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Corrosion inhibition of mild steel in acidic medium by butyl alcohol

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Abstract The corrosive behavior of mild steel in 1 M H₂SO₄ solutions contaminated with 3.5 % recrystallized sodium chloride at specific concentrations of butyl alcohol was investigated using potentiodynamic polarization and weight loss technique. The results obtained showed butyl alcohol to be an efficient inhibitor in the acid environment with general decrease in corrosion rate as the concentration of the alcohol increases. The adsorption of the inhibitor on the mild steel obeys the Langmuir adsorption isotherm. The thermodynamic parameters of adsorption deduced reveal a mixed interaction with the steel surface and spontaneous adsorption of butyl alcohol.

Keywords Butyl alcohol · Sulfuric acid · Corrosion · Inhibitor

Introduction

The corrosion of metals remains a worldwide scientific problem as it affects the metallurgical, chemical, construction and oil industries. The increasing interest in the manufacture and use of sulfuric acid in applications involving the extensive use of mild steel has created the need for obtaining information on the corrosion resistance of mild steel to sulfuric acid attack. Sulfuric acid is a very important commodity chemical, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength [1]. Sulfuric acid is widely used in industries such as pickling, cleaning and descaling, industrial cleaning agent, production of chemicals, etc. Mild steel is used in these environments due to its easy availability, low cost and excellent physical properties, but its use and lifespan is restricted in

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these conditions due to its susceptibility towards corrosion. To complement its low cost and economic value, the most effective means of addressing the corrosion of mild steel is with the use of inhibitors, especially organic compounds. Though many compounds show good anticorrosive activity, most of them are highly toxic to both human beings and the environment. These toxic effects and ecological problems associated with the discharge of such materials have resulted in the development of other efficient and environmentally acceptable inhibitors. Hence, the recent trend is the search for environmentally friendly chemicals. Most natural products are non-toxic, bio-degradable and readily available in abundance for use in aggressive solutions in contact with the steel surface in order to inhibit the corrosion reaction and significantly influence the kinetics of the electrolytic process. A number of organic compounds [2–9] are known to be applicable as corrosion inhibitors for steel in acidic environments. Such compounds typically contain nitrogen, oxygen or sulfur in a conjugated system, and function via adsorption of the molecules on the metal surface, creating a barrier to corrosive attack [10]. This investigation aims to assess the inhibitive effect of butyl alcohol (BUT) on the electrochemical corrosion behavior of mild steel in dilute sulfuric acid chloride. BUT is a primary alcohol with a 4-carbon structure and the molecular formula of C_4H_9OH . It belongs to the higher and branched-chain alcohols without any record of harm to humans and the environment.

Experimental procedure

Material

The mild steel used for this work was obtained in the open market and analyzed at the Applied Microscopy and Triboelectrochemical Research Laboratory, Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, South Africa. The mild steel has the nominal per cent composition: 0.401C, 0.169Si, 0.440Mn, 0.005P, 0.012S, 0.080Cu, 0.008Ni, 0.025Al, 0.0114Ph, the rest being Fe.

Inhibitor

Butyl alcohol (BUT), a brownish, translucent liquid, is the inhibitor used. The structural formula of BUT is shown in Figs. 1 and 2. The molecular formula is C_4H_9OH while the molar mass is 74.122 g/mol.

BUT was prepared in various concentrations of 2.5, 5, 7.5, 10, 12.5, and 15 % which were used as the inhibiting compound.



Fig. 1 Chemical structure of butyl alcohol (BTU)

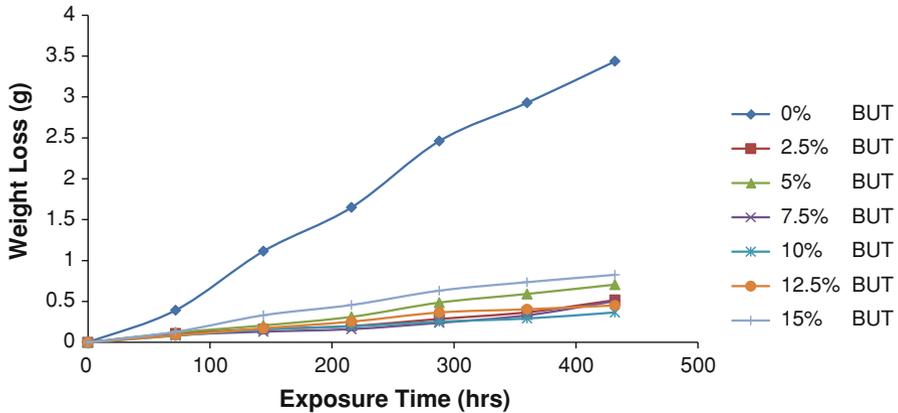


Fig. 2 Variation of weight-loss with exposure time for samples (A–G) in 0–15 % BUT concentrations

Test media

The test medium used for the investigation consists of 200 ml of 1 M dilute H_2SO_4 of Analar grade with 3.5 % recrystallized sodium chloride in addition to specified concentrations of BUT.

Preparation of test specimens

A cylindrical mild steel rod with a diameter of 14.5 mm was carefully machined and cut into a number of test specimens of average dimensions of length 6 mm. A 3-mm hole was drilled at the centre for suspension. These mild steel specimens were then thoroughly rinsed with distilled water and cleansed with acetone before analysis.

Weight-loss experiments

Weighed test pieces were totally immersed in each of the various prepared test media contained in a 200-ml plastic container for 432 h with and without inhibitor addition. They were taken out every 72 h, washed with distilled water, rinsed with acetone, dried and re-weighed. The tests without inhibitors were done for comparison with the tests in inhibited environments to observe the corrosion reactions behavior of the tested specimens. The corrosion rate (R) in millimeters per year was calculated from Eq. 1 below;

$$R = \left[\frac{87.6W}{DAT} \right] \quad (1)$$

where W is the weight loss in milligrams, D is the density in g/cm^3 , A is the area in cm^2 , and T is the time of exposure in hours. Curves of corrosion rate (calculated) versus time of immersion were also plotted.

The % inhibitor efficiency, P , was calculated from the relationship:

$$P = \left[\frac{W_1 - W_2}{W_1} \right] \times 100 \quad (2a)$$

where W_1 and W_2 are the corrosion rates in the absence and the presence, respectively, of a predetermined concentration of inhibitor. The percentage inhibitor efficiency was calculated for all the inhibitors throughout the exposure period.

The degree of surface coverage (θ) is calculated from Eq. 2b

$$\theta = \left[\frac{W_1 - W_2}{W_1} \right]. \quad (2b)$$

Linear polarization resistance

Linear polarization measurements were carried out using, a cylindrical coupon embedded in resin plastic mounts with exposed surface of 1.65 cm². The electrode was polished with different grades of silicon carbide paper, polished to 6 m, rinsed by distilled water and dried with acetone. The studies were performed at ambient temperature with Autolab PGSTAT 30 ECO CHIMIE potentiostat and electrode cell containing 200 ml of electrolyte, with and without inhibitor addition. A graphite rod was used as the auxiliary electrode and silver chloride electrode (Ag/AgCl) was used as the reference electrode. The steady state open circuit potential (OCP) was noted. The potentiodynamic studies were then made from -1.5 V versus OCP to $+1.5$ mV versus OCP at a scan rate of 0.002 V/s and the corrosion currents were registered. The corrosion current density (j_{corr}) and corrosion potential (E_{corr}) were determined from the Tafel plots of potential E (v) versus log current I . The corrosion rate (R) and the percentage inhibition efficiency (% IE) were calculated as follows:

$$R(\text{mm/yy}) = \frac{0.00327 i_{\text{corr}} \text{eq.wt}}{D} \quad (4)$$

Where i_{corr} is the current density in $\mu\text{A}/\text{cm}^2$, D is the density in g/cm^3 ; eq.wt is the specimen equivalent weight in grams;

The percentage inhibition efficiency (%IE) was calculated from corrosion current density values using the equation.

$$\%IE = 1 - \left[\frac{C_2}{C_1} \right] 100 \quad (5)$$

where C_1 and C_2 are the corrosion current densities in absence and presence of inhibitors, respectively.

Results and discussion

Weight-loss measurements

The weight-loss of mild steel was studied at various time intervals, in the absence and presence of stated concentrations of (BTU) in 1 M H₂SO₄ + 3.5 % NaCl at

25 °C. The values of weight-loss (W), corrosion rate (R) and the percentage inhibition efficiency (%IE) are presented in Table 1. The corrosion rate decreased drastically with the application of BUT due to the interaction of inhibitor molecules with the steel surface. Observation of Table 1 shows the influence of the inhibitor to be independent of the value inhibitor concentration as the results of the electrochemical kinetics were slightly similar. The weight-loss measurements are not linearly proportional to the value of BUT concentration most probably due to formation of a protective film which prevents the diffusion of the harmful anions onto the steel irrespective of its concentration.

Figures 2, 3 and 4 show the variation of weight-loss, corrosion rate and %IE with exposure time at the various BUT concentrations, while Fig. 5 shows the variation of %IE with inhibitor concentration. The curves obtained indicate similar electrochemical reactions with the addition of BUT. The variations are almost insignificant as there was generally minimal change in corrosion rate and inhibition efficiency with increase in concentration of BUT.

Polarization studies

The potential was scanned from -1.50 to 1.50 V versus Ag/AgCl at a rate of 0.002 V/s, which allows for quasi-stationary state measurements. The inhibitive effect of the addition of BUT on the potentiodynamic corrosion behavior of mild steel in the acid chloride solution was studied. Figure 6 a, b shows the polarization curves of mild steel in absence and presence of BUT concentrations. Anodic and cathodic reactions were inhibited effectively with increasing concentrations of the inhibitor. BUT appeared to act as mixed type inhibitor since anodic (metal dissolution) and oxygen reduction reactions were significantly influenced by its presence in the corrosive medium. All scans exhibited slightly similar polarization behavior over the potential domain examined, indicating that similar electrochemical reactions took place on the metal. The electrochemical parameters, such as corrosion potential (E_{corr}), corrosion current (i_{corr}), corrosion current density (I_{corr}), cathodic Tafel constant (bc), anodic Tafel slope (ba) and percentage inhibition

Table 1 Data obtained from weight loss measurements for austenitic stainless steel in 1 M H_2SO_4 in presence of specified concentrations of the BUT at 432 h

Sample	Weight loss (g)	Corrosion rate (mm/yy)	Molarity (M)	Inhibitor concentration (%)	Inhibition efficiency (%)	Surface coverage (θ)
A	3.436	22.04	0	0	0	0
B	0.517	2.23	0.00034	2.5	85.0	0.8495
C	0.706	2.95	0.00068	5	79.5	0.7945
D	0.505	2.38	0.00101	7.5	85.3	0.8530
E	0.366	1.53	0.00135	10	89.4	0.8935
F	0.452	2.25	0.00169	12.5	86.9	0.8685
G	0.826	4.23	0.00202	15	76.0	0.7596

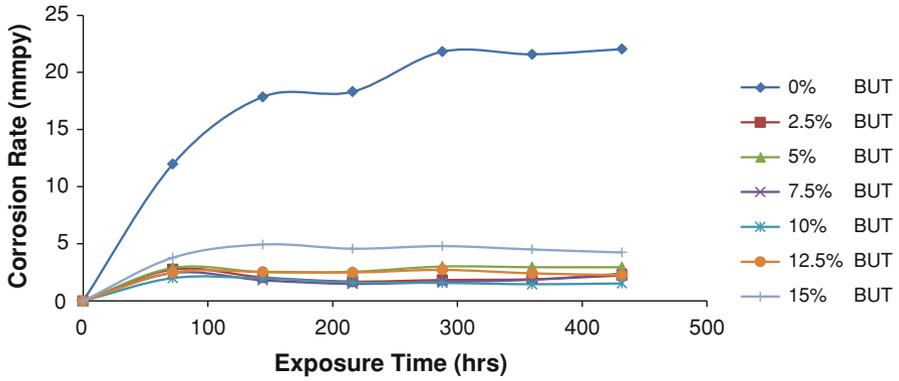


Fig. 3 Effect of percentage concentration of BUT on the corrosion rate of austenitic stainless steel

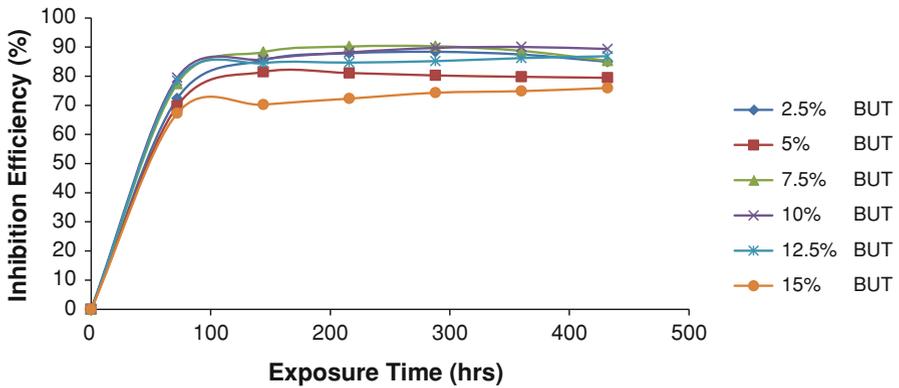


Fig. 4 Variation of inhibition efficiencies with exposure time for samples (A–G)

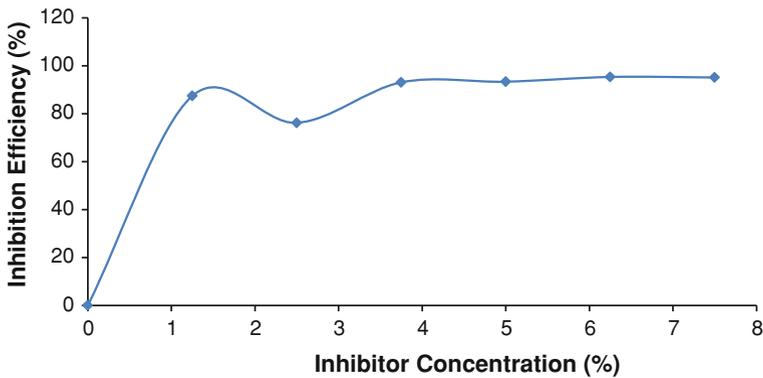


Fig. 5 Variation of % IE percentage inhibition efficiency with BUT at concentrations at 432 h

efficiency (%IE), were calculated and are given in Table 2. The values of %IE, corrosion rate and corrosion current density reduced drastically but varied slightly with the addition of BUT at different concentrations. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were determined by the intersection of the extrapolating anodic and cathodic Tafel lines; % IE was calculated from Eq. 6

$$\% \text{ IE} = \frac{\text{CR1} - \text{CR2}}{\text{CR1}} \% \quad (6)$$

As shown from Table 2, there is a strong inhibition effect of the BUT at higher concentrations. With the increase of BUT concentration, both anodic and cathodic currents were inhibited, but the reduction of anodic currents was slightly more significant than that of cathodic currents. A compound can be classified as an anodic- or a cathodic-type inhibitor on the basis of shift in E_{corr} value. If displacement in E_{corr} is greater than 85 mV towards anode or cathode with reference to blank, then an inhibitor is categorized as either anodic- or cathodic-type inhibitor. Otherwise, the inhibitor is treated as mixed type [11, 12]. In this investigation, maximum displacement in E_{corr} value was around 30 mV indicating that the inhibitor is a mixed type inhibitor. The inhibitor molecules are first absorbed onto the mild steel surface and therefore impede corrosion by merely blocking the reaction sites of the mild steel surface. In this way, the surface area available for H^+ ion reduction is decreased while the actual reaction mechanism remains unaffected. A higher coverage of the inhibitor on the surface was obtained in solutions with higher inhibitor concentration. The formation of surface inhibitor film on the mild steel surface provides consideration protection to the mild steel against corrosion. This film reduces the active surface area exposed to the corrosive medium and delays the hydrogen evolution and iron dissolution.

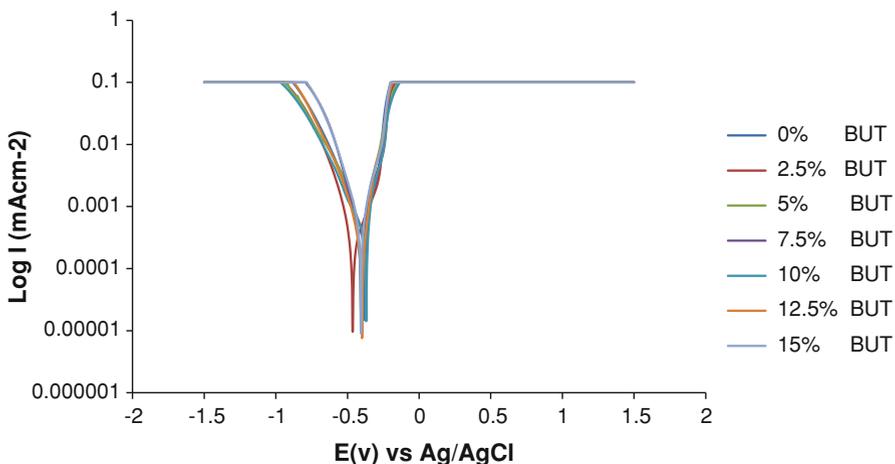


Fig. 6 Comparison plot of linear polarization scans for mild steel in 1 M H_2SO_4 + 3.5 % NaCl solution in the absence and presence of 0–15 % BUT at ambient temperature

Table 2 Data obtained from polarization resistance measurements for mild steel in 1M H₂SO₄ + 3.5 % NaCl in presence of different concentrations of the BUT

Sample	Inhibitor concentration (%)	ba (V/dec)	bc (V/dec)	$E_{\text{corr, obs}}$ (V)	j_{corr} (A/cm ²)	i_{corr} (A)	Corrosion rate (mm/year)	Polarization resistance (Ω)	Inhibition efficiency (IE %)
A	0	0.263930	0.077079	-0.37759	6.73E-04	1.11E-03	7.823	23.32	0
B	2.5	0.057517	0.081147	-0.40357	6.63E-05	1.09E-04	0.770	133.65	90.2
C	5	0.040919	0.045165	-0.40673	8.02E-05	1.32E-04	0.931	70.49	88.0
D	7.5	0.043093	0.049484	-0.40518	5.91E-05	9.75E-05	0.687	102.59	91.2
E	10	0.033804	0.026674	-0.36888	4.49E-05	7.40E-05	0.521	87.46	93.3
F	12.5	0.030828	0.088841	-0.39814	6.32E-05	1.04E-04	0.735	95.28	90.6
G	15	0.056160	0.102250	-0.40578	4.84E-04	1.33E-04	1.459	74.79	81.4

The observed phenomenon is generally described as the corrosion inhibition of the metal with the formation of a protective layer of adsorbed species at the metal surface. It is clear from the linear polarization plots that both the anodic and cathodic current values were considerably higher in uninhibited acid chloride due to excess dissolution of iron. It is evident that the corrosion current density of mild steel in BUT is considerably smaller than in the uninhibited solution and the corrosion potential shifts in the anodic direction [13–15].

Mechanism of inhibition

In the presence of BUT, corrosion is inhibited by adsorption of the organic molecules on the metal surface. Protection by BUT alcohol is generally enhanced by the presence of iron ions. This is explained by the participation of iron ions in the condensation and polymerization reactions leading to the production of surface films [16]. Alcohol protonizes in an acid environment to form $R-OH^+$ type species owing to the existence of the negative zero charge potential of iron in hydrochloric acid. The adsorption of protonated alcohol molecules on the metal surface takes place resulting in corrosion inhibition [17].

For an inhibitor to have a high coverage on the surface, a chemical bond between the inhibitor and the metal atom stronger than the one for water molecules should be formed. The adsorption of corrosion inhibitors at the metal/solution interface is due to the formation of either electrostatic or covalent bonding between the adsorbates and the metal surface atoms. To form strong electrostatic bonding, if the corrosion potential is not at the point zero charge (pzc), the inhibitor should either carry a charge of the proper sign or have a large dipole moment. For iron in acid solutions, the electrode is positively charged at the corrosion potential. Thus, an inhibitor with a negative charge is preferred. Alcohols protonize in acid environments to form $R-OH^+$ -type species. Owing to existence of negative zero charge potential of iron in acidic solution, the adsorption of protonized alcohol molecules on the metal surface takes place resulting in corrosion inhibition. Furthermore, because of the large dipole moment of water (1.8 D), an inhibitor relying on electrostatic bonding is usually not strong enough to be a good inhibitor for iron, and a covalent bonding should be involved. In order to form strong and effective covalent bonds between the surface metal atoms and the adsorbate, the energy levels of the donor's filled orbitals and the acceptor's empty orbitals, as well as their symmetry, should match.

To determine the inhibiting properties and the behavior of the BUT molecules adsorbed on the metallic surfaces, it is preferable to suppose that physiochemical reaction is responsible for the main inhibiting effect. Thus, they are good inhibitors for iron. Furthermore, it is well known that iron corrosion inhibition by organic compounds, particularly these presenting π -bonding, is favored whenever a strong adsorption process takes place on the metal surface [18]. The single bond of a BUT can be considered to be the active center for adsorption of the molecule onto the metal surface. The π -electrons of the single bond form a chemical type of bond with d-orbitals of the transition metals, which results in the inhibition of corrosion reaction. As a parallel view, it can be said that BUT also has good inhibition efficiency for mild steel in 1M H_2SO_4 .

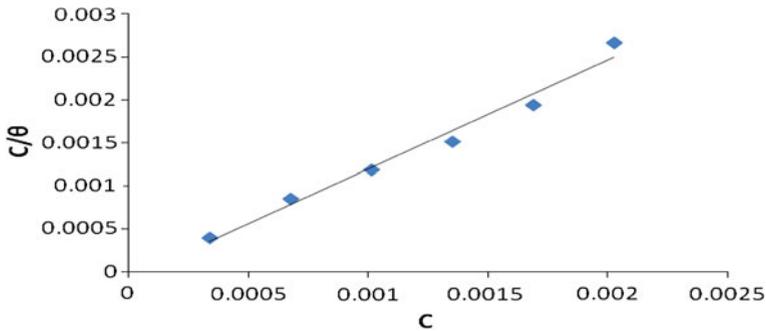


Fig. 7 Relationship between $\frac{C}{\theta}$ and inhibitor concentration C

Adsorption isotherm

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals and alloys has been deduced in terms of adsorption characteristics of the inhibitor. The adsorption behavior of the inhibitor molecules on the metal surface can be applied to explain the inhibition mechanism of inhibitors [19, 20]. Several adsorption isotherms can be used to assess the adsorption behavior of the inhibitors. The Langmuir adsorption isotherm was found to be the best description of the adsorption behavior of BUT on the mild steel surface, which obeys the following equation [21, 22].

$$\theta = \frac{KC}{1 + KC} \quad (7)$$

where C is the inhibitor concentration, K is the adsorption equilibrium constant, and Θ the surface coverage of the inhibitor. The linear relationship of C/θ versus C in different concentration BUT solutions is displayed in Fig. 7.

Generally, two modes of adsorption are considered. The process of physical adsorption requires the presence of an electrically charged metal surface and charged species in the bulk solution. Chemisorption process involves charge sharing or charge transfer from the inhibitor molecule to the metal surface. This is possible in the case of positive charges as well as negative charges on the metal surface. The presence of a transition metal having vacant low energy electron orbital and an inhibitor molecule having relatively loose bound electrons or hetero atoms with a lone pair of electrons facilitates this adsorption. On the other hand, the BUT containing oxygen atoms in its structure can readily accept protons to form positively charged ions. These ions can be adsorbed by the metal surface because of attractive forces between the positively charged ions and the negatively charged metals [23, 24, 25].

The deviation of the slopes from unity is attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation. The Langmuir isotherm assumes that:

- (i) The metal surface contains a fixed number of adsorption sites and each site holds one adsorbate.

Table 3 Data obtained for the values of Gibbs free energy, surface coverage and equilibrium constant of adsorption at varying concentrations (M) of BUT

Sample	Molarity	Equilibrium constant of adsorption (K)	Free energy of adsorption (ΔG)	Surface coverage (θ)
A	0	0	0	0
B	0.00034	16753.8	-34064	0.8495
C	0.00068	5728.67	-31382	0.7945
D	0.00101	5735.14	-31382	0.8530
E	0.00135	6217.92	-31610	0.8935
F	0.00169	3913.32	-30469	0.8685
G	0.00202	1561.17	-28187	0.7596

- (ii) ΔG_{ads} is the same for all sites and it is independent of θ .
 (iii) The adsorbates do not interact with one another, i.e. there is no effect of lateral interaction of the adsorbates on ΔG_{ads} [26].

The large negative value for Δ_{ads} suggests that the inhibitor is spontaneously adsorbed on the mild steel surface by strong interaction between the inhibitor molecules and the steel surface [27]. It has been reported that the Δ_{ads} value up to -20 kJ mol^{-1} or lower indicates a physical adsorption, while a value more negative than -40 kJ/mol involves sharing or transfer of electron from the inhibitor molecules to the metal surface to form a coordinate type bond (chemisorption) [28]. As can be seen from Table 3, the values of Δ_{ads} vary between (28–34) kJ/mol, indicating that the adsorption of inhibitor on mild steel surface is typically physiochemical. The high value of K_{ads} reveals that the BUT molecule possesses strong adsorption ability onto the mild steel surface.

Conclusion

1. The potentiodynamic polarization resistance and weight loss technique reveals BUT to be an efficient inhibitor for mild steel in the sulfuric acid/chloride medium.
2. The inhibition efficiency increases with the increase in concentration of BUT with maximum inhibition at 15 %.
3. This is a mixed type inhibitor whose adsorption is on mild steel is physiochemical.
4. It mainly acts by film formation, thus blocking the active sites on the cathodic and anodic regions.
5. The adsorption of this inhibitor obeys Langmuir's adsorption isotherm.

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