

Exploring the role of Sodium dodecyl sulphate in presence of 2-thioureidobenzoxazole as enhancer of corrosion inhibition of mild steel in 2M HCl solution

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In the current communication, we report the role of sodium do-decyl sulphate (SDS) as the corrosion inhibition enhancer for 2-thioureidobenzoxazole (BOT) on mild steel (MS) in 2M Hydrochloric acid electrolyte. Though, 2-thioureidobenzoxazole shows limited inhibition due of the presence of oxygen atom, addition of small quantity of SDS enhances the inhibition by 10-fold. Electrochemical impedance spectroscopy, Tafel measurements and weight loss studies were used in the current work. The variation of temperature on the inhibition efficiency of SDS+BOT on MS surface was explored. The Gibbs free energy of adsorption values showed that inhibition process is spontaneous. Langmuir adsorption was prevalent and the morphological characterization was carried out using scanning electron microscope which indicated the role of SDS as a versatile performance enhancer for BOT. This combination, act as an anodic mixed type inhibitor.

Keywords: Corrosion inhibition, mild steel, Impedance, Adsorption.

1. INTRODUCTION

Mild steel (MS) is a versatile material for many industrial applications such as infrastructure development, automobiles, pipelines and storage tanks. Mild steel is preferred owing to its favorable mechanical properties, availability and economical advantage[1][2]. Protection of metals from oxidation using chemical compounds which mitigate the corrosion process esp. localized attacks is a well-known practice in various industries. The performance enhancement of BOT using an anionic surfactant is the main objective of the current work. The standard inhibitors are organic compounds involving, aromaticity, long carbon chained structures and heteroatoms (N, S, O, P) [3][4][5]. These compounds are adsorbed over the MS surface leading to the formation of thin film on the MS surface. This offsets

the acidic attack from the electrolyte thus preventing metal degradation. The inhibitor molecules are adsorbed prominently by virtue of physico-chemical properties such as presence of functional groups, steric factors, aromaticity, p-orbital character of the donor atoms. These functional groups contribute to the formation of a thin protective layer by contributing electrons towards the metal surface [6].

Sodium dodecyl sulphate (SDS) is a well-known anionic surfactant used in varied applications such as cleaning, detergent, pharmaceutical, food products etc. The structure of SDS involves 12 carbon chains attached to a sulphate group. SDS is amphiphilic in nature due to the presence of hydrocarbon tail and polar headgroup[7]. In recent times, synergism is one of the key factors in the formulation of novel corrosion inhibitors. The addition of surfactant to the organic inhibitor has proven to be one of the most effective ways to inhibit corrosion[8].

Surfactants have a long history of being extensively used as inhibitors to prevent metallic corrosion. Surfactant molecules possess amphiphilic nature which enables the surfactant to effectively retard corrosion process at the metal/metal-oxide-water interface[9]. The important factors that determine the adsorption of inhibitors on the metal surface are the properties of the surfactants and interaction of the surfactant on the metal surface[10].

Because of the characteristic property of the surfactant to form aggregates at the metal/solution interface, it is vastly chosen as the corrosion inhibitor for metallic corrosion. Surfactants function by forming hemimicelles, admicelles in the form of mono or bilayer on the metal surface that reduce the corrosion attack[5]. When only the surfactant is used for preventing corrosion, the observed effect is minimal, whereas SDS in combination with organic compounds enhances their inhibition performance substantially. 2-thioureidobenzoxazole (2-BOT) when combined with SDS exhibits synergism in reducing corrosion effectively.

In the present study, which is in continuation of the work carried out by the authors of the publication[11]. we investigated the synergistic role of organic inhibitor 2-BOT in combination with SDS at a very low concentration in 2 M HCl solution. Electrochemical techniques such as electrochemical impedance spectroscopy, polarization measurements and weight loss studies were carried out. In addition, surface morphology studies are carried out using SEM to elucidate the synergistic effect of 2-BOT and SDS surfactant.

2. MATERIALS AND METHODS

2-thioureidobenzoxazole which was synthesized [11] [16] and characterized was used in the present study.

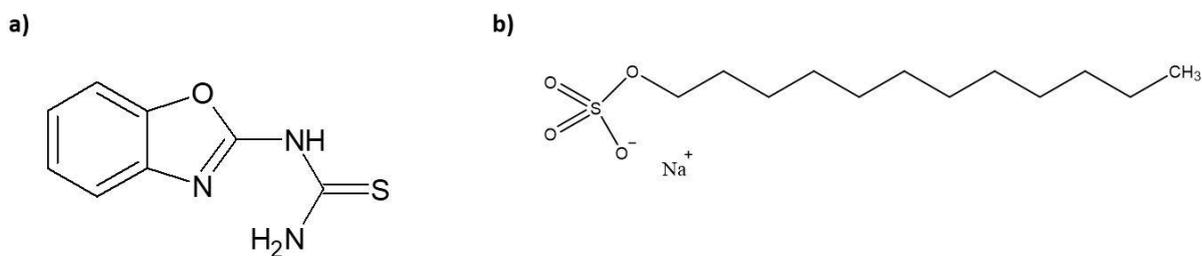


Figure 1. Structure of a) 2-thioureidobenzoxazole b) sodium do-decyl sulphate

2.1. Metal specimen and test solution preparation

Experiments were performed using Carbon Steel Type CS1084 (Carbon – 0.86%, Manganese – 0.75%, Phosphorous –0.04%, Sulphur – 0.05%, Silicon – 0.22%, and Nickel – 0.04%). The electrolyte test solution 2 M HCl solution was prepared by appropriately diluting the acid solution (using 37 % HCl obtained from SDFINE) and Millipore grade water used for diluting the stock acid solution.

2.2 Preparation of working electrode – MS

The working electrode MS was subjected to pre-treatment by abrading with different grades of Si/C paper i.e., 200, 400, 600, 800 1000 and 1200. The metal was washed with distilled water. Further, the metal was immersed in HCl solution for about 5 min by the process known as acid pickling. Subsequently, metal was washed with ethanol to remove traces of organic contaminants. The MS specimen was then dried and used for electrochemical corrosion experiments where only 1 cm² of surface area was exposed to the acidic electrolyte.

2.3 Characterization

The analytical grade solvents were used without further purification for all the experiments. Electrothermal melting point apparatus was utilized to determine the melting point of the synthesized compounds. The test solutions were prepared by using Hydrochloric acid of AR grade and diluted appropriately using Millipore water. JEOL scanning electron microscope JSM-IT 300 was used to obtain SEM images of MS specimen.

2.4 Electrodes and chemicals

Electrochemical measurements

The electrochemical measurements were performed using CHI 660E workstation in potentiodynamic mode with MS as working electrode (WE), platinum wire as counter electrode (CE) and saturated calomel electrode (SCE) as the reference electrode (RE). Impedance measurements were

performed within the frequency range of 100 kHz to 0.1 Hz at the open circuit potential by applying a small signal amplitude perturbation of 5 mV. Polarization measurements were obtained at a scan rate of 0.005 Vs^{-1} over a range of +250 mV to -250 mV versus the open circuit potential. Weight loss of metal specimen were determined using an analytical balance of $\pm 0.1 \text{ mg}$ accuracy. Initially the metal specimen was immersed in 2 M HCl solution for 1 h at 298 K and then metal specimen was washed thoroughly with distilled water after the exposure. Weight loss of the material was obtained from initial and final weight loss of the metal specimen.

3. RESULTS AND DISCUSSION

3.1 UV-Vis spectroscopic analysis

The UV-Vis spectrum was recorded for the solution containing 2-thioureidobenzoxazole (BOT) in 2M HCl and compared with the spectrum of SDS-BOT in 2M Hydrochloric acid solution. It is evident from the below (Fig.1) that BOT shows a λ_{max} value of 278 nm. Upon addition of SDS, hypsochromic/blue shift was observed as the λ_{max} values shifts to lower wavelength of 274 nm, which arises due to the synergistic interaction of SDS and BOT contributing to enhanced inhibition vis-a-vis BOT. The inhibitor displays n to π^* transition, where oxygen containing unshared electron pair is excited to π^* antibonding orbital.

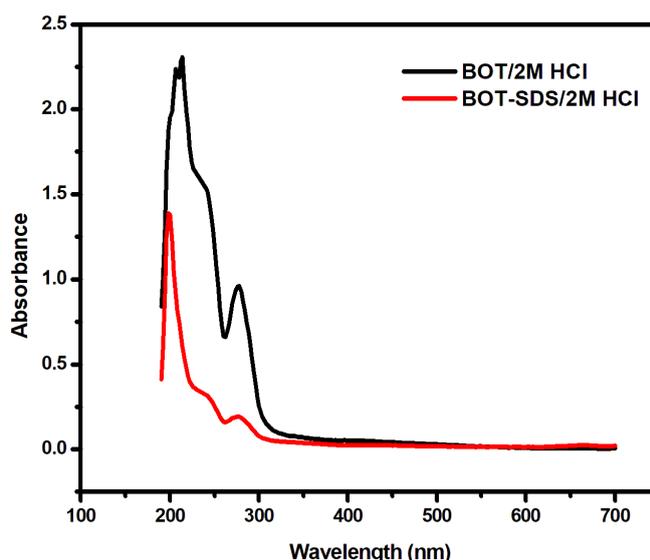


Figure 1.1. UV-Vis spectrum of BOT in 2M HCl solution and BOT-SDS in 2M HCl solution at 298 K.

3.2 Electrochemical Impedance Spectroscopy (EIS)

EIS technique is used to measure charge transfer resistance offered by the organic inhibitor on the metal surface. BOT acts as a good corrosion inhibitor, whose performance is enhanced by addition

of small concentration of 0.01 mM of SDS. Adsorption of surfactant and inhibitor on the mild steel surface increased the resistance and decreased the corrosion rate (Fig.2). This decrease in corrosion rate is due to the micelle formation at the metal/solution interface[12]. The equivalent circuit diagram consisting of parallel combination of capacitance double layer and charge transfer resistance in series with solution resistance ($R_s[R_{ct}-C_{dl}]$) was used to fit experimental Nyquist data. This was used to calculate various impedance parameters such as solution resistance, charge transfer resistance and capacitance double layer values. These parameters implied increased charge transfer resistance due to the addition of SDS. It is observed that the plots exhibit single capacitive loop. The surfactant inhibitor aggregates over the metal surface and efficiently reduces the surface tension. The highest R_{ct} value of 1547-ohm cm^{-2} (Fig.2) was observed at 0.5 mM concentration, which partially decreased, due to the constant penetration of acid electrolyte. The adsorption layer thickness is maximum at 0.5 mM concentration. Also, the capacitance double layer reduces at higher concentrations, which reiterates that BOT and SDS inhibitor acts synergistically to reduce the surface tension contributing to maximum inhibition at the metal/solution interface[13]. The charge transfer resistance peaks by the virtue of adsorption of SDS and BOT at the interface of MS/solution. The optimum concentration of 0.5 mM is sufficient to achieve effective corrosion inhibition.

Table 1. EIS Parameters BOT without and with SDS in 2M HCl

Conc. (mM) BOT	SDS (mM)	R_s (ohm cm^{-2})	R_{ct} (ohm cm^{-2})	C_{dl} (μF cm^{-2})	IE (%)
Blank 2M HCl	Nil	2.58	30.86	105.4	-----
2M HCl	SDS	2.46	127.9	3.69	90.73
0.05	0.01	2.5	40.54	4.36	70.74
0.1	0.01	2.64	188.1	2.38	93.69
0.5	0.01	2.53	1547	3.17	99.23
1.0	0.01	2.51	806.6	1.76	98.53
2.0	0.01	2.48	889	2.94	98.67
0.05	Nil	2.46	47.29	56	43.73
0.1	Nil	2.55	335.8	24	92.07
0.5	Nil	2.55	767.7	17	96.54
1.0	Nil	2.82	674.5	6.68	96.06
2.0	Nil	3.63	358	3.13	92.58

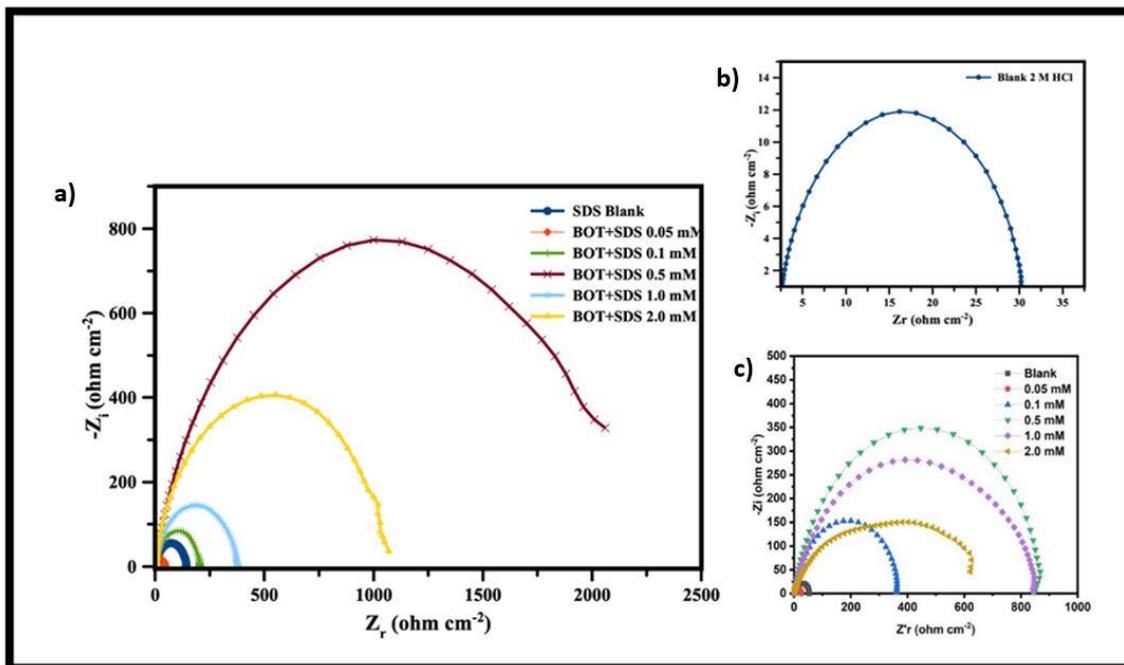


Figure 2. Nyquist plots indicating the charge transfer resistance at room temperature in 2M HCl; a) SDS-BOT b) Blank 2M HCl c) BOT inhibitor.

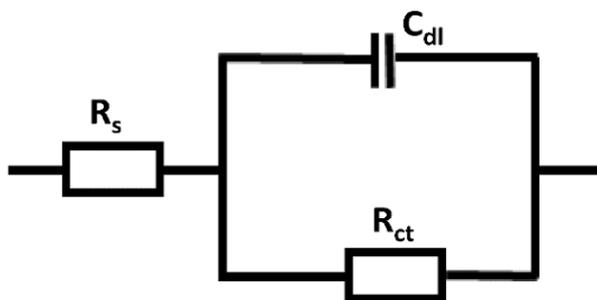


Figure 3. Equivalent circuit diagram for SDS-BOT inhibitor at 298 K.

3.3 Potentiodynamic Polarization Studies (PDP)

The corrosion inhibition of behavior of BOT in presence of SDS in 0.5 M H_2SO_4 was investigated using potentiodynamic polarization studies at various concentrations. From the below (Fig. 4) it is evident that the anodic and cathodic reactions have significantly shifted to lower current densities. The impedance exhibited at the corrosion potential directly correlates with the corrosion rate from the conventional electrochemical measurements. It is also evident from Tafel measurements that as the concentration of the inhibitor increases the corrosion current density decreases significantly. In addition, both of the anodic and cathodic branches of polarization was observed and the tendency of the Tafel curves was in both the directions. This can be attributed to the fact that; the inhibitor readily blocks the susceptible corrosion sites from oxidation and acts as anodic mixed type inhibitor[14]. To further quantify PDP results, various Tafel parameters such as corrosion potential, anodic and cathodic Tafel

slopes, corrosion current density was determined using extrapolation technique. The below equation was used to determine corrosion inhibition efficiency.

$$IE (\%) = \frac{I_{corr} - I_{corr,o}}{I_{corr}} \text{ -----}[1]$$

where I_0 and I are corrosion current densities in the absence and presence of the organic inhibitor respectively.

Table 2. Tafel parameters of BOT without and with SDS at various concentrations at 298 K.

Conc. (mM) BOT	SDS (mM)	-E _{corr} (mV)	-b _a (mV dec ⁻¹)	b _c (mV dec ⁻¹)	I _{corr} (mA cm ⁻²)	IE (%)
Blank 2M HCl	Nil	479	84	128	10.76	-----
2M HCl	SDS	488	109	144	0.57	94.70
0.05	0.01	532	204	303	3.51	67.38
0.1	0.01	540	109	238	1.79	83.36
0.5	0.01	517	32	123	0.083	99.23
1.0	0.01	522	30	126	0.106	99.07
2.0	0.01	519	35	113	0.076	99.29
0.05	Nil	524	242	172	1.66	46.1
0.1	Nil	523	213	122	0.48	84.20
0.5	Nil	532	207	133	0.27	91.17
1.0	Nil	535	173	124	0.25	91.82
2.0	Nil	521	163	37	0.11	96.33

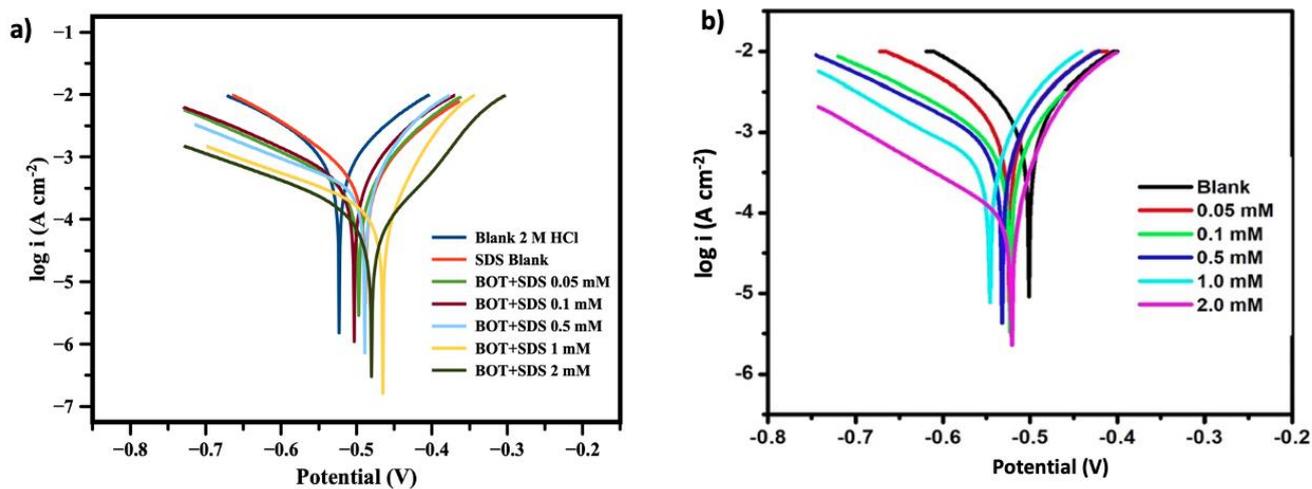


Figure 4. Tafel plots depicting the polarization behavior of a) SDS-BOT inhibitor b) BOT inhibitor in HCl solution at various concentrations.

3.4 Weight loss

The corrosion phenomenon was further validated through weight loss studies at different concentration of SDS-BOT inhibitor. The weight loss was obtained by measuring initial and final weights of the specimen at 298K. Before measuring the weight of the specimen, the metal specimen was cleaned and dried. These values were used to calculate the inhibition efficiency of the organic inhibitors. The inhibition efficiency values obtained reinforces the fact that corrosion rate is substantially reduced by BOT in the presence of SDS.

Table 3. Weight loss inhibition efficiency for BOT without and with SDS at various concentrations at 298 K.

Conc. (mM) BOT	SDS (mM)	Weight Loss (g)	Surface Coverage (θ)	IE (%)
Blank 2M HCl	Blank	0.0062	-----	-----
0.05	0.01	0.002	0.67	67.74
0.1	0.01	0.001	0.83	83.87
0.5	0.01	0.0004	0.93	93.55
1.0	0.01	0.0005	0.91	91.94
2.0	0.01	0.0003	0.95	95.16
0.05	Nil	0.0037	0.40	40.3
0.1	Nil	0.0031	0.50	50.0
0.5	Nil	0.0021	0.66	66.0
1.0	Nil	0.0022	0.64	64.5
2.0	Nil	0.0008	0.87	87.1

3.5 Adsorption isotherm

The adsorption mechanism of BOT in the presence of SDS on the metal surface was investigated. The adsorption isotherms such as Langmuir, Temkin and Frumkin isotherms were fitted with the surface coverage data values at different concentrations. BOT in the presence of SDS possess enhanced tendency to adsorb on the metal surface either individually or by forming aggregates.

The surfactant molecules function by tail-tail interactions leading to the formation of aggregates and headgroups facing the surface of the working electrode[15]. This phenomenon limits or quenches the availability of electrons, thus mitigating the electron transfer. The adsorption isotherms is described according to the following equation:

$$\text{Langmuir isotherm: } \frac{C}{\theta} = \frac{1}{K_{ads}} + C \text{ -----(2)}$$

Where K is the adsorption-desorption of BOT and SDS on metal surface, θ is surface coverage value, C is the concentration of the inhibitor SDS-BOT. The BOT in the presence of SDS surfactant

obeyed Langmuir adsorption model isotherm (Fig. 5), which indicates adsorption is finite, uniform throughout the metal surface and there are no vacant sites.

The standard free energy of adsorption ($-\Delta G_{ads}$) of SDS-BOT is calculated by using equation below:

$$K_{ads} = (1/55.5) \exp (-\Delta G_{ads}/RT) \text{ ----- (3)}$$

Terms for the above equation remain the same as reported in the literature. From the Table 4. It is evident that ($-\Delta G_{ads} = -8.12 \text{ kJmol}^{-1}$) is negative which confirms that the adsorption is spontaneous. The adsorption value is less than -20 kJ mol^{-1} which ratifies physisorption as the primary adsorption phenomenon at the metal/solution interface. Physisorption occurs due to electrostatic interaction between the metal surface and inhibitor molecules.

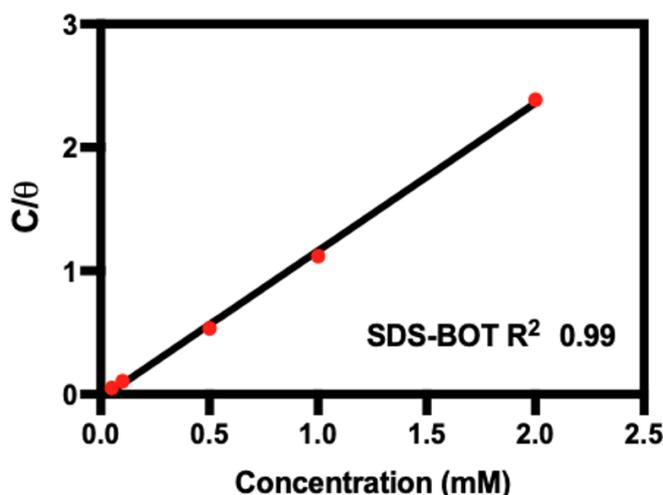


Figure 5. Langmuir fitted adsorption isotherm for SDS-BOT inhibitor in 2 M HCl solution at 298 K.

Table 4. Thermodynamic parameters obtained for BOT without and with SDS inhibitor at 298 K.

Inhibitor	$K_{ads} [M^{-1}]$	R^2	$E_a [kJ mol^{-1}]$	$-\Delta G_{ads} [kJmol^{-1}]$	Reference
BOT	3.4×10^3	0.98	28.76	-29.81	[11]
SDS-BOT	127.61×10^3	0.99	9.94	-8.12	Current work

3.6 Effect of Temperature

The effect of temperature on the adsorption of BOT in presence of SDS was studied in the range of 30 °C to 70 °C in both uninhibited and inhibited conditions. The corrosion rate gradually peaked with increase in the temperature due to disintegration of the adsorption layer formed on the metal surface. To understand the thermodynamic factors influencing the corrosion process, Arrhenius equation was used

to determine factors viz., enthalpy of adsorption, entropy of adsorption and energy of activation values. The linear plots were obtained from variation of temperature on corrosion rate. The data is given in below table 5 and plotted using the following Arrhenius equation.

$$k = A \text{Exp} \left(\frac{-E_a}{RT} \right) \text{----- (4)}$$

k is corrosion rate, ‘A’ is Arrhenius factor, E_a is energy of the activation, the activation energy obtained from the slope of the plots are shown in table 4. The values of E_a 9.94 kJ mol⁻¹ for SDS-BOT is much lower compared to BOT inhibitor of 28.76 kJ mol⁻¹, which imply that the corrosion inhibition is enhanced in the presence of the surfactant. Also, the adsorption is spontaneous and favored.

Table 5. Weight loss results of metal specimen in 2 M HCl solution in presence of SDS-BOT inhibitor at different temperatures.

		Temperature				
Medium		303 K	313 K	323 K	333 K	343 K
2M HCl	Weight loss(g)	0.0048	0.0061	0.0096	0.0126	0.0162
BOT-SDS	Weight loss (g)	0.0008	0.001	0.0011	0.0019	0.0029
	Corrosion rate (inches per year)	21.91	27.39	30.13	52.04	79.43

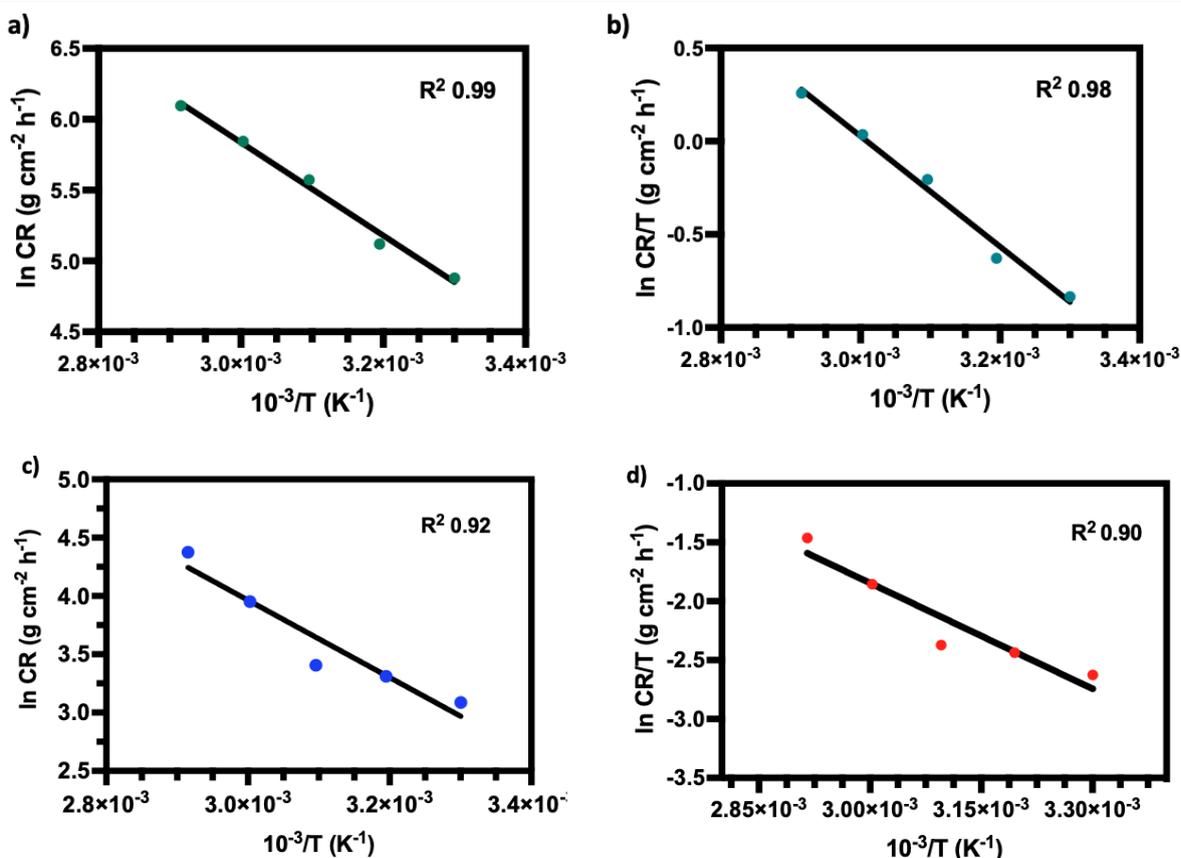


Figure 6. Arrhenius plots (a) and (c) represents ln CR vs 1/T of blank and SDS-BOT inhibitor respectively, (b) and (d) represents ln CR/T vs 1/T of blank and SDS-BOT respectively in 2 M HCl at different temperatures.

3.7 SEM Analysis

The morphological changes of mild steel under the acidic conditions are studied using SEM. The mild steel is exposed to acid electrolyte for a time period of 1 hr at 298 K. The below (Fig 7.a) shows polished metal surface [Fig. 7.b) and (7.c), 7.d), 7.e)] show metal surface under uninhibited and inhibited solution conditions. The presence of surfactant aids the mild steel to retain its smooth surface, whereas MS in presence of acid solution, loses its structural property by undergoing rapid corrosion leading to formation of pits and crevices. The use of BOT+SDS results in decrease of the surface tension, micellar formation at the interface of metal/solution. The inhibitor forms a protective layer on the metal surface blocking the active corrosion sites retarding the corrosion rate. Hence, in presence of BOT+SDS inhibitor, the inhibition efficiency is enhanced.

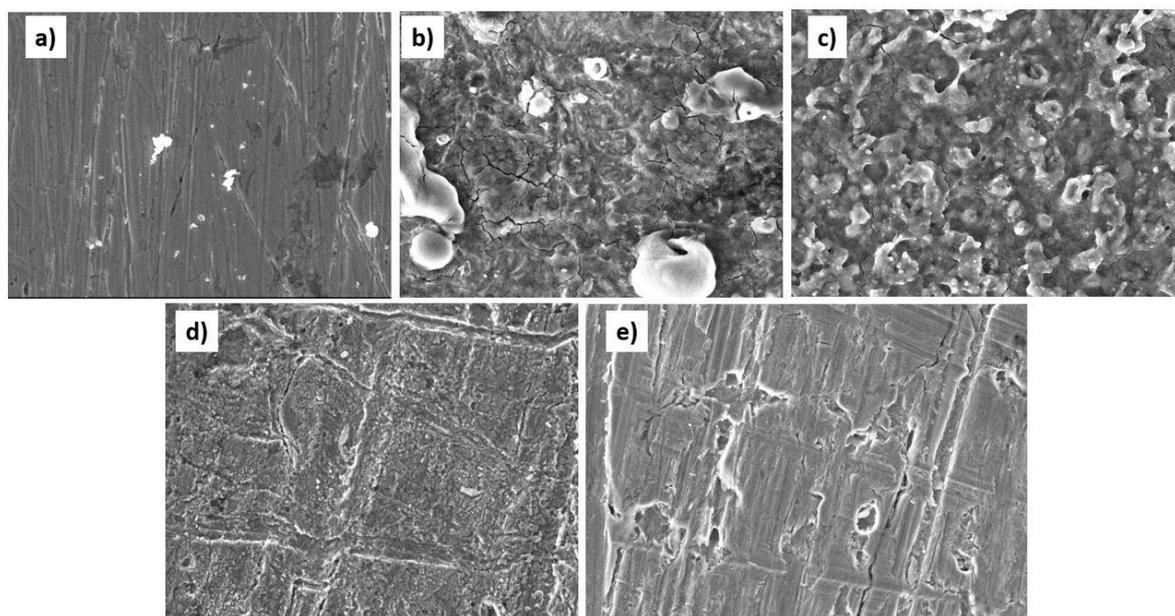


Figure 7. SEM micrographs representing corrosion inhibition a) Polished MS b) MS-2M HCl c) MS-2M HCl+SDS d) MS-BOT e) MS-BOT+SDS.

4. CONCLUSIONS

Primary conclusion of the study are as follows:

1. Synergistic effect of surfactant sodium do-decyl sulphate in combination with 2-thioureidobenzoxazole was evaluated using EIS, Tafel measurements, weight loss studies.
2. The combined inhibition performance of BOT and SDS was found to increase from 89% to 98%. This established the superior performance of BOT in the presence of SDS.

3. The SDS-BOT inhibitor functioned as anodic mixed-type inhibitor, which acts by forming micellar aggregates at the metal/solution interface.

4. Adsorption studies indicated that SDS-BOT obeyed Langmuir adsorption isotherm, with physisorption as the adsorption phenomenon.

5. The surface morphology studies further proved that although BOT retards corrosion. The presence of SDS surfactant enhances the inhibition efficiency. From the SEM micrographs it is evident that in presence of SDS-BOT the surface is far smoother compared to BOT inhibitor alone.

The above factors corroborate that SDS surfactant enhances the inhibition property of BOT, SDS acts as enhancer of corrosion inhibition.

CONFLICT OF INTEREST

There is no conflict of interest to report.

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SUPPLEMENTARY INFORMATION

S1. Synthesis of 2-Thioureidobenzoxazole [1]

A magnetically stirred suspension of isoperthiocyanic acid (0.01 mol) and 2-aminophenol (0.01mol) in 30 mL absolute alcohol was refluxed for 7-30 hours. Copious evolution of H₂S occurred after five minutes of heating. The reaction mixture was then cooled and poured into a china dish and the solvent was left to evaporate on a steam bath.

The leftover residue was extracted with 1N NaOH solution (3 × 20 mL) and the insolubles were then filtered. The filtrate was neutralised to pH 7 by adding 2N HCl solution. It was then cooled in an ice bath for two hours. The precipitate formed was filtered, washed with water and dried in vacuum at 80 °C. The compound was recrystallized using absolute alcohol and the yield of the compound was 80 % and the melting point was determined to be 195 °C.

S1.1 Characterization: 2- Thioureidobenzoxazole (BOT)

IR (KBr): 3345, 3240, 3170, 3120, 1620, 1600, 1575, 1450, 1230, 1060 and 740 cm⁻¹.

¹H NMR [DMSO]: 7.75 (4H, m), 8.73 (s, 1H; exchangeable with D₂O), 9.91 (s, 1H; exchangeable)

Mass m/z (% abundance): M 193 (43) 176 (3) 134 (100) 105 (10) 91 (11) 79 (23).

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