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# Assessment of electrochemical behaviour for X65-steel: part A: OCP and PDP

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**Abstract** : The adsorption of sodium diethyl dithiocarbamatetrihydrate (NaDDCT) and 3,6diamino-10-methylacridin-10-ium chloride (DAMAC) inhibitors on X65-steel in 0.05M  $H_2SO_4$  is investigated using electrochemical techniques. The polarization curves and the open circuit potential results obtained indicate that NaDDCT and DAMAC compounds behave as mixed type inhibitors. The results show the efficiency of corrosion inhibition increases with corrosion inhibitor concentration and also as a function of the structure of the inhibitor. The adsorption isotherms are found to obey Langmuir's adsorption isotherm with high correlation values. The effect of temperature is studied on the corrosion rate in the presence of  $1 \times 10^{-3}$ M of NaDDCT and DAMAC inhibitors over the temperature range 298.15K to 318.15K and the activation energy value, adsorption equilibrium constant and free Gibbs energy of adsorption of corrosion inhibitor for X65-steel.

**Keywords :** Corrosion inhibition, X65-steel, corrosion, open circuit potential, inhibitors, Langmuir adsorption.

# Introduction

Generally, steel alloys are important materials, which are commonly used in many day-to-day applications<sup>1</sup>. These metals and alloys are characterized by high mechanical characteristics and their susceptibility to be joined easily using welding techniques. As they are characterized by especially high toughness and resistance to extreme stress, they are commonly used for pipes, pumps, tanks and other similar applications  $^{1-3}$ . The use of X -65 steel is commonplace, partly because of its low cost compared to the top leading steels. The major problem, which besets pipeline steels, usually in industrial applications, is their tendency to suffer from corrosion when exposed to aggressive media, such as those containing chloride ions and acidic solutions <sup>1,4-8</sup>. Corrosive substances receive much attention in academic studies and are a cause for industrial concern as iron and its alloys are used widely in various industries. However, although it is subject to severe erosion damage in aggressive environments, it should not be forgotten, that these effects generally arise from acidic solutions used to remove unwanted products in many industrial processes <sup>9-11</sup>. Corrosion of carbon steel is a significant problem in the gas and transportation systems and oil production and causes significant economic loss <sup>12</sup>. Corrosion inhibitors are substances that, when added in small concentrations to aggressive solutions used in industries will reduce metal corrosion rate <sup>13</sup>. Thus, the use of corrosion inhibitors is one of the most practical ways to protect steel from corrosion, especially in acidic solutions where the prevention consumption from exposure to unexpected mineral acid solutions is critical <sup>14-18</sup>. Usually, these are organic compounds that already tend to condense on the surface of the metal and therefore can be used as effective corrosion inhibitors <sup>19-24</sup>. Studies have indicated that the adsorption of organic inhibitors depends mainly on

physico-chemical properties of the molecule attached to the functional group(s) <sup>25,26</sup>. Previous work to study the prevention of corrosion in carbon steel in acidic solutions has evaluated piperazine compounds <sup>27</sup>, *Ilex paraguariensis* extracts <sup>28</sup>, dimethyl pyrimidine derivatives <sup>29</sup>, gibberellic acid as a green corrosion inhibitor <sup>30</sup>, triazole derivatives <sup>31</sup>, and the aminolysis of poly(ethylene terephthalate) waste<sup>32</sup>.

In this work, sodium diethyl dithiocarbamatetrihydrate (NaDDCT) and 3,6-diamino-10-methylacridin-10-ium chloride (DAMAC) are used as corrosion inhibitors for X65-steel in the 0.05M  $H_2SO_4$  acidic solution. This is studied by using open circuitpotential (OCP) and potentiodynamicpolarization (PDP) techniques in order to study the corrosion efficiency, corrosion rate and the effect of temperature on the corrosion process.

## 1. Experimental

#### 2.1. Materials and solutions

X65-steel was used as a working electrode in an electrochemical cell to investigate the corrosion inhibition in 0.05M  $H_2SO_4$  acidic solution over a temperature range from 298.15K to 318.15K in the absence and the presence of NaDDCT and DAMAC inhibitors. Table 1 shows the chemical composition of X65 steel, that was taken from Iraq's fields, obtained by optical emission spectroscopy (PMI MASTER Pro Oxford,UK). The specimens were prepared by cutting the pipes using an electrical saw to dimensions (1cm x1cm) with thickness (1cm) and covered with an epoxy resin. The specimens were then polished using emery paper at different sizes and used an aqueous alumina to obtain a mirror-like surface. Thus, the specimens were cleaned by using by hot benzene (*care:* carcinogen risk), acetone, distilled water and dried by passing nitrogen over the surface. The cross-sectional area that was exposed to the test solution was 1cm<sup>2</sup>.

#### Table 1 : shows the chemical compositions of X65-steel obtained by optical emission spectroscopy

Elements	С	Si	Mn	Cr	Mo	Ni	Cu	Fe
Wt.%	2.180	3.100	1.360	0.102	0.127	0.213	0.596	Balance

All experiments were carried at constant temperature by using a regulated circulating bath (HYSC company, Korea). The test solution was freshly prepared with distilled water in sulfur acid (analytical reagent grade 97% which obtained from Scharlaucompany). Thus, to study of inhibitive action of NaDDCT and DAMAC compounds towards X65 steel, an 0.05M  $H_2SO_4$  acidic solution was prepared at various concentrations ( $1 \times 10^{-3}$  M to  $3 \times 10^{-3}$  M) over a temperature range (298.15 - 318.15)K. Fig. 1 shows the chemical structure of the organic compounds that were studied as corrosion inhibitors.



## Fig. 1. Chemical structures of sodium diethyl dithiocarbamatetrihydrate (left) and 3,6-diamino-10methylacridin-10-ium chloride (right).

#### 2.2. Electrochemical measurement

A five necked Pyrex glass cell was constructed containing three electrodes: X65-steel as the working electrode, a platinum electrode as a counter electrode and a saturated Calomel electrode Hg | Hg<sub>2</sub>Cl<sub>2(s)</sub> | KCl) as the reference electrode. The remaining necks were used to admit the nitrogen gas (purity 99.99%) and to allow it to. The X65-steel working electrode was covered by epoxy resin with a 1cm<sup>2</sup> area exposed to the test solution and the platinum electrode was coated with black platinum to increase the large surface area and catalytic activity. The saturated Calomel electrode that was used as reference electrode was put in a glass capillary "Luggin capillary tube" and the fine tip was immersed in the solution and used in this state to reduce the drop in

Ohmic potential<sup>33</sup>. After that, each of the aforementioned electrodes were placed in the corrosion cell and the contents measured by a Potentiostat/Galvanostat Research Grade Interface 1000(GAMRY company, USA) to determine the open circuitpotential as a function of time and obtain the potentiodynamic polarization curve. The data were analyzed by an Echem Analyst (version 6.23) to obtain the electrochemical parameters at a polarizedvalue  $\pm$  100 mV according to the free corrosion potential (E *vs.* SCE).

#### 3. Results and Discussion

#### **3.1. Open Circuit Potential**

Figs. 2 and 3 exhibit the variation in the OCP as a function of immersion time (10 min.) in the absence and the presence of NaDDCT and DAMAC inhibitors at various concentrations in 0.05M H<sub>2</sub>SO<sub>4</sub> acidic solution at 298.15K. Fig. 2 shows a slight drift in the OCP values towards the negative showing the presence of NaDDCT inhibitor, this behaviour is attributed to adsorption of the inhibitor or/and deposition of the products of the corrosion reaction on the X65 steel<sup>34</sup>. The magnitude of the OCP shift suggests that NaDDCT inhibitor at the same time affects the anodic and cathodic reactions. Meanwhile, the exact classification of the organic compounds as either an anodic or cathodic inhibitor involves the displacement of the OCP values by more than 85mV with respect to the OCP value in the absence of the NaDDCT inhibitor <sup>35</sup>. At low concentrations of the NaDDCT inhibitor (see Supplementary information) the initial OCP data are negative when compared with the increasing concentration in the inhibitor. The value of the potential drifts to less negative values, even though the change was not excessive but only a few mV. This means at a NaDDCT molarity of  $1 \times 10^{-4}$  M, the inhibitor cannot provide a completely protective film rapidly in the X65 steel electrode surface and this leads to a big cathodic area compared with anodic areas on the electrode surface and is a cause of the corrosion  $^{36}$ . The OCP values are shown in a Fig. 3, for the addition of the DAMAC inhibitor to the 0.05M H<sub>2</sub>SO<sub>4</sub> solution. The values of OCP become increasingly positive with increasing the concentration of DAMAC inhibitor; this is particularly marked at a concentration of  $1 \times 10^{-3}$  M.This clearly indicates that high concentrations of corrosion inhibitor will possess less activity and do not give adequate protection of the surface under the conditions of the OCP at the non-polarized electrode. The potentiodynamic measurements in the following section.confirm these tentative conclusions.



Fig.2. The open circuit potential of X65-steel in the absence and the presence of different concentrations of NaDDCT in  $0.05M H_2SO_4$ 



Fig.3.The open circuit potential for X65-steel in the absence and the presence of different concentrations of DAMAC in 0.05M H<sub>2</sub>SO<sub>4</sub>

#### 3.2. Potentiodynamic Polarization (PDP) Curve

Using a polarized electrode and applying a varying potential and scan rate yielded a series of potentiodynamic polarization curves. These are commonly used to evaluate the parameters affecting corrosion and thus understand the mechanism of the corrosion processes  $^{37-40}$ . Figs. 4 and 5 illustrate the overall kinetics of anodic and cathodic reactions that occur on the surface of the X65-steel electrode at various concentrations of NaDDCT and DAMAC inhibitors in 0.05M H<sub>2</sub>SO<sub>4</sub> solution at 298.15K. When the data presented in Figs. 4 and 5 are assessed, it can be seen that both the anodic and cathodic currents become lower when the inhibitors are added into the test solution. This reveals the role of the NaDDCT and DAMAC as inhibitors by protecting the surface from the aggressive medium. The magnitude of the shifts in a current density values will increase with increasing the concentration of the inhibitors, *i.e.* by increasing the range of the concentration of the inhibitors, the anodic and cathodic reactions are both retarded. The hypothesis is that the inhibitors operate by obstructing the cathodic process illustrated, by retarding the liberation of hydrogen interaction; in the anodic reaction the release of free iron ions in solution is impeded. Thus, there is a reduction in the dissociation reaction of X65-steel, especially at high concentrations and this enhances the resistance to corrosion in environments similar to those under study.



Fig. 4.Potentiodynamic polarization curves for the corrosion X65-steelin 0.05 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of different concentrations of NaDDC at 298.15K.



Fig. 5.Potentiodynamic polarization curves for the corrosion of X65-steel in 0.05 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of different concentrations of DAMAC at 298.15K.

The kinetic parameters of the electrochemical corrosion reaction (*e.g.* current density  $i_{Cor}$ , corrosion potential  $E_{Cor}$ , anodic and cathodicTafel slopes,  $\beta_a$ ,  $\beta_c$ , respectively), which were obtained from the extrapolation of polarization curves, and the corrosion rate are shown in Table 2. The latter also includes the percentage of corrosion inhibition, %IE, calculated by using Eq.(1) as well estimated the coverage degree ( $\Theta$ ) of surface X65-steel electrode as given in Eq.(2) [41-43].

$$IE\% = \left(\frac{i_{corr.uninh.} - i_{corr.inh.}}{i_{corr.uninh.}}\right) \times 100 \dots \dots \dots \dots \dots (1)$$
$$\theta = \left(\frac{i_{corr.uninh.} - i_{corr.inh.}}{i_{corr.uninh}}\right) \dots \dots \dots \dots \dots \dots (2)$$

The *i*<sub>corr.uninh</sub>.and*i*<sub>corr.inh</sub>. parameters relate to the absence and the presence of inhibitors, respectively.

Table 2. The kinetic parameters of corrosion, percentage inhibition efficiencies and coverage degree for X65steel in various concentrations of NaDDCT and DAMAC inhibitors in 0.05M H<sub>2</sub>SO<sub>4</sub> solution at 298.15K.

		<b>i</b> <sub>Corr</sub>	E <sub>Corr</sub>	β <sub>a</sub>	β <sub>c</sub>	Corrosion		
inhibitors	Conc.(M)	$(\mu A/cm^2)$	( <b>mV</b> )	(mV/decade)	(mV/decade)	Rate(mpy)	%IE	Θ
NaDDCT	blank	86.10	-508.0	68.50	170.8	31.96		
	$1 \times 10^{-4}$	64.50	-574.0	95.20	94.60	27.66	25.08	0.25
	$3x10^{-4}$	22.30	-579.0	62.60	86.40	8.280	74.09	0.74
	6x10 <sup>-4</sup>	14.70	-576.0	61.50	71.80	5.454	82.92	0.82
	$1 \times 10^{-3}$	12.70	-574.0	57.20	79.20	4.710	85.24	0.85
	3x10 <sup>-3</sup>	4.740	-586.0	70.10	56.80	1.760	94.49	0.94
DAMAC	1x10 <sup>-4</sup>	74.00	-513.0	61.40	127.5	27.49	14.05	0.14
	3x10 <sup>-4</sup>	57.40	-507.0	60.60	129.6	21.30	33.33	0.33
	6x10 <sup>-4</sup>	56.70	-503.0	63.90	137.6	21.05	34.14	0.34
	$1 \times 10^{-3}$	55.20	-504.0	71.40	131.7	20.48	35.88	0.35
	$3x10^{-3}$	41.50	-496.0	66.50	129.2	15.39	51.80	0.51

It seems very clear from Table 2 that the corrosion current densities reduce and shift the corrosion potentials towards a noble direction in presence of NaDDCT and DAMAC inhibitors in the 0.05M H<sub>2</sub>SO<sub>4</sub>acidic solution, corresponding to a decrease in the corrosion rate. This is also reflected in the calculated percentages of inhibition efficiencies Fig.6, which are high, as well as the increased degree of surface coverage. This indicates access to high corrosion resistance and a reduction in feasibility of corrosion. Thus, the drift in corrosion

potential towards the noble direction refers to the tendency of X65-steel in  $0.05M H_2SO_4$ solution to decrease from a purely thermodynamic point of view <sup>44</sup>.



Fig. 6. The inhibition efficiency for X65-steel in 0.05 M H<sub>2</sub>SO<sub>4</sub> in the presence of NaDDCT and DAMAC inhibitors

The changes of corrosion potentials become less negative (increasingly more positive) in the presence of the DAMAC inhibitor when compared with the addition of NaDDCT. This result was consistent with the values obtained for the OCP. Despite the different experiments natures of the experiments, comparisons between the OCP and the values of E<sub>corr</sub> are important to understand the elementary work of the corrosion inhibitor than the change in OCP Figs. 2 and 3. The measured value of  $E_{corr}$  in the presence of inhibitor is often a beneficial sign to indicate which reaction is more affected: the anodic or the cathodic<sup>45-48</sup>. Moreover, the variation in the Tafel slopes for the anodic and cathodic reactions give a clear indication about the change in the mechanism of the electrochemical reaction associated with the corrosion process <sup>49-53</sup>. The data in Table 2 show that the decrease in the values of the Tafel slopes in present study can be interpreted both in terms of the anodic and cathodic reactions occurring in the X65-steel electrode under the conditions of controlled addition of these inhibitors, *i.e.* to achieve a mixed control for both anodic and cathodic reactions <sup>54-57</sup>. Likewise, the reduction in the anodic Tafel slope means that the dissociation of metal is retarded by the inhibition effect that is introduced by blocking the active site on the electrode surface <sup>58-61</sup>. Thus, this phenomenon is essential to enable the adsorption of inhibitor molecules on the X65-steel electrode surface. On the other hand, the values of the cathodic slope in the presence of the DAMAC inhibitor are noticeably higher than those for NaDDCT. This indicates that the reaction to liberate hydrogen has diminished relatively by blocking the active site, even though accompanied by a decrease in the cathodic current density <sup>62</sup>. Thus, the percentage of corrosion inhibition for DAMAC inhibitor is lower than NaDDCT and acts as a good inhibitor under these conditions.

#### 3.3 Adsorption isotherm and effect of temperature

Generally, the adsorption process on the surface did not reach a sufficient degree of corrosion to achieve a true equilibrium, but rather tends to reach a steady state of adsorption. However, when a corrosion rate issufficiently high, the steady state of the adsorption tends to become a quasi-equilibrium condition. Thus, to a reasonable approximation a semi-equilibrium isotherm may be used to represent the thermodynamic equilibrium isotherm <sup>38</sup>. The isotherm adsorption can give important information about the inhibitor and its interaction with the metal surface. So, Langmuir, Frumkin and Temkin type isotherms were all tested to evaluate the adsorption of the DAMAC and NaDDCT inhibitors on the X65-steel surface, according to the Eqs.( 4, 5 and

where Kis defined as the adsorption/desorption equilibrium constant, C represents the concentration of the DAMAC and NaDDCT inhibitors, *g* is the parameter relating to the adsorbate interaction and  $\theta$  is the degree of surface coverage. It is important to determine which of the applied isotherms give the best fit to the degree of coverage degree and then calculate the adsorption parameter for the free energy by using Eq.(6)<sup>65</sup>. Figs.7 a,b,c illustrate the kinds of adsorption isotherm and indicate that the DAMAC and NaDDCT inhibitors were adsorbed on X65 steel. Fig.7a shows the data obtained display good correlation values:  $r^2 = 0.9932$  and 0.9420 for NaDDCT and DAMAC respectively, for the adsorption of the inhibitors on the X65-steel electrode according to the Langmuir isotherm. While the  $r^2$  values for applied Frumkin and Temkin isotherms are 0.9505 and 0.6979 for the NaDDCT inhibitor, and 0.9223 and 0.8840 for the DAMAC inhibitor. Thus, the  $\Delta G^{\circ}_{ads}$  values are calculated from the slopes of the Langmuir isotherms usingEq.(6).

 $\Delta G^{\circ}_{ads} = -RTln(55.5K_{ads})\dots\dots\dots$  (6)

The presence of 55.5 in Eq. (6) refers to the water concentration in a solution in  $\frac{g}{1L}$ , R is the gas constant and T an absolute temperature value.



Fig.7. Types of adsorption isotherms (a-Langmuir , b- Frumkin and c- Temkin ) for the adsorption of NaDDCT and DAMACinhibitors on X65-steel in 0.05M H<sub>2</sub>SO<sub>4</sub> solution at 298.15K

The equilibrium constants of the adsorption-desorption process were determined as 4985.12 molL<sup>-1</sup> and 253.531 molL<sup>-1</sup> for the NaDDCT and DAMAC inhibitors, respectively. Therefore, the values of the Gibbs' free energy of adsorption,  $\Delta G^{\circ}_{ads}$ , become-31.0667 kJmol<sup>-1</sup> and -23.6816 kJmol<sup>-1</sup>. The higher value of adsorption constant reflects the strong adsorption of inhibitor molecules on a surface electrode as is clearly the case with the NaDDCT; whilst the negative values of  $\Delta G^{\circ}_{ads}$  refer to the spontaneous adsorption of an inhibitor on the X65-steel surface electrode, In addition to giving an idea of the strength of interaction between the surface and the inhibitor molecules. Generally, the values of  $\Delta G^{\circ}_{ads}$  that were calculated lie in a range between (-31.0667 and -23.6816) kJmol<sup>-1</sup> where a value less than 40kJmol<sup>-1</sup> is usually interpreted as the presence of a stronger physical adsorption and formation of a protective film on the surface electrode. This reflects a chemical adsorption feature <sup>66</sup> and is stronger in the case of NaDDCT inhibitor and coincides with the value representing the efficiency of the inhibition of the corrosion reaction as shown in a Table2. These results suggest similar adsorption thermodynamics to those previously published in research relating to the adsorption of corrosion inhibitors in H<sub>2</sub>SO<sub>4</sub> acidic solution on the surface of X65-steel  $^{67}$ . Fig.(7b) shows that the r<sup>2</sup>value is also high when using the Frumkin isotherm, which indicates the good correlation between the experimental data; lower in the Temkin isotherm which yields negative values for the g parameters (-0.9631 and -2.506 for NaDDCT and DAMAC inhibitors respectively). This indicates the presence of a side reaction that involves repulsive interactions besides the adsorption process 68.

The effect of temperature on the corrosion process in the presence of inhibitors is very complicated because there are several changes that may occur on the metal surface: rapid etching as well the desorption process of the inhibitor molecules that may be caused especially at high temperatures <sup>69-70</sup>. Thus, these parameters are very useful to evaluate and study the inhibition of the corrosion process. Generally, when the temperature is raised the corrosion rate or corrosion current density increase exponentially in corrosive media, due to the decrease in the over-potential of the evolution of hydrogen <sup>71</sup>. The Arrhenius modified Eq.7 that is shown below gives the relationship between the corrosion current density and temperature <sup>72-74</sup>.

$$logi_{Corr.} = logA - \frac{-E_a}{2.303RT} \dots \dots \dots 7$$

where  $E_a$  is the apparent activation energy, A is a pre-exponential factor (a constant), R is the gas constant, T is the absolute temperature in Kelvin and  $i_{Corr.}$  is the corrosion current density. Thus, the  $E_a$  values are estimated to interpret the inhibition mechanism of the inhibitors under study by measuring the polarization curves over the range of temperature from 298.15 to 318.15K in the absence and presence of NaDDCT and DAMAC inhibitors ( $3x10^{-3}$ M) in acidic solution. Generally, there are no dramatic changes in the form of polarization curves at temperatures up to 298.15K and the results are illustrated in Table 3. Moreover, the corrosion potential drifts towards a more negative direction except in the presence of the NaDDCT inhibitor, which encourages a shift to less negative values when the temperatures are increased. The values of corrosion current densities and corrosion inhibition decrease. Note, the presence of the aggressive medium results in an increase in the value of  $i_{Corr}$  as a result of the loss of the protective film and resulting metal dissolution, which controls the corrosion process. The values of  $E_a$  calculated from the Eq. (7) as shown in Fig.8 were 22.9085kJ mol<sup>-1</sup> and 73.71017 kJ mol<sup>-1</sup> in the absence and the presence of the NaDDCT inhibitor, respectively.The calculated value of the activation energy for the NaDDCTinhibitor, in conjunction with the values of the protection efficiency, are shown in Table 3.



Fig. 8. Arrhenius plot of X65-Steel in 0.05M  $\rm H_2SO_4$  acidic solution and in the presence of  $~1\times10^{-3}M$  NaDDCT inhibitor

Thus, the results of the apparent activation energy are in agreement with the protection efficiency and the  $E_a$  value in the presence of inhibitor is noticeably higher than in the absence of the NaDDCT inhibitor. This may interpreted as being due to NaDDCT inhibitor retarding the general process of corrosion at normal temperatures <sup>75-77</sup>, while the inhibition is greatly reduced at high temperatures.

T(K)	i <sub>Corr</sub> (µA/cm <sup>2</sup> )	E <sub>Corr</sub> (mV)	β <sub>a</sub> (mV/decade)	β <sub>c</sub> (mV/decade)	Corrosion Rate(mpy)	%IE			
Blank									
298.15	86.10	-508.0	68.50	170.8	31.96				
308.15	86.40	-565.0	77.80	88.50	32.05				
313.15	87.50	-544.0	55.50	91.40	32.36				
318.15	155.0	-542.0	56.30	88.50	57.28				
NaDDCT									
298.15	4.740	-586.0	70.10	56.80	1.76	94.49			
308.15	5.600	-542.0	60.90	52.60	2.33	93.51			
313.15	10.50	-541.0	75.70	70.40	3.87	88.00			
318.15	34.90	-539.0	141.5	100.0	12.93	77.48			
	DAMAC								
298.15	41.50	-496.0	66.50	129.2	15.39	51.80			
308.15	50.20	-518.0	57.30	94.00	32.49	41.89			
313.15	141.0	-497.0	44.30	126.9	52.19	aggressive			
318.15	425.0	-496.0	57.70	160.4	157.4	aggressive			

Table 3.The kinetic parameters of corrosion, percentage inhibition efficiencies for X65-steel at optimum concentration  $(3x10^{-3}M)$  of NaDDCT and DAMAC inhibitors in 0.05M H<sub>2</sub>SO<sub>4</sub> solution in temperature range from 298.15K to 318.15K.

Furthermore, the value of  $E_a$  is higher for the inhibited system, which suggests that the physical adsorption occurs during the first stage and explains the nature of the interactions of the organic molecules with the metal <sup>78-79</sup>, and is correlated with and increasing thickness for the double layer. In other words, the physical adsorption corresponds to the lower values of activation energy from *ca.* 30 kJ mol<sup>-1</sup>to 50 kJ mol<sup>-180-81</sup>. However, in spite of this, this criterion cannot be considered as conclusive evidence for a competitive adsorption with molecules of water that are removed from the surface of the X65-steel, which also possesses an activation energy <sup>82</sup>.

#### 3.4. Mechanism of inhibition corrosion

The corrosion inhibition of X65-steel in 0.25M  $H_2SO_4$  in the presence of NaDDCT and DAMAC inhibitors is explained on the basis of an interpretation of the adsorption process. Thus, the molecular inhibitors inhibit the corrosion process *via* controlling the anodic and cathodic reactions. The generally accepted first step in the adsorption of an inhibitor molecular on the surface electrode of X65-steel involves the replacement of water molecules, which are adsorbed on the electrode's surface <sup>75,83</sup>. The action of inhibition in the presence of inhibitors correlates with freshly produced charged iron species and leads to the formation of complexes on the surface X65-steel.

 $Fe \rightarrow Fe^{2+} + 2e$ 

 $Fe^{2+} + Inh_{(ads)} \rightarrow [Fe - Inh]^{2+}_{(ads)}$ 

In other words, as well the physical adsorption, the adsorption of NaDDCT and DAMAC inhibitors occurs on the basis of the phenomenon of donor-acceptor interactions between the  $\pi$ -electrons of the double bonds and the nitrogen/sulfur atoms of the neutral molecules. Additionally, the  $\pi$ -electrons of the DAMAC cationic inhibitor interact with the *d*-orbitals of iron to block the anodic sites causing a reduction in the anodic dissolution of X65-steel. Therefore, the inhibitor molecules adsorb on the cathodic sites to retard the evolution of hydrogen <sup>84-92</sup>.

## 3.5. Conclusions

The open circuit potential drift toward the positive values with increasing concentrations of NaDDCT and DAMACinhibitors indicate the formation of a film layer on the X65 steel surface. The results from potentiodynamic polarization confirm that NaDDCT and DAMAC act as good inhibitors in acidic medium under the conditions that were selected in the present work, whereas the loss of protection efficiency occurs for the DAMAC inhibitor at high temperature. The results confirmed that NaDDC and DAMAC inhibitors act as mixed-type inhibitor. The negative values of  $\Delta G_{ads}$  showed that the adsorption of inhibitor molecules on the X65 steel surface is spontaneous. The apparent activation energy values for the process were also high in the presence of inhibitors, which is explained by the increasing energy barrier for the corrosion reaction and a change in the mechanism of the corrosion process. The corrosion inhibition efficiencies increased with inhibitor concentration and decreased with increasing temperature. The adsorption of both inhibitors obeys the Langmuir isotherm with excellent correlation values.

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