors is under both anodic and cathodic control. The magnitude of the shift in E_{corr} in presence of Triton X-100 suggests that it acts as a mixed inhibitor and affects both anodic and cathodic reaction. In presence of Triton X-100 and Triton X-100-GS mixture the values of E_{corr} shifts to more negative values indicating that Triton X-100 alone and in combination with GS should predominantly control the cathodic reaction. The values of IE as obtained by potentiodynamic polarization studies are highly consistent with the results of the weight loss measurements.

Table 3 Calculated values of kinetic/thermodynamic parameters for aluminium in 1 M HCl in the absence and presence of Triton X-100 and GS from weight loss measurement

Surfactant	E_a (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol-K)	-Q (kJ/mol)	$-\Delta G_{ads}$(kJ/mol)			
					30°C	40°C	50°C	60°C
Blank	41.86	37.53	-53.04	-	-	-	-	-
Triton X-100	51.52	46.91	-37.70	28.34	30.42	31.02	31.61	32.16
GS	68.91	64.72	10.35	13.12	47.13	47.57	47.92	49.08
Triton X-100+GS	68.66	62.99	9.96	29.68	63.02	63.56	65.15	66.15

$$(\%)\,IE = \left(1 - \frac{i_{corr}}{i^o_{corr}}\right) \times 100 ....(9)$$

where, i_{corr} is the inhibited current density and i^o_{corr} is uninhibited current density.
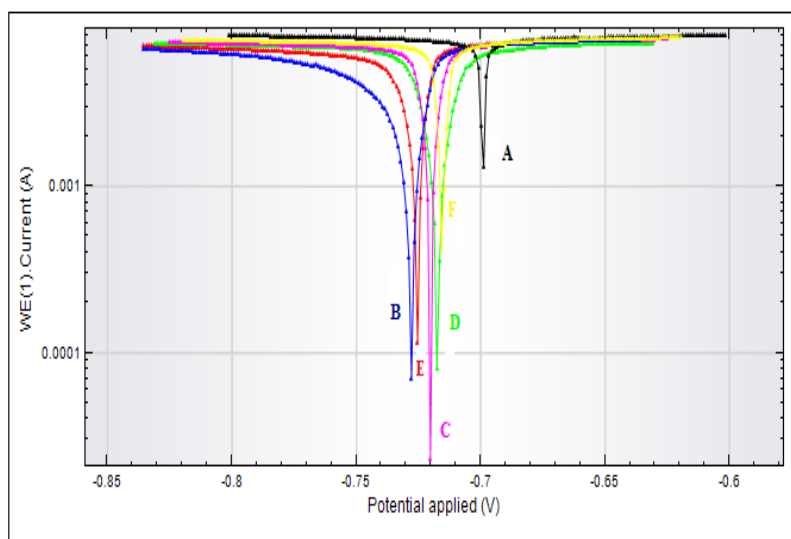

Figure 7 (A) Potentiodynamic polarization curves for aluminium in 1 M HCl in absence and presence of different concentration of Triton X-100 alone, (A) Blank, (B) 1×10^{-3} M, (C) 7×10^{-4} M, (D) 1×10^{-4} M, (E) 7×10^{-5} M, (F) 1×10^{-5} M

Electrochemical impedance spectroscopy (EIS) measurements

Electrochemical impedance spectroscopy is more advanced technique in studying corrosion mechanisms and adsorption phenomena [19]. The EIS provides important mechanistic and kinetic information for an electrochemical system involved. Bode modulus and Nyquist plots obtained for the aluminium working electrode at respective

corrosion potentials after 15 min immersion in 1M HCl in presence and absence of various concentrations of Triton X-100 alone and in combination with GS is shown in Figure 8 (A and B) and 9 (A and B). EIS parameters for corrosion of aluminium 1 M HCl in absence and presence of Triton X-100 alone and in combination with GS, at 30°C is given in Table 5.
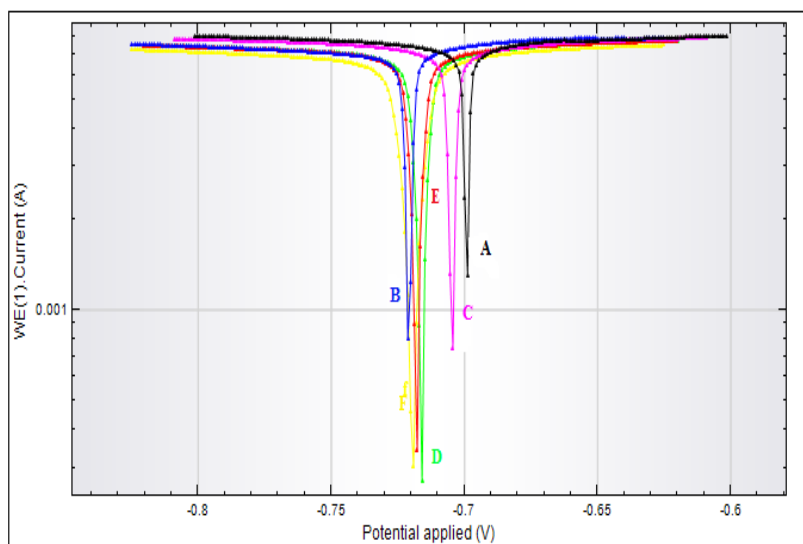

Figure 7 (B) Potentiodynamic polarization curves for aluminium in 1 M HCl in absence and presence of different concentration of Triton X-100 + GS (1×10^{-7} M), (A) Blank, (B) 1×10^{-3} M + 1×10^{-7}M, (C) 7×10^{-4} M + $\times10^{-7}$M, (D) 1×10^{-4} M + 1×10^{-7}M, (E) 7×10^{-5} M + 1×10^{-7}M, (F) 1×10^{-5} M + 1×10^{-7}M

Table 4 Potentiodynamic polarization parameters for corrosion of aluminum in 1 M HCl in absence and presence of Triton X-100 alone and in combination with GS concentration at 30°C

Triton X 100 (M)	GS (M)	E_{corr} (mV)	I_{corr} (mA/cm^2)	β_a (mV/dec)	β_c (mV/dec)	Polarisation Resistance (mΩ)	CR (mmpy)	%IE
Blank	-	-699.24	75.89	-396.72	103.13	797.50	881.83	-
1×10^{-5}	-	-715.47	38.67	1.49	80.45	954.91	449.37	49.04
7×10^{-5}	-	-725.57	35.21	-134.84	70.78	1837.00	409.16	53.60
1×10^{-4}	-	-717.42	28.29	454.62	246.37	2452.40	328.80	62.72
7×10^{-4}	-	-720.00	24.47	180.14	116.69	1257.00	284.32	66.91
1×10^{-3}	-	-728.01	18.21	-131.92	61.54	2750.00	211.59	76.00
1×10^{-5}	1×10^{-7}	-720.11	32.47	296.20	230.45	1770.00	377.34	57.21
7×10^{-5}	1×10^{-7}	-717.63	27.95	405.34	75.28	978.84	324.78	63.17
1×10^{-4}	1×10^{-7}	-715.54	22.60	130.34	72.43	978.32	262.61	70.22
7×10^{-4}	1×10^{-7}	-709.86	10.19	69.71	30.23	981.33	118.52	86.56
1×10^{-3}	1×10^{-7}	-721.56	6.67	79.23	10.99	635.04	77.51	91.21

It is evident from the Table 5 that in presence of surfactant, the values of R_{CT} increases whereas, the value of C_{dl} decreases. An increase in the R_{CT} value in presence of surfactants is due to the formation of a protective film on the metal/acid solution interface. A decrease in the C_{dl} values in presence of additives is attributed to the increased thickness of the electrical double layer. The IE was obtained from the following equation:

Table 5 EIS parameters for corrosion of aluminium 1 M HCl in absence and presence of Triton X-100 alone and in combination with GS at 30°C

Triton X-100 (M)	GS (M)	$R_S(\Omega)$	$R_{CT}(\Omega)$	C_{dl}(mF)	%IE
lank	-	0.67	1.09	145.93	
1×10^{-5}	-	0.69	2.15	0.42	49.30
1×10^{-3}	-	2.06	5.03	0.38	78.33
1×10^{-5}	1×10^{-7}	1.18	2.73	0.43	60.07
1×10^{-3}	1×10^{-7}	1.83	14.90	0.32	92.68

$$\% IE = \frac{R_{CT} - R_{CT}^0}{R_{CT}} \times 100 ....(10)$$

The R_{CT} and $R°_{CT}$ are charge transfer resistance of inhibited and uninhibited solution.
Where C_{dl} values were calculated from the frequency at which the imaginary component of impedance was maximum $(Z_{im\ max})$ using the following equation:

$$C_{dl} = 1 / 2\pi f_{max} \times 1 / R_{CT} .... (11)$$
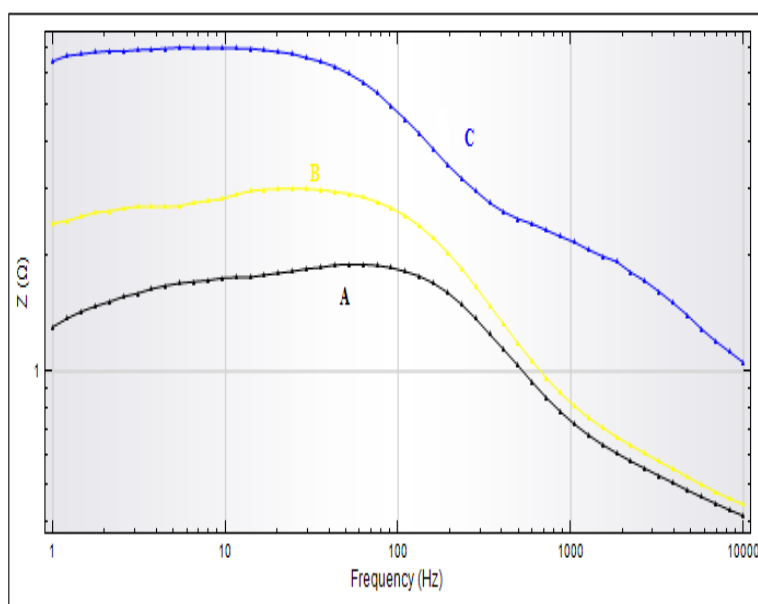
Figure 8 (A) Bode modulus of aluminium immersed in 1 M HCl at highest and lowest concentrations of Triton X-100 alone, (A) Blank, (B) 1×10^{-5} M, (C) 1×10^{-3} M

Surface morphological studies

The SEM was done to observe morphological changes on surface of polished, uninhibited and inhibited aluminium samples. The SEM photomicrographs are shown in Figures 10 (A-D). The polished surface shows scratches due to polishing with emery papers. But the surface is free from any defects such as pits or cracks [Figure 10(A)]. Figure 10 (B) shows SEM photomicrographs of the aluminium surface obtained after immersion in uninhibited acid HCl
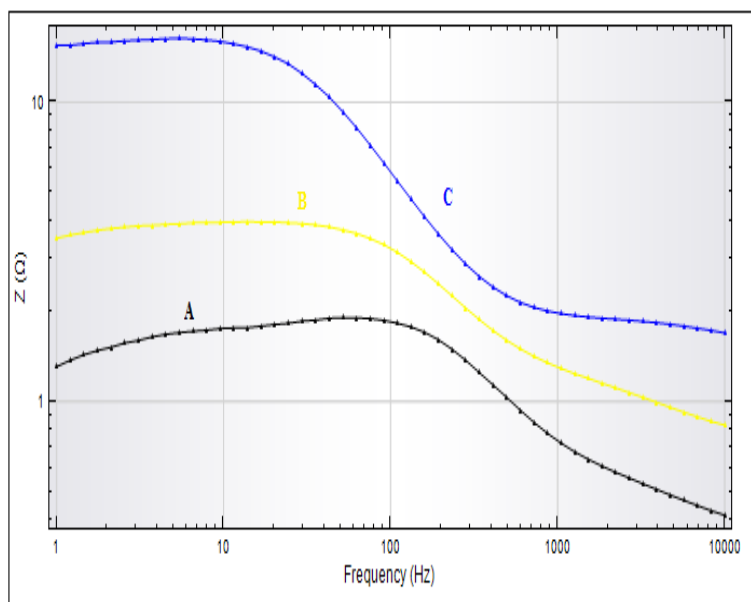
Figure 8 (B) Bode modulus of aluminium immersed in 1 M HCl at highest and lowest concentrations of Triton X-100+GS(1×10^{-7} M), (A) Blank, (B) 1×10^{-5} M+ 1×10^{-7} M, (C) 1×10^{-3}M +1×10^{-7} M
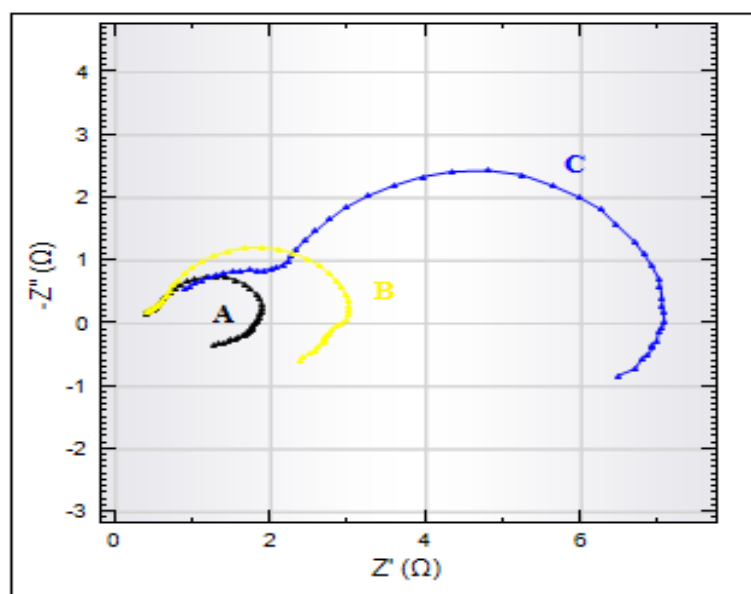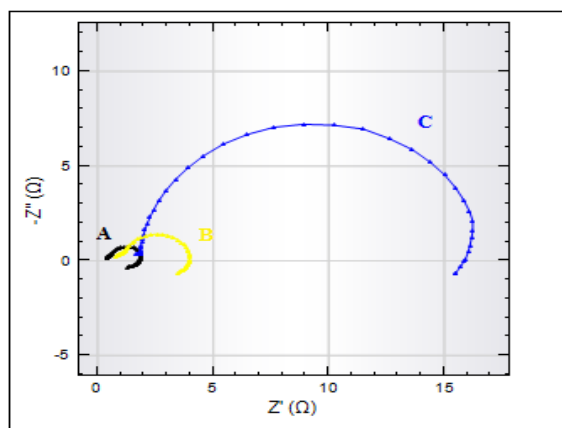

Figure 9 (A) Nyquist plot of aluminium immersed in 1 M HCl at highest and lowest concentrations of Triton X-100 alone, (A) Blank, (B) 1×10^{-5} M, (C) 1×10^{-3} M

solution at 30°C. The aluminium surface is severely damaged by corrosive action of acid and a rough and pitted corroded surface is evident. In Triton X-100 inhibited HCl solution the corroded area was found to be diminished due to adsorption of Triton X-100 on the aluminium surface [Figure 10 (C)]. Better inhibition was shown by aluminum dipped in Triton X-100 + GS inhibited acid solution [Figure 10 (D)] as compared to solution inhibited alone by Triton X-100. A smooth surface is noticed which is easily comparable with the photograph of polished aluminium surface.

Figure 9 (B) Nyquist plot of aluminium immersed in 1 M HCl at highest and lowest concentrations of Triton X-100 +GS (1×10^{-7} M), (A) Blank, (B) 1×10^{-5} M+ 1×10^{-7} M, (C) 1×10^{-3} M +1×10^{-7} M
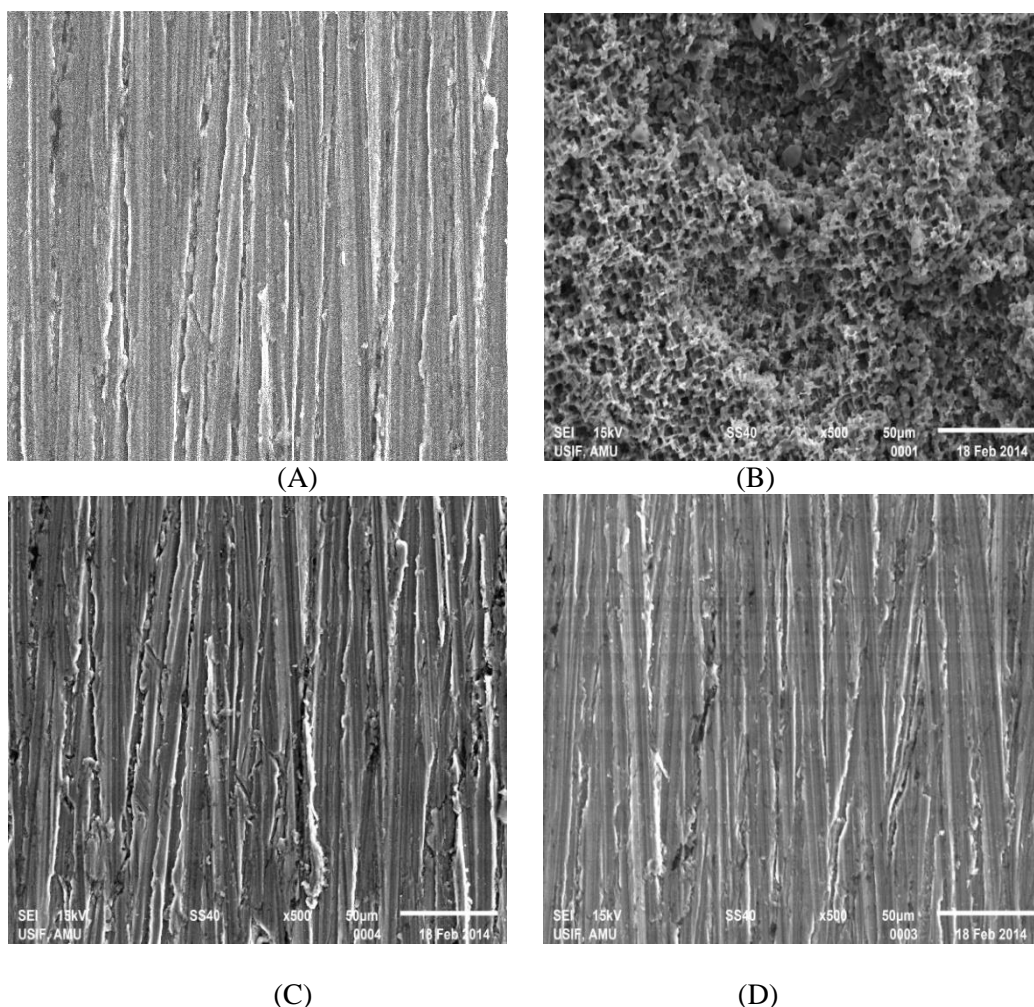

(A)	(B)
(C)	(D)

Figure 10 SEM photomicrographs of aluminium sample, (A) Polished, (B) Dipped in 1 M HCl , (C) Dipped in Triton X-100 inhibited 1 M HCl, (D) Dipped in Triton X-100 +GS inhibited 1 M HCl

SEM results are further confirmed by the results of EDAX studies. The EDAX spectra of polished, uninhibited and inhibited aluminium surface are shown in Figures 11 (A-D). In case of polished sample only Al is present as indicated

by the single signal of Al [Figure 11 (A)]. In uninhibited acid sample aluminium oxide is present as indicated by the Al and O signals   [Figure 11 (B)]. In Triton X-100 inhibited acid, EDAX spectra showed an additional line characteristic of the existence of C due to the C atoms of the Triton X-100. In addition, the Al and O signals are significantly suppressed relative to the sample obtained in uninhibited acid solution. The suppression in the signals occurs because of the overlying Triton X-100 inhibitor film [Figure 11 (C)]. The above data confirmed that a carbonaceous material containing oxygen atoms has covered the aluminium electrode surface. This layer is undoubtedly due to Triton X-100, because the C signal and the lower contribution of O signal are not present on the surface of aluminium exposed to uninhibited acid solution. In Triton X-100 + GS inhibited sample, EDAX spectra showed a more suppressed C and O line but high contribution of Al signal [Figure 11 (D)].
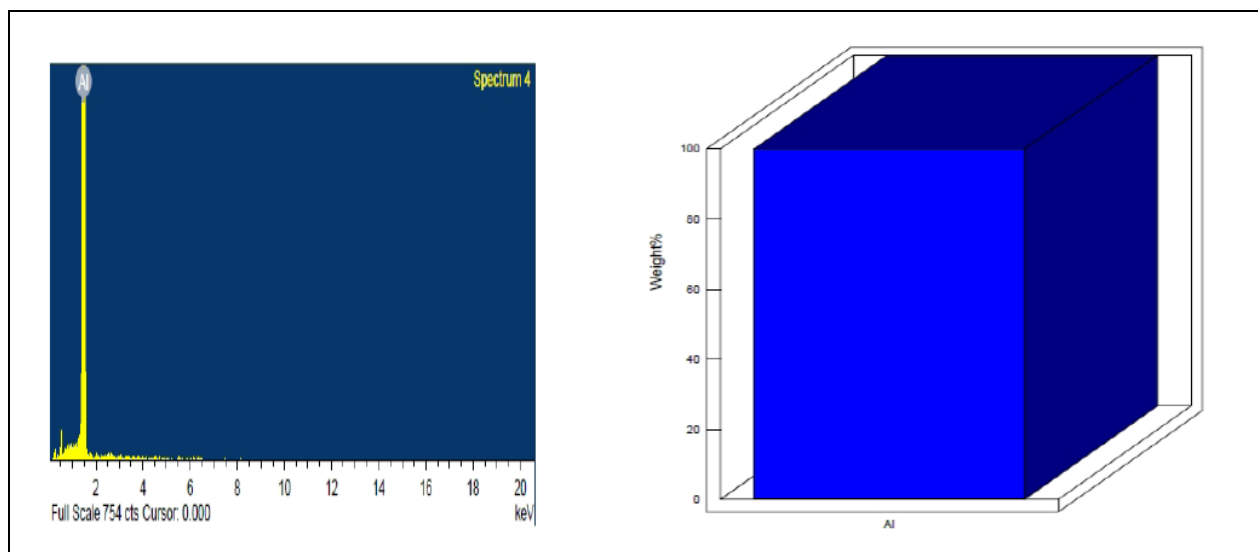

Figure 11 (A) EDAX spectrum and plot of weight% vs. element of polished aluminium sample
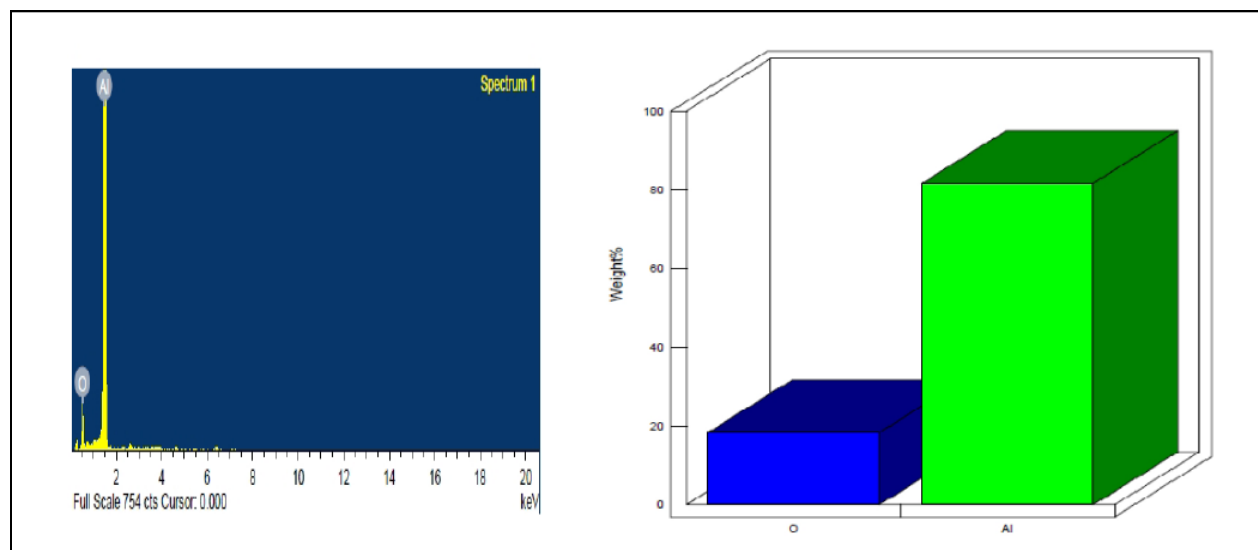

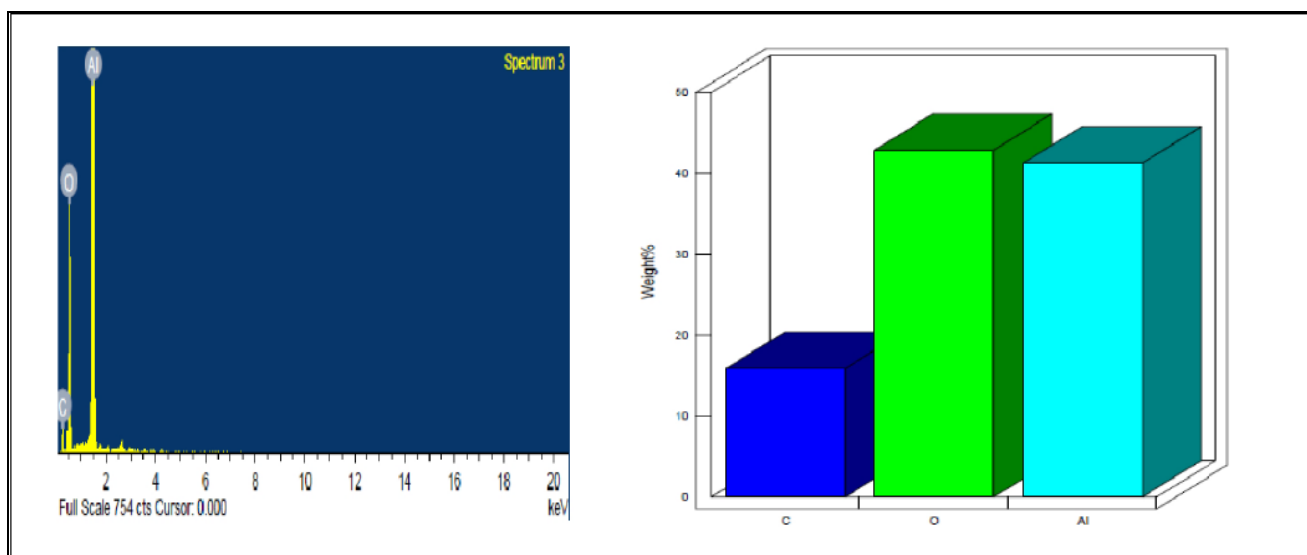**Figure 11 (B)** EDAX spectrum and plot of weight% vs. element of aluminium sample dipped in 1 M HCl

Figure 11 (C) EDAX spectrum and plot of weight% vs. element of aluminium sample dipped in Triton X-100 inhibited 1 M HCl
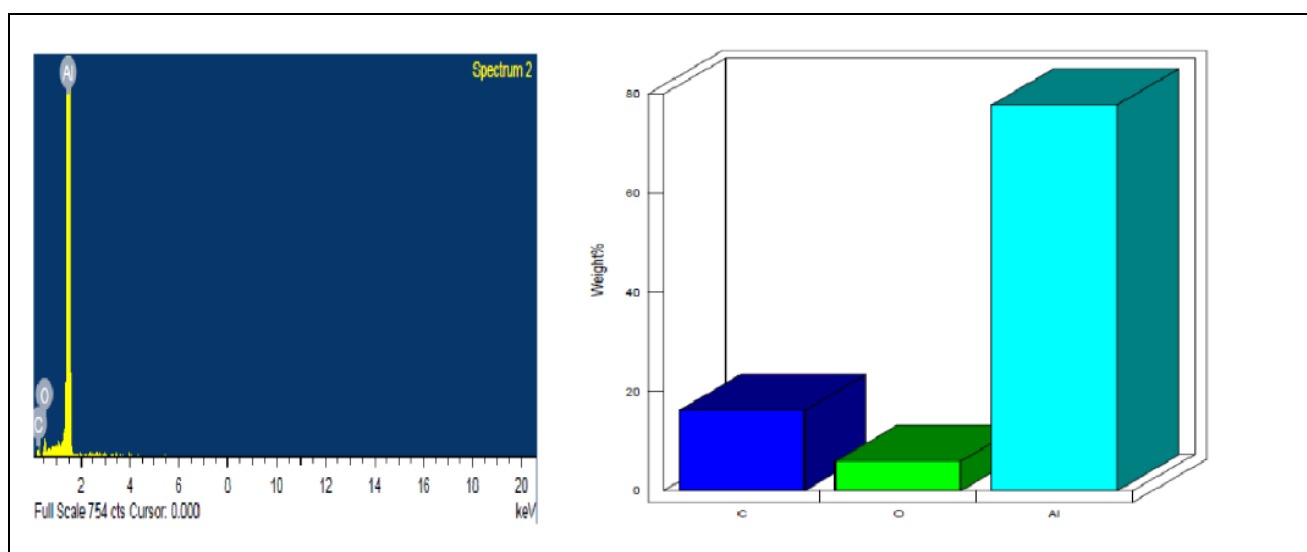

Figure 11 (D) EDAX spectrum and plot of weight% vs. element of aluminium sample dipped in Triton X-100+GS inhibited 1 M HCl

Conclusions

Triton X-100 was found to be an efficient corrosion inhibitor for aluminium in 1M HCl. The inhibition efficiency increased with an increase in surfactant concentration and reached a value of 76.00% at 1×10^{-3} M at 30°C, but decreased with rise in temperature. The corrosion process is inhibited by adsorption of the Triton X-100 on the aluminium surface following the Langmuir adsorption isotherm. Addition of GS synergistically increased the inhibition efficiency of Triton X-100 and a maximum inhibition efficiency of 94.26% was observed. The negative free energy of adsorption, ΔG_{ads} indicates strong and spontaneous adsorption of Triton X-100 on the aluminium surface. The results of electrochemical measurements are in reasonably good agreement with the weight loss measurements. SEM and EDAX studies further confirm the inhibitive character of the additives.

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