



Evaluation of corrosion inhibition of carbon steel in 0.25M H₂SO₄

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ABSTRACT

The effect of sodium diethyl dithiocarbamate trihydrate (NaDDCT) on the corrosion of carbon steel in O₂-saturated 0.25M H₂SO₄ solutions have been studied using the open circuit potential (OCP) and potentiodynamic polarization (PDP) techniques. The results of open circuit potential showed that slightly shifts toward positive direction with increasing the concentration of NaDDCT inhibitor due to form a layer protected film on the carbon steel surface. The potentiodynamic polarization (PDP) results referred to the NaDDCT as a good inhibitor in O₂ - saturated acidic medium as well acts as a mixed-type inhibitor. The inhibition efficiency increases with increasing of concentration of NaDDCT to exceeds 96.55%. The adsorption of the NaDDCT inhibitor on the electrode surface is well depended to on the Langmuir adsorption isotherm. The ΔG_{ads} values indicated that the adsorption of NaDDCT on the surface of carbon steel spontaneously.

Keywords: carbon steel, O₂ gas, NaDDCT, corrosion inhibition, sulfuric acid

INTRODUCTION

The carbon steel in the petroleum industry is the most common material that is used in piping and tank in both the downstream and upstream is domain due its relatively low cost and high behavior compared with higher alloyed materials. The corrosion impedance of the carbon steel in O₂ free aqueous solutions is depended to the surface layer that consists of the carbon steel. This layer commonly consists of siderite (FeCO₃) and cementite (Fe₃C); however these deposits are nor dense neither compact [1]. The carbon steel of corrosion is a problem in petroleum industries that attracted the attention of researchers. In some industrial processes such as etching, cleaning with acid, and pickling using aggressive media such as acids, bases, and salts, leads to corrode the steel. A number of ways such as material cathodic or anodic protection, selection, coatings and the use of corrosion inhibitors have been used to inhibit corrosion of the installation industry [2-5]. Organic compounds are most active inhibitors because of containing electronegative functional groups and pi- electrons in double or triple bonds [6-9]. The organic compounds also have heteroatoms (such as N, P, O, and S) [10-12]. The effect of such organic compounds on the corrosion of carbon steel in acidic solution has been investigated by several researchers [13-15]. The aim of this work to investigate the NaDDCT inhibitor on the corrosion behavior of the carbon steel in 0.25M H₂SO₄ solutions by using electrochemical methods.

EXPERIMENTAL SECTION

2.1. Materials and solutions

The carbon steel alloys were used as working electrode to investigate the corrosion inhibition in oxygenated acidic solution at constant temperature 298.15K in the absence and presence of sodium diethyl dithiocarbamate trihydrate (NaDDCT) inhibitor. The chemical compositions of carbon steel by Optical Emission Spectroscopy (PMI MASTER Pro Oxford UK) were shown in Table(1) that taken from Iraq's oil fields. The samples were cut to dimensions (1cm x 1cm) and thickness (1cm). The samples polished to mirror finish, using emery paper following by aqueous alumina suspensions to become surface soft. After that, cleaned by hot benzene and acetone with double distilled water and finally dried.

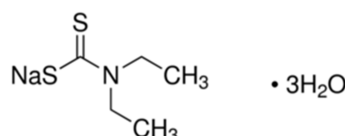
Table (1): Chemical composition of carbon steel by Optical Emission Spectroscopy

Elements	C	Si	Mn	Cr	Mo	Ni	Cu	Fe
Wt.%	2.18	3.10	1.36	0.102	0.127	0.213	0.596	Balance

The working steel specimen cut from cylindrical rods of carbon steel was covered with epoxy, so that its cross-sectional area, 1cm, was in contact with the solution. Experiments were carried out at constant temperature 298.15K by using a calibrated thermostat bath circulator from HYSC company. The solutions for all the experiments were prepared freshly with double distilled water, in sulphuric acid (which obtained from Scharlau company). 0.25M H₂SO₄ solutions were prepared by dilution of an analytical reagent grade 97% H₂SO₄ with distilled water.

2.2. Corrosion Inhibition Study

In order to study the inhibitive action of sodium diethyl dithiocarbamatetrihydrate (NaDDCT) as inhibitor (which supplied from SIGMA-ALDRICH Company) towards the corrosion of carbon steel in acidic solutions, experiments were carried out in 0.25M H₂SO₄ in absence and the presence of NaDDCT inhibitor in various concentration 1×10^{-3} M to 3×10^{-3} M at 298.15K. The chemical structure of the investigated compound is given Figure (1).

**Figure (1): The chemical structure of sodium diethyl dithiocarbamatetrihydrate**

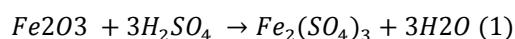
2.3. Electrochemical measurement

For the electrochemical measurement used a conventional five necks Pyrex glass cell, three-electrodes, including a working electrode (carbon steel), a platinum electrode as an auxiliary and Saturated Calomel electrode (Hg | Hg₂Cl_{2(s)} | KCl) as a reference. While, two necks, one to enter the gas and the other to get out oxygen gas (purity 99.99%). The working electrodes were made of carbon steel which was holder using epoxy resin with a square surface of 1cm². The auxiliary electrode was a platinum foil and coating by black platinum in all the experiments to increase a large surface area and high catalytic activity, The saturated Calomel electrode with a fine Luggin capillary tube positioned close to the working electrode surface in order to minimize Ohmic potential drop (IR). After that, The working electrode, Platinum auxiliary electrode and reference electrode with a fine Luggin capillary immersed in the test solution and connected by Potentiostat/Galvanostat for measurement the open circuit potential (OCP) and the potentiodynamic, After that, using an Echem Analyst (version 6.23) to obtain the electrochemical parameters for Tafel polarization curves at a polarizing value ± 100 mV with respect to the free corrosion potential.

RESULTS AND DISCUSSION

3.1- Open circuit potential

Figure 2 shows the potential of carbon steel immersed in O₂ – saturated 0.25M H₂SO₄ solution was measured as a function of time in the absence and presence of (1×10^{-4} to 3×10^{-3} M) of NaDDCT inhibitor. Open circuit potential measurements apparent from Figure(2) that the open circuit potential of 0.25M H₂SO₄ in the absence of the inhibitor decreases with time and the end of reaches a steady state value at (10 min). In without of addition of sodium diethyldithiocarbamatetrihydrate inhibitor, the potential at steady state (E_{ocp} at $t = \text{steady state}$) become more negative than the immersion potential (E_{ocp} at $t = 0$), suggests that before the steady-state condition is investigated; which represents the dissolve pre-immersion air formed oxide film the presence on the carbon steel surface according to the following equation(1)[16].



At low concentration of inhibitor shifts values of the steady state potential towards noble direction (positive direction) values and without changing in the E–t curves features and the shifts become more by increasing of NaDDCT concentration. The noble shifts for the open circuit potential enhanced the formation of a protective layer of the NaDDC inhibitor on the carbon steel surface [17]. These results may indication to the formation of a stable Fe(II)-complexes with the sulfur atom as ligands in the (NaDDCT) molecule [18].

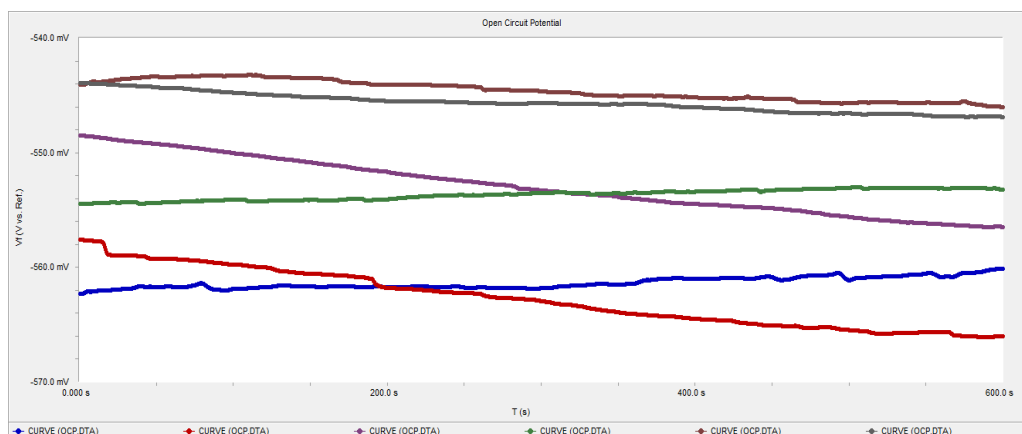


Figure (2): Show the open circuit potential (OCP) for the carbon steel in O_2 – saturated $0.25M H_2SO_4$ solution in the presence of the various concentration ($0 M, 1 \times 10^{-4} M, 3 \times 10^{-4} M, 6 \times 10^{-4} M, 1 \times 10^{-3} M$ and $3 \times 10^{-3} M$) of NaDDCT at $298.15K$

3.2- Potentiodynamic Polarization Curve

Potentiodynamic polarization curves of the cathodic and the anodic for the carbon steel surface recorded at scan rate $0.5mVs^{-1}$ in O_2 – saturated $0.25M H_2SO_4$ solution and the presence of different concentration of NaDDCT inhibitor at $298.15K$ are given in Figure 3. The increasing of the NaDDCT concentration inhibitor decreases both the anodic and the cathodic corrosion current density with reducing of current density values. Thus, the decrease in the corrosion current density suggested the inhibitive action of NaDDCT. Electrochemical parameters such as the corrosion current density (i_{corr}), corrosion potential (E_{corr}), the anodic Tafel constant (β_a) and the Cathodic Tafel constant (β_c) were calculated from Tafel plots and shown in Tables 2.

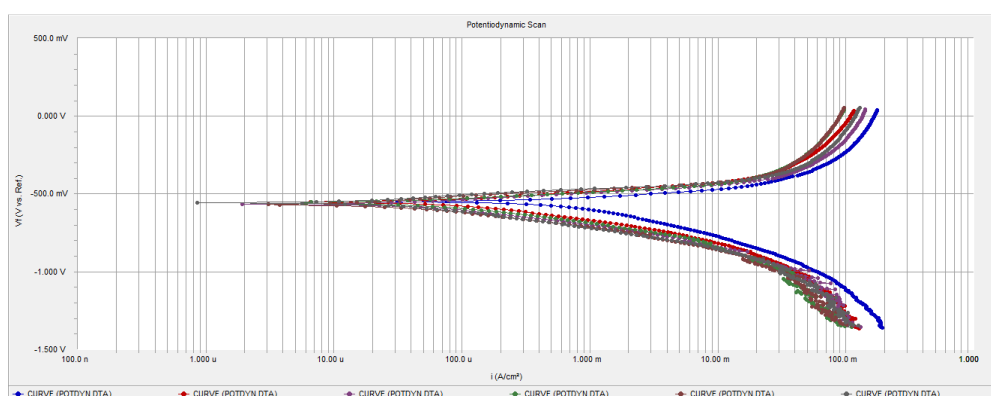


Figure (3): Shows potentiodynamic polarization curves for carbon steel in O_2 – saturated of $0.25M H_2SO_4$ in the absence and presence of different concentration of NaDDCT inhibitor ($0M, 1 \times 10^{-4}M, 3 \times 10^{-4}M, 6 \times 10^{-4}M, 1 \times 10^{-3}M$ and $3 \times 10^{-3}M$) at $298.15 K$

Table (2): Shows the kinetic parameter for carbon steel in O_2 – saturated of $0.25M H_2SO_4$ and the absence and presence of different concentration of NaDDCT inhibitor at $298.15 K$

Conc. Inh. (M)	i_{corr} (μAcm^{-2})	E_{corr} (mV)	β_a (mV/decade)	β_c (mV/decade)
0	374.0	-549.0	54.30	127.7
1×10^{-4}	48.30	-552.0	52.20	82.80
3×10^{-4}	41.10	-567.0	57.30	98.30
6×10^{-4}	34.40	-556.0	46.20	80.60
1×10^{-3}	26.90	-568.0	81.20	98.40
3×10^{-3}	12.90	-558.0	51.90	64.20

The results in a table(2) show that in the presence of NaDDC inhibitor, the value of corrosion current density (i_{corr}) was decreased. These behaviors prove its ability to inhibit the corrosion of the carbon steel in O_2 - saturated $0.25M H_2SO_4$ solution. The corrosion current densities were decreased as shown in Figure 4, indicating that the NaDDCT inhibitor inhibits both the anodic and cathodic reactions through adsorption on the carbon steel surface [19]. Whereas, changes in values Tafel slope anodic Tafel constants (β_a) and cathodic Tafel constant (β_c) upon addition of NaDDCT inhibitor which indicates that NaDDCT inhibitor is adsorbed at both anodic and cathodic sites [20]. The corrosion potential shift small in the range of $-568mV$ around the corrosion potential of $-549mV$ and this shift towards the positive direction (noble direction) in Table 2. These results show that the addition of NaDDCT

compound inhibited of iron oxidation and in a lower extent hydrogen evolution, consequently these of NaDDCT compounds can be classified as mixed – type corrosion inhibitors [21].

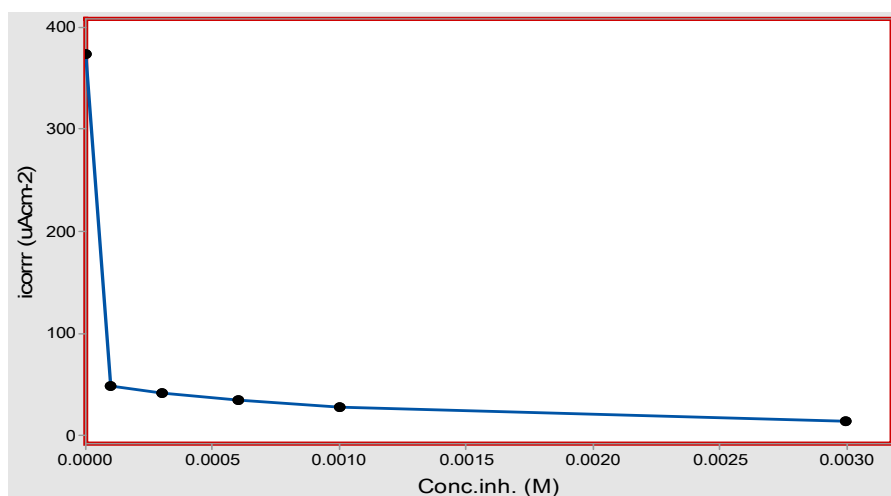


Figure (4): Shows decrease i_{corr} with increasing of NaDDCT concentration

The surface coverage (θ) and inhibition efficiency were calculated as [22]:

$$\theta = \left(\frac{i_{corr.uninh.} - i_{corr.inh.}}{i_{corr.uninh.}} \right) \quad (2)$$

$$IE = \theta \times 100 \quad (3)$$

Where, $i_{corr.uninh.}$ and $i_{corr.inh.}$ represents absence and presence inhibitors respectively, are given in table 3.

From data in Table, 3 shows decrease the corrosion rate and increase the inhibition efficiency (%IE) and the fractional surface coverage (θ) as in shown figure 5 and 6. This behavior indicates that the NaDDCT inhibitor adsorbed on the carbon steel surface [23].

Table 3: Shows corrosion rate, inhibition efficiency, and surface coverage degree for carbon steel in O_2 – saturated of 0.25M H_2SO_4 in the presence and absence of different concentration of NaDDC inhibitor at 298.15 K

	Corrosion Rate(mpy)	%IE	θ
0	138.8	---	---
1×10^{-4}	17.93	87.08	0.87
3×10^{-4}	15.25	89.01	0.89
6×10^{-4}	12.78	90.80	0.90
1×10^{-3}	9.973	92.80	0.92
3×10^{-3}	4.777	96.55	0.96

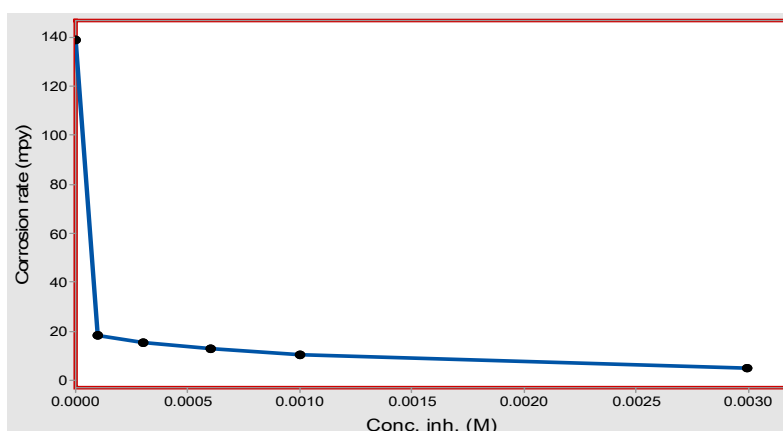


Figure (5): Shows the relationship between the corrosion rate and the NaDDCT concentration

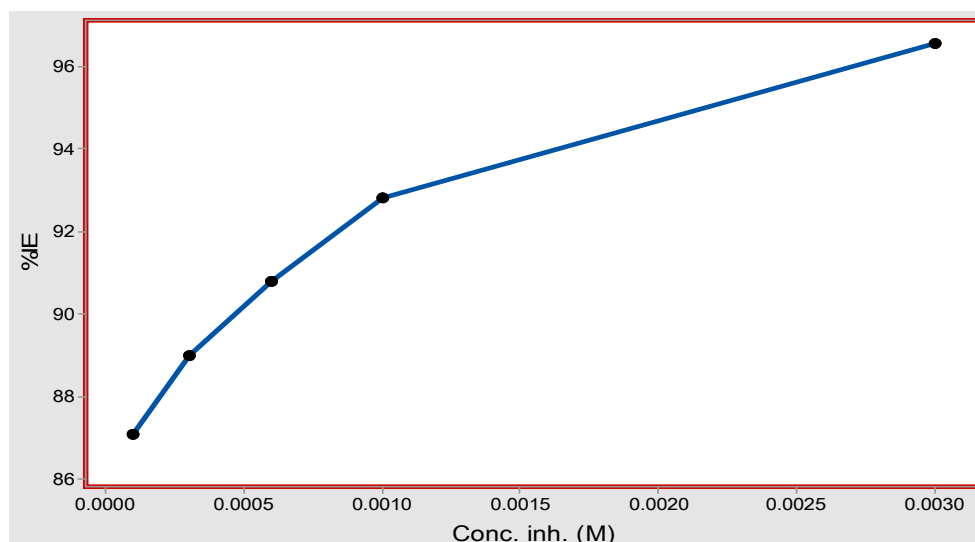


Figure (6): Shows the relationship between the inhibition efficiency and NaDDCT concentration

3.3- ADSORPTION ISOTHERM

It is generally assumed that the adsorption of the inhibitors on the metal surface is an essential step in the inhibition mechanism [24]. Several adsorption isotherms were assessed and the Langmuir adsorption isotherm was found to be the best description of the adsorption behavior of the studied inhibitor, which obeys to [25-28]:

$$\frac{C_{inh.}}{\theta} = \frac{1}{K_{ads}} + C_{inh.} \quad (4)$$

$$\Delta G^{\circ}_{ads} = -RT \ln(55.5K_{ads}) \quad (5)$$

Where K_{ads} the equilibrium constant of the adsorption reaction and $C_{inh.}$ is the inhibitor concentration in the bulk of the solution and the standard adsorption free energy (ΔG_{ads}), R is the gas constant ($8.314 \text{ kJ mol}^{-1}$) and T is the temperature in Kelvin (298.15K). 55.5 is the concentration of water in solution in mol L^{-1} . Plots of $C_{inh.}/\theta$ versus $C_{inh.}$ yielded a straight line as shown in Figure 7, the intercept is represent $1/K_{ads}$ and give in table 4. The calculation the standard adsorption free energy (ΔG_{ads}) from equation (4) and give in table 4.

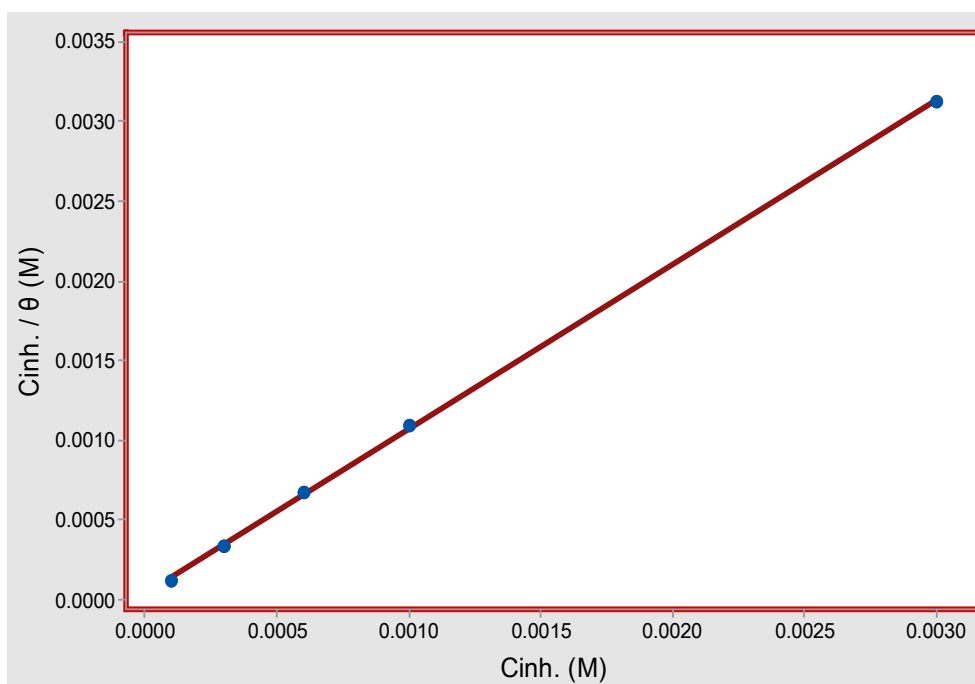


Figure (7): Langmuir isotherm adsorption model of NaDDCT on the surface of carbon steel in 0.25M H_2SO_4

Table (4): shows the Langmuir isotherm parameters of inhibitors on carbon steel surface in 0.25 M H₂SO₄ solutions

R ²	Slope	Intercept	K _{ads}	-ΔG(KJ mol ⁻¹)
1.000	1.034	0.000032	31250	35.61

The slopes close to 1.034 and the linear correlation coefficients(R) are close to 1, as shown in Table 4, indicating that the adsorption of the NaDDCT inhibitor on the carbon steel surfaces is well depended to the Langmuir adsorption isotherm [29]. The relatively high value of the adsorption equilibrium constant (K_{ads}) in Table 4 shows the high adsorption ability of NaDDCT inhibitor on the carbon steel surface [30]. K_{ads} large values of implying more efficient adsorption hence better inhibition efficiency [31]. The ΔG_{ads} negative values indication of adsorption of NaDDCT on the carbon steel surface is spontaneous. Generally, the values of ΔG_{ads} to (-20 kJ mol⁻¹) are consistent with the electrostatic interaction between the charged metal and the charged molecules (physical adsorption) while those more negative than (-40 kJ mol⁻¹) involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorptions) and ΔG_{ads} values between 20 and 40 KJ mol⁻¹ are mixed - adsorption [32]. In the present study, the ΔG_{ads} values obtained for NaDDCT on carbon steel in O₂-saturated 0.25M H₂SO₄ solution are -35.61KJ mol⁻¹. This indicates that the adsorption of studied inhibitors is mixed- typical (physical and chemisorption adsorption).

3.4- Mechanism of inhibition

The results which obtained from electrochemical measurements concluded that the (NaDDCT) inhibit the corrosion process of carbon steel in 0.25M H₂SO₄. As shown in Figure 1 which explained NaDDCT structure, contain nitrogen group (N) and C=S bond. It is general assumption that the adsorption of NaDDCT molecules may adsorb on the carbon steel surface by 4 types [33, 34].

1. Electrostatic interaction between the charged of Na⁺ - DDCT molecules and the charged of Fe²⁺ on the carbon steel surfaces.
2. Interaction of unshared electron pairs (N, S) in the NaDDCT molecule inhibitor with d-orbitals on the carbon steel surface by coordination bonds, form Fe (II) complexes.
3. Interaction of π - electron pairs for C=S bonds with the carbon steel surface.
4. A combination of step 1 and step 3.

CONCLUSIONS

The changed in the OCP values to noble direction explained formation a protective layer from NaDDCT inhibitor on the carbon steel surface. The results from potentiodynamic polarization (PDP) indicated that NaDDCT as a good inhibitor in acidic medium. Thus, the potentiodynamic polarization results showed that NaDDCT as a mixed-type inhibitor due to inhibiting both anodic metal dissolution and also cathodic hydrogen evolution reactions. The inhibition efficiency increases with increasing the concentration of NaDDCT. The adsorption of the NaDDCT inhibitor on the carbon steel surfaces is well dependent to the Langmuir adsorption isotherm. The higher values of the equilibrium constant (K_{ads}) indicated higher adsorption of the NaDDCT on the carbon steel surface. The negative value of ΔG_{ads} indicates spontaneity in the NaDDCT adsorption on the carbon steel surface and the adsorption type is mixed – adsorption type (physical and chemisorption).

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