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Triton X-100 and Sodium Lauryl Sulfate Surfactants as Environmentally Friendly Corrosion Inhibitors for Steel in 0.5 M H_2SO_4

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Abstract The effect of anionic surfactant Sodium Lauryl Sulfate and neutral surfactant Triton X-100, as environmentally friendly corrosion inhibitors for carbon steel in 0.5 M H_2SO_4, has been tested. The inhibition efficiency has been determined by weight loss and impedance measurements. Adsorption of Sodium Lauryl Sulfate and Triton X-100 on carbon steel in 0.5 M H_2SO_4 obeyed Langmuir adsorption isotherm. Mechanism of adsorption has been studied and explained. Effect of TX 100 on the kinetics of the dissolution of steel in 0.5 M H_2SO_4 was studied. The activation parameters E_a, ΔH^* and ΔS^* were calculated and explained.

Keywords Surfactants, Acid Corrosion, Adsorption, Inhibition, Weight loss, Impedance

1. Introduction

Metal corrosion is electrochemical interaction between the metal and the surrounding environment leading to degradation of the metal properties. Loss of metal by corrosion is not only waste of the metal, but also waste of energy, water, and human effort that are used to fabricate the metal structures. The main reasons for the importance of corrosion are: safety, economics and conservation. Corrosion can affect the safety of operating equipment by causing failure to pressure vessels, boilers, metallic containers for toxic chemicals and airplane components. Also, it is a critical issue in the design of equipment for nuclear power plants and for disposal of nuclear wastes. Direct economic losses include the costs of replacing corroded structures and machine or their components, such as condenser tubes, pipelines and the extra cost of using corrosion - resistant metals and alloys instead of carbon steel where the latter has suitable mechanical properties but not sufficient corrosion resistance. Indirect economic losses includes; Shutdown of the unit and loss of product, loss of efficiency because of diminished heat transfer through accumulated corrosion products, Contamination of product, Overdesign in which equipment is often designed many times heavier than normal operating pressures. Losses would be cut at least in half because less power would be required to operate [1, 2]. Although there are a large number of organic compounds used as corrosion inhibitors, there was a general trend for many decades to find new trends of corrosion inhibitors for metals. Nowadays, there are restrictions to the use of ordinary corrosion inhibitors like chromates, nitrites, molybdates, and all organic inhibitors due to their chemical hazards. This has prompted the search for eco-friendly corrosion inhibitors for metals. Thus, there has been increased interest in employing environmentally benign corrosion inhibitors for metals in acid solution for sustainable development. Plants extracts are one of these sources. Plant extracts serve as environmentally friendly corrosion inhibitor materials [3, 4]. Among these newly discovered inhibitors are surfactants. Although, they are chemical compounds but they are environmentally acceptable, inexpensive, readily available and renewable source of materials [5-7]. Surfactants are widely used in our daily life and in industrial applications [8]. Surfactants nowadays find its role as corrosion inhibitors [9, 10]. The advantages of using surfactants as corrosion inhibitors are its low toxicity, low price, and easy production [11]. The mechanism of action of surfactants as corrosion inhibitor is adsorption on the metal surface in such a way that the polar or ionic part (hydrophilic) attaches the metal surface while the non-polar part (hydrophobic) extends in the solution [12]. It was also reported that the adsorption behavior depends on the structure of the surfactant [13]. Leema Rose et al. [14] studied the effect of Sodium Dodecyl Sulphate and Calcium Propionate in biocidal activity and corrosion inhibition of mild Steel immersed in an aqueous acidic solution using weight loss and biocidal efficiency method. The results showed that addition of SDS increases the inhibition efficiency and a protected film is formed. El-Tabei el al. [15]

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studied the synthesis and inhibition effect of a novel tri-cationic surfactant on mild steel corrosion in 0.5 M H_2SO_4 solution using potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss techniques. The three techniques showed that prepared Tricationic surfactant acted as mixed-type inhibitor for mild steel in 0.5 M H_2SO_4 and the corrosion inhibition increased with increasing the inhibitor concentration and temperature. In our previous work, [16, 17] we studied the effect of the cationic surfactant Cetyl trimethyl ammonium bromide on the electrochemical behavior of steel in 0.5 M H_2SO_4 solution and the effect of Tween 80 neutral surfactant on aluminum in 0.5 M HCl.

The aim of this study is to focus on the effect of surfactants: Sodium Louryl Sulphate (SLS), TritonX-100 on the electrochemical behavior of mild steel in sulfuric acid and to study the adsorption mechanism of those surfactants on the metal surfaces using electrochemical impedance spectroscopy (EIS) and weight loss techniques in this medium.

2. Materials and Methods

2.1. Electrochemical Measurements

A frequency response analyzer potentiostat (ACM 604) was used to carry out the electrochemical impedance and polarization measurements. The frequency range for EIS measurements was 0.1 x 10^4 to 0.01 Hz with applied potential signal amplitude of 10 mV around the rest potential. A three electrode mode cell contains an auxiliary graphite electrode and saturated calomel reference electrode was used. The working electrode was fabricated in cylindrical form. Steel was encapsulated in epoxy resin in such a way that only one surface was left uncovered. The working electrode has the chemical composition (% wt) Fe 96.86; C 0.21; S 0.04; Mn 2.5; P 0.04; Si 0.35. The exposed area (0.28 cm^2) sample was wet hand-polished using different grade 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 newly polished electrode. Before EIS measurements, the working electrode was introduced into the test solution and left for 20 min at the open circuit potential. All the measurements were done at 30.0 ± 0.1°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.

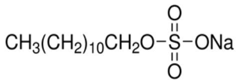
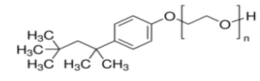
2.2. Weight Loss Measurements

Rectangular specimens of mild steel with dimensions (2.0 cm x 5.0 cm x 0.05 cm) were used during weight loss measurements. The weight loss coupons were polished, cleaned and weighted, then suspended in beakers containing 100 ml acidic solution with and without different concentrations of surfactant. After definite time, the coupons were removed from the solution, washed with distilled water, ethanol and then dried by acetone and reweighed. The weight loss was then determined (gm/cm^2), the experiment was then repeated for different time intervals up to 6 hours. To test the reliability and responsibility of the measurements, duplicate experiments were performed in each case of the same conditions.

2.3. Solution Preparation

The test solutions were prepared from analytical grade reagents and distilled water. 98% H_2SO_4 was purchased from Aldrich chemicals. Stock solution, of 3 M of H_2SO_4 and 0.02 M of surfactant were used to prepare the test solution. Prior each experiment, certain volume of 3 M of H_2SO_4 is added to an appropriate volume of 0.1 M surfactant solution and double distilled water to obtain a solution of 0.5 M H_2SO_4 and the required concentration of the surfactant. Triton X-100 (TX 100) and Sodium Lauryl Sulphate (SLS) were obtained from Alpha Chemica, their molecular structures are given in Table 1.

Table 1. Chemical structure of Triton X-100 (TX 100) and Sodium Lauryl Sulphate (SLS)

Surfactant	Chemical formula	Molecular structure
Sodium Louryl Sulphate	$CH_3(CH_2)_{11}OSO_3Na$	 $CH_3(CH_2)_{10}CH_2O-\underset{\underset{O}{\Vert}}{\overset{\overset{O}{\Vert}}{S}}-ONa$
Tritonx-100	$C_{14}H_{22}O(C_2H_4O)_n$	 n= 40

3. Results and Discussion

The effect of neutral surfactant Triton X-100 (TX 100) and anionic surfactant Sodium Lauryl Sulfate (SLS) on the electrochemical behavior of steel in 0.5 M H_2SO_4, was studied using weight loss and electrochemical impedance spectroscopy (EIS) techniques.

3.1. Mass Loss Measurements

Tables 2 and 3 present the mass loss results obtained for the corrosion of steel in 0.5 M H_2SO_4 in absence and presence of different concentrations of TX 100 and SLS surfactants at different immersion times.

The data in both tables 2 and 3 indicate that the mass loss values decrease and the inhibition efficiency increases with increasing the concentration of both surfactants indicating that both surfactants have positive effect on the protection of steel in sulfuric acid solution. In the mean time the inhibition efficiency in presence of the neutral surfactant TX 100 is higher to large extent than that in presence of the ionic surfactant SLS. The fact, that TX-100 surfactant has very high inhibition efficiency approaches 97% at 5 x 10^{-5} M, reflected the very high efficiency of TX-100 as corrosion inhibitor for steel in 0.5 M H_2SO_4.

Figures 1 and 2 present the relation between the mass losses of steel immersed in 0.5 M H_2SO_4 and the immersion time in absence and in presence of different concentrations of both surfactants TX 100 and SLS.

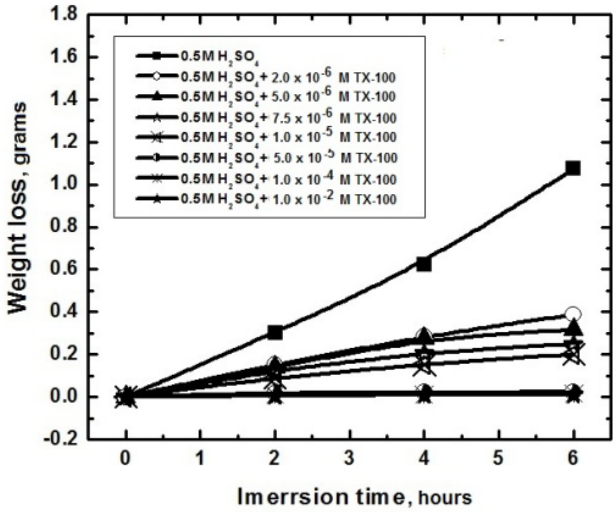


Figure 1. Mass loss measurements of steel immersed in 0.5 M H_2SO_4 in presence and absence of different concentrations of Triton X 100 surfactant against different immersion times (at 30°C)

By inspection of both figures 1 and 2, it is clear that the mass loss values increase with increasing the immersion time of the steel in the corroding medium which is logic regarding of the aggressiveness of the medium used in this study. Also, the mass loss values as a whole decrease with increasing the concentration of both surfactants. Comparing the mass loss results obtained in presence of both surfactants we can notice that the mass loss values in case of TX 100 is smaller and consequently the protection efficiency is higher in case of TX 100 than in case of SLS confirming the better performance of the neutral surfactant TX 100 as corrosion inhibitor than the anionic surfactant SLS.

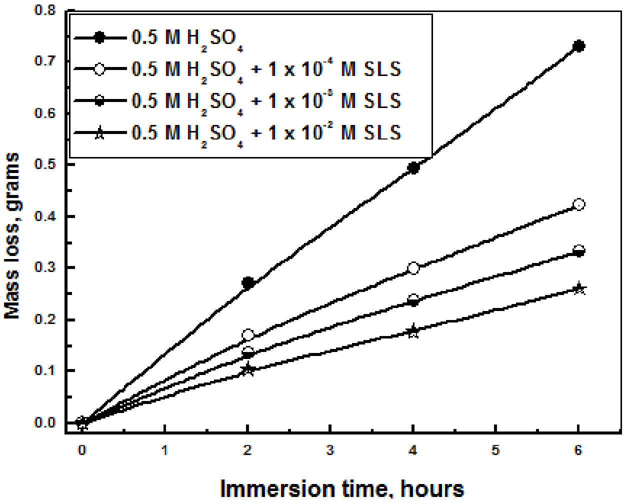


Figure 2. Mass loss measurements of steel immersed in 0.5 M H_2SO_4 in presence and absence of different concentrations of SLS surfactant against different immersion times (at 30°C)

Table 2. Weight loss measurements of steel immersed in 0.5 M H_2SO_4 in presence and absence of different concentrations of Triton X 100 surfactant at different immersion times (at 30°C)

	2h		4h		6h	
	Weight loss	%p	Weight loss	%p	Weight loss	%p
Blank	0.2708	-	0.4927	-	0.7309	-
2.0 x 10^{-6}	0.1521	43.83	0.2853	42.09	0.3876	46.96
5.0 x 10^{-6}	0.1407	48.04	0.2756	44.06	0.3164	56.71
7.5 x 10^{-6}	0.1263	53.36	0.2070	57.98	0.2496	65.85
1.0 x 10^{-5}	0.0905	66.58	0.1521	69.12	0.2018	72.39
5.0 x 10^{-5}	0.0179	93.38	0.0199	95.96	0.0219	97.00
1.0 x 10^{-4}	0.0086	96.82	0.0107	97.82	0.0153	97.90
1.0 x 10^{-2}	0.0048	98.22	0.0088	98.21	0.0108	98.52

Table 3. Weight loss measurements of steel immersed in 0.5 M H_2SO_4 in presence and absence of different concentrations of SLS surfactant at different immersion times (at 30°C)

	2hr		4hr		6hr	
	Weight loss	%p	Weight loss	%p	Weight loss	%p
Blank	0.2708	-	0.4927	-	0.7309	-
5.0 x 10^{-4}	0.1689	37.60	0.2993	39.25	0.4231	42.11
5.0 x 10^{-3}	0.1371	49.35	0.2377	51.76	0.3325	54.51
5.0 x 10^{-2}	0.1050	61.21	0.1779	63.89	0.2610	64.29

3.2. Electrochemical Impedance Spectroscopy Measurements (EIS)

Figures 3 and 4 represent Nyquist plots for steel immersed in 0.5 M H_2SO_4 in presence and absence of different concentrations of TX 100 and SLS respectively.

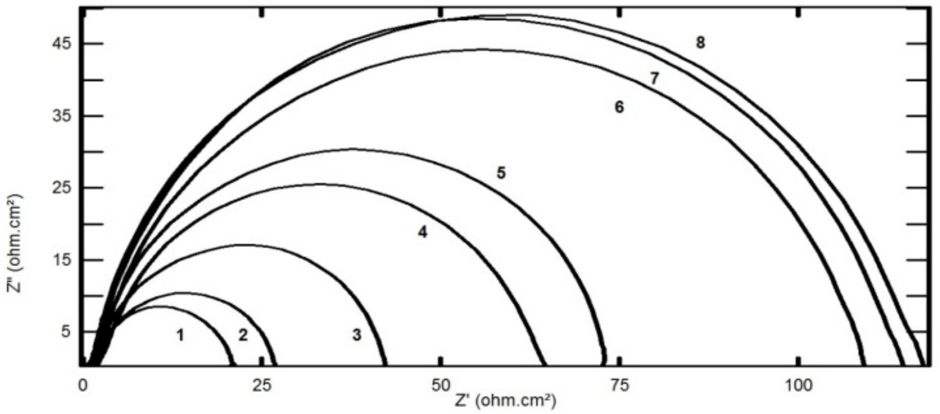


Figure 3. Nyquist plots for steel immersed in 0.5 M H_2SO_4 in presence and absence of different concentrations of TX 100; 1. 0.5 M H_2SO_4; 2. 0.5 M H_2SO_4 + 1 x 10^{-6}; 3. 0.5 M H_2SO_4 + 2 x 10^{-6}; 4. 0.5 M H_2SO_4 + 4 x 10^{-6}; 5. 0.5 M H_2SO_4 + 1 x 10^{-5}; 6. 0.5 M H_2SO_4 + 5 x 10^{-5}; 7. 0.5 M H_2SO_4 + 1 x 10^{-2}; 8. 0.5 M H_2SO_4 + 2 x 10^{-6}

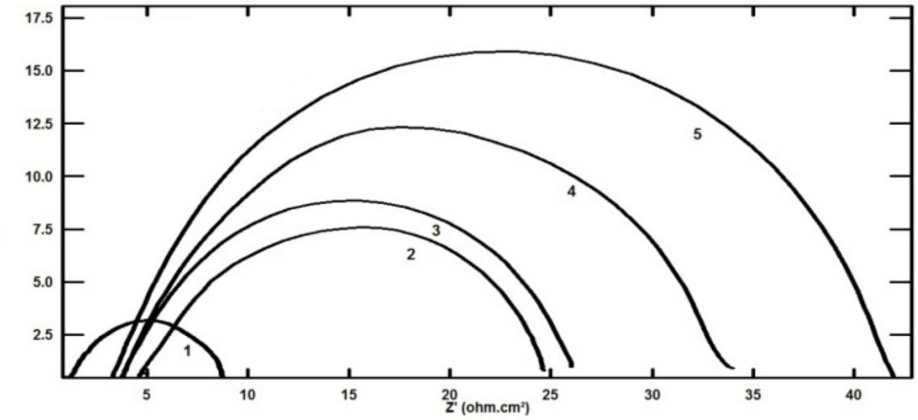


Figure 4. Nyquist plots for steel immersed in 0.5 M H_2SO_4 in presence and absence of different concentrations of SLS; 1. 0.5 M H_2SO_4; 2. 0.5 M H_2SO_4 + 1 x 10^{-3} M SLS; 3. 0.5 M H_2SO_4 + 2.5 x 10^{-3} M SLS; 4. 0.5 M H_2SO_4 + 5 x 10^{-3} M SLS; 5. 0.5 M H_2SO_4 + 5 x 10^{-2} M SLS

Table 4. Impedance parameters for steel in 0.5 M H_2SO_4 in absence and presence of different concentrations of TX 100

Concentration mol/L	R_S ohm.cm^2	Q_{dl} µF	n	R_{CT} ohm.cm^2	% P
0.0	1.14	570	0.80	20.49	-
1 x 10^{-6}	1.42	922	0.81	26.33	22.18
2 x 10^{-6}	1.17	481	0.80	42.33	51.59
4 x 10^{-6}	1.92	538	0.81	64.2	68.08
1 x 10^{-5}	1.61	427	0.81	75.21	72.75
5 x 10^{-5}	1.32	191	0.81	111.3	81.59
1 x 10^{-2}	1.04	147	0.84	117.2	82.51
2 x 10^{-2}	0.86	135	0.85	118.9	82.76

Table 5. Impedance parameters for steel in 0.5 M H_2SO_4 in absence and presence of different concentrations of SLS

Concentration mol/L	R_S ohm.cm^2	Q_{dl} µF	n	R_{CT} ohm.cm^2	% P
0.0	1.22	450	0.86	19.05	-
1 x 10^{-3}	4.54	770	0.76	20.98	9.19
2 x 10^{-3}	3.65	640	0.80	23.05	17.35
5 x 10^{-3}	3.74	400	0.81	30.37	37.27
5 x 10^{-2}	3.27	300	0.84	39.02	51.17

The Nyquist plots showed only one depressed capacitive semicircle in which its diameter increases with increasing the concentration of surfactant. Analysis of the experimental data was done by using Zsimpwin program by fitting the data to the suitable equivalent circuit given in figure 5. 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}.

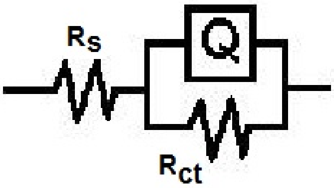


Figure 5. Equivalent circuit

The impedance parameters for steel in 0.5 M H_2SO_4 in absence and presence of TX 100 or SLS surfactants and the protection efficiency which can be calculated from the following equation are presented in tables 4 and 5.

$$\% \text{ P.} = [(R_{ct} - R_{ct0}) / R_{ct}] \times 100 \quad (1)$$

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

The results showed that the charge transfer resistance and hence the protection efficiency is higher to a great extent only in the presence of the neutral surfactant TX 100. On the other hand, it shows very small charge transfer resistance and consequently small percentage inhibition in case of the presence of the anionic surfactant SLS. This observation results in the conclusion that both the TX 100 and SLS can be used as corrosion inhibitors for steel in 0.5 M H_2SO_4 solution taking into consideration that the efficiency of TX 100, as neutral surfactant, in controlling the corrosion of steel in 0.5 M H_2SO_4 solution is better than the anionic surfactant SLS.

The protection efficiency was found to increase with increasing the concentration of both surfactants reaching a value of 81% at concentration 5 x 10^{-5} M of TX 100. Also, the values of the capacitance of double layer decrease with increasing the concentration of both surfactants confirming the adsorption of the surfactants on the metal surface and their interference in the electric double layer structure and change the chemical composition at the interface.

3.3. Application of Langmuir Adsorption Isotherm

It is known that the surfactant molecules have a tendency to associate at interfaces and in solution to form aggregates [5]. Adsorption of the surfactant molecules on to the 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. The variation of the percentage inhibition, which was calculated from the mass loss measurements, with different concentrations of both SLS and TX 100 surfactants is plotted in figure 6.

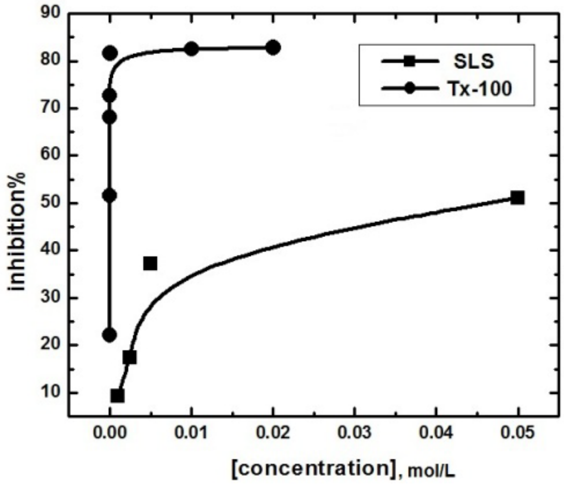


Figure 6. Variation of the percentage inhibition of the corrosion of steel in 0.5 M H_2SO_4 with concentrations of SLS and TX 100

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 ΔG_{ads}, the experimental data was fitted to Langmuir adsorption isotherm which is given by the following equation [18, 19]:

$$C/\theta = 1/K + C \quad (2)$$

Where, K is the adsorptive equilibrium constant which represent the extent of interaction between the surfactant and the steel substrate; C is the concentration of surfactant in mol/L and θ is the degree of surface coverage by the surfactant molecules. The application of Langmuir to the experimental data is given in figure 7.

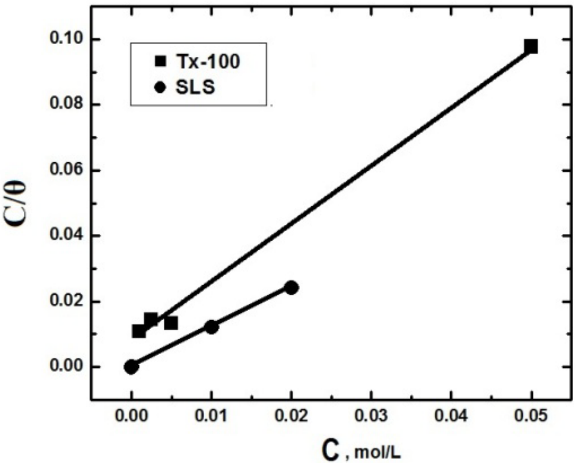


Figure 7. Application of Langmuir adsorption isotherm to the results of adsorption of SLS and TX 100 on steel surface in 0.5 M H_2SO_4

The slope of the above relation is nearly unity which means that the data obtained fit the Langumir model. The values of K which is the reciprocal of the slope of the relation and the values of the free energy change of adsorption ΔG_{ads} which is calculated from the following relation [20], is given in table 6.

$$K = 1/C_{solvent} \exp(-\Delta G_{ads}/RT) \quad (3)$$

Where, R is the universal gas constant, T is the absolute temperature, $C_{solvent}$ is the molar concentration of solvent which is in this case water and equal to 55.5 mol/L. It is reported that low values of ΔG°_{ads} equal to or less than -20 kJ/mol are consistent with (physical adsorption) which can be discussed on the basis of an electronic interaction between the inhibitor molecule and the metal surface. If ΔG°_{ads} values equal to or higher than - 40 kJ/mol can be an evidence of chemical adsorption. In other words, formation of coordinate bond between the inhibitor molecules and the metal surface by charge sharing or charge transfer from the inhibitor molecules to the metal surface [21].

Table 6. The values of the binding constant K and the free energy change of adsorption ΔG_{ads} for the adsorption of SLS and TX 100 on steel surface in 0.5 M H_2SO_4

Surfactant	K	ΔG_{ads} kJ/mol
SLS	1.26×10^2	-22.31
TX 100	5.15×10^5	-43.24

The large values of K obtained in both cases indicate strong interaction between the two surfactants and the steel surface. The negative values of ΔG°_{ads} obtained in both cases indicative that the adsorption of both surfactants SLS and TX 100 on the steel is spontaneous. The values of ΔG°_{ads} obtained in both cases strongly indicate that the adsorption of SLS is physical adsorption while in case of TX 100 it is chemical adsorption in nature. The fact that TX-100 is chemically adsorbed is good proof for explaining the higher efficiency of TX-100 over SLS.

3.4. Effect of TX 100 on the Kinetics of the Dissolution of Steel in 0.5 M H_2SO_4

The effect of TX 100 on the kinetics of the dissolution of steel in 0.5 M H_2SO_4 was studied by comparing the activation parameters of the dissolution reaction of steel in the free acid in absence and in presence of two different concentrations of TX 100 surfactant. The results obtained are applied in the linear square fit of ln W and ln (W/T) versus (1/T) according to Arrhenius and Transition State equations [22] as following:

Arrhenius equation:

$$\ln W = \ln A - (Ea/RT) \quad (5)$$

Where Ea is the apparent effective activation energy, T is the absolute temperature, R is the universal gas constant and A is the Arrhenius pre-experimental factor.

Transition state equation:

$$W = (RT/Nh)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \quad (6)$$

Where, N is the Avogadro's number, h is the Planks constant, ΔH* is the enthalpy of activation and ΔS* is the entropy of activation. Figures 8a and 8b show the linear plots produced when we plot (ln W) versus (1/T) and (ln W/T) versus (1/T) using data collected in experiments where steel was immersed in 0.5 M H_2SO_4 in the absence or the presence of 2×10^{-6} and 5×10^{-5} M TX 100.

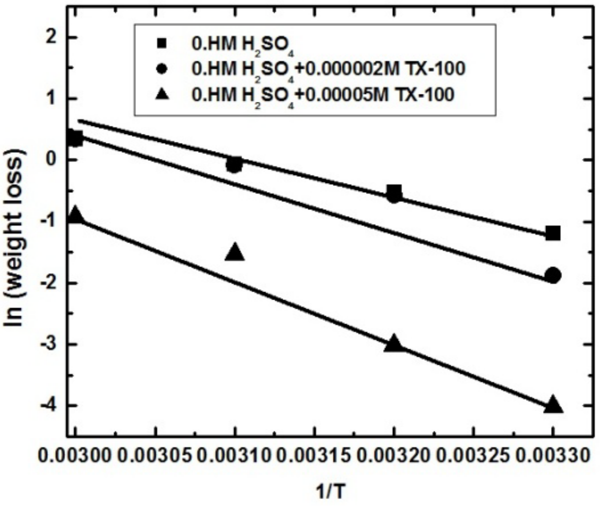


Figure 8a. Linear fit for (ln W) data vs. (1/T) for steel dissolution in 0.5 M H_2SO_4 solutions in the absence and presence of 2×10^{-6} and 5×10^{-5} M TX 100

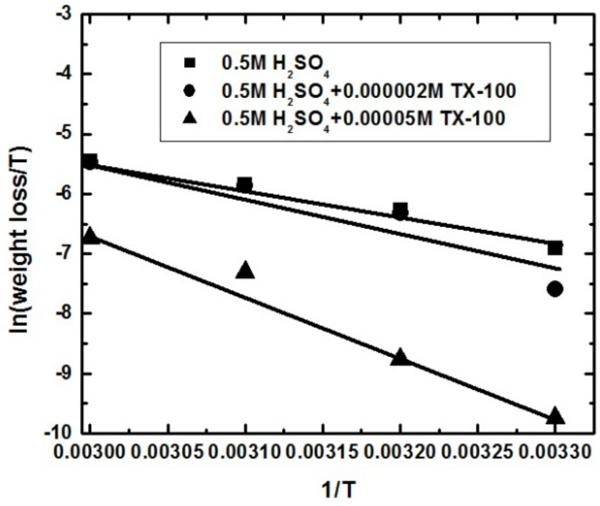


Figure 8b. Linear fit for (ln W/T) data vs. (1/T) for steel dissolution in 0.5 M H_2SO_4 solutions in the absence and presence of 2×10^{-6} and 5×10^{-5} M TX 100

These data were used to calculate the values of the activation parameters E_a, ΔH^* and ΔS^*. The resulting values of the activation parameters are given in table 7.

Table 7. Activation parameters for steel dissolution in 0.5 M H_2SO_4 solutions in the absence and presence of 2×10^{-6} and 5×10^{-5} M TX 100

	E_a (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K)
0.5 M H_2SO_4	42.31	39.70	-123.36
0.5 M H_2SO_4 + 2×10^{-6} M TX-100.	59.48	56.87	-70.85
0.5 M H_2SO_4 + 5×10^{-5} M TX-100.	89.39	86.77	8.15

It can be seen that the values of the E_a, ΔH^* in presence of the surfactant are higher than those of the free acid solution.

This behavior can be discussed on the basis that the adsorption of the surfactant at the steel/solution interface increases the energy barrier of the dissolution reaction of steel. The negative values of ΔS^* in the absence of surfactant indicates that the activated complex represents association rather than dissociation step [23]. The values of ΔS^* in presence of the surfactant becomes less negative or (more positive), this means that the entropy increases in presence of surfactants which is the driving force for the adsorption of the surfactants on the steel surface [24].

3.5. Mechanism of Adsorption of Surfactants

The adsorption of surfactant onto the metal surface can be explained by considering the changes that could happen to the structure of the double layer formed at the metal/solution interface. Characteristics of this region is the existence of a specific structure of particles and the presence of an electric field of significant intensity across it which is caused by the separation of charges that are in contact. The surface phase can be considered as a parallel plate condenser, with one plate on the center of the ions that have been brought to the electrode. At the distance of their closest approach to it, and with the second plate at the metal surface, between the two plates and acting as a dielectric are oriented water molecules. This structure is known as the electric double layer. Thermal motion of the positive ions in the solution makes the condenser plate on the electrolyte side of the interface diffuse. This condition justifies the potential gradient from the metal surface through the bulk of the solution. The picture is further complicated by the presence of ions in the surface layer of the electrode in addition to those that are present due to the force of attraction or repulsion between electric charges. Such electrode surface layer ions are said to be specifically adsorbed on the electrode surface [25].

Adsorption of surfactants on the metal surface can change their interfacial properties such as hydrophobicity, surface charge and corrosion inhibition. 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 desolvation. The overall adsorption process is a mixture of all these forces [26].

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 [27]. There are a number of mechanisms by which surfactants molecules may adsorb onto metal surface from aqueous solution [28-30]. It is reported that [31] the adsorption of ionic surfactants on oppositely charged metal surface can be explained by considering that, 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 step 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 which is the case in presence of SLS. The adsorption of SLS on the steel surface 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 a previous work, A. Kumar studied the effect of SLS surfactant as corrosion inhibitor for steel in hydrochloric acid by using mass loss and polarization techniques. The results obtained are in good agreement with the current results indicating that SLS adsorbed on the steel surface in acidic solution regardless the type of anionic species present in solution [32].

The adsorption of cationic surfactant Cetrimide on steel surface, which is positively charged, in 0.5 M H_2SO_4 were explained in our previous work by assuming the important role played by the counter ion Br^- during the adsorption process. The driving force for the adsorption of cationic surfactant Cetrimide onto the steel surface is the intermediate bridge formed by Br^- ion between the negative ends of the bromide-steel 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 steel 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 [33].

The adsorption of the neutral surfactant TX-100 on the steel surface can be explained by considering one or all the following proposed mechanisms: Adsorption by polarization of π – electrons which takes place by the electron-rich aromatic nuclei in its chain and their attraction to the solid metal which has strongly positive sites; adsorption by dispersion forces which takes place via London–van der Waals dispersion forces between metal and the large number of ethylene oxide units in the TX 100 surfactant chain, where by this mechanism adsorption of the surfactant increases with an increase in its molecular weight; hydrophobic bonding which takes place when the attraction between hydrophobic groups of the surfactant molecules due to their tendency to escape from an aqueous environment becomes large enough to permit them to adsorb onto the metal by aggregating their chains.

4. Conclusions

The results showed that both TX-100 and SLS can be used as environmentally friendly corrosion inhibitors for steel in 0.5 M H_2SO_4. TX-100 has very high efficiency for protection of steel in 0.5 M H_2SO_4 as it has 97% inhibition efficiency at very low concentration 5 x 10-5 M.

Langumir adsorption isotherm was applied to the experimental data. The results showed that Langumir fit the results. ΔG_{ads} was calculated and found to be -22.1 kJ/mol for SLS indicating physical adsorption and -43.2 kJ/mol for TX-100 indicating chemical adsorption.

The activation parameters were calculated by applying Arrhenius equation. E_a, ΔH^* in presence of the surfactants were found to be higher than those of the free acid solution indicating that the adsorption of the surfactants at the steel/solution interface increases the energy barrier of the dissolution reaction of steel.

ΔS^* has negative values in the absence of surfactant indicates that the activated complex represents association rather than dissociation step. The values of ΔS^* in presence of the surfactants are less negative or (more positive), meaning that the entropy increases in presence of surfactants which is the driving force for the adsorption of the surfactants on the steel surface.

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