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Influence Of N-(4-Diethylaminophenyl)-N'-Phenylthiourea On Corrosion Inhibition Of Carbon Steel In 0.5M H_2SO_4

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ABSTRACT

The inhibition of the corrosion of carbon steel in 0.5M H_2SO_4 by N-(4-diethylaminophenyl)-N'-phenylthiourea(DAPPTU) has been investigated in relation to the concentration of the inhibitor using weight loss and electrochemical measurements as potentiodynamic polarisation, linear polarisation and impedance. Results obtained show that this organic compound is an excellent inhibitor in 0.5M H_2SO_4 solution. Polarisation curves reveal that DAPPTU is a mixed type inhibitor without change of the mechanism of the hydrogen evolution. The inhibition efficiency of DAPPTU increases with the inhibitor concentration to reach 97.8 at 1.6×10^{-3}M. Changes in impedance parameters(charge transfer resistance and double layer capacitance) were indicative of adsorption of DAPPTU on the metal surface, leading to the formation of a protective film. Adsorption of DAPPTU on the carbon steel surface is found to obey the Langmuir adsorption isotherm. From the adsorption isotherm some thermodynamic data for the adsorption process (K and ΔG_{ads}) are calculated and discussed. The effect of the temperature on the corrosion behaviour of carbon steel in 0.5M H_2SO_4 without and with addition of DAPPTU at 4×10^{-4}M was studied in the range of temperatures from 30 to 60^0C.

KEYWORDS

Carbon steel;
N-(4-diethylaminophenyl)-N'-phenylthiourea;
Acid, Adsorption;
Corrosion inhibition.

INTRODUCTION

The corrosion of steels in acidic media and its inhibition constitute a very important problem in chemistry and metallurgy. The use of acid solution during pickling, descaling and industrial cleaning leads to the corrosive attack on metals and alloys. For this reason a variety of organic additives as corrosion inhibitors have been tested in these processes[1-5]. Compounds containing both nitrogen and sulphur groups are often better than either type alone. For example, the efficiency of the inhibition of iron and steel corrosion in acidic media by thiourea and some of its derivatives has been studied by several workers.

Thus, the literature is replete with information on the effect of thiourea derivatives on the corrosion of metal in different environments. Ozcan et al.[6] studied the effect of thiourea, methylthiourea and phenylthiourea on corrosion behaviour of mild steel in 0.1MH_2SO_4 and reported that these compounds revealed a good corrosion inhibition, phenylthiourea being the most efficient and thiourea the least. Tandel et al[7] used the thermometry technique for evaluation of corrosion inhibition by thiourea, urea and their derivatives for mild steel in binary acid mixture($HCl+HNO_3$). Thiourea, allylthiourea and phenylthiourea have been investigated as corrosion inhibitors for Al-4%Cu alloy in trichloracetic acid by Pandya and Daraji[8]. These authors showed that the substitution of amino H atoms by a phenyl or allyl groups affected the inhibitive action and suggested that the resonance effect increased more with phenyl than with allyl groups. Yadaw and Vadhawani[9] studied the effect of thiourea and some of its derivatives namely phenylthiourea, o-tolylthiourea, m-tolylthiourea, p-tolylthiourea, 1,3-di-o-tolyl-thiourea, 1,3-di-m-tolylthiourea, 1,3-di-o-tolylthiourea and 1,3-di-p-tolylthoiurea on corrosion of 1100 aluminum in 1% HCl and concluded that the inhibition of the inhibitors increased with increase of temperature from 25 to 45^{0}C. In order to give more information about the inhibition mechanism of thiourea derivatives, Singh[10] investigated the effects of thiourea, allylthiourea, N,N'-diethylthiourea, N,N'-di-isopropylthiourea, phenylthiourea, thiocarbanilide and sym-di-o-tolylthiourea on the corrosion reaction of cold rolled mild steel in 1M H_2SO_4 at 40^{0}C. This investigation revealed that cathodic reaction was inhibited at higher concentration and that the higher inhibitors concentrations decreased H_2 pickup. The effects of temperature and immersion time as well as of polarisation on the inhibitive action of urea, thiourea and phenylthiourea on the corrosion inhibition of copper in HNO_3, was studied by Mansour et al.[11]. Oza et al.[12] studied the corrosion inhibition by thiourea and its derivatives for AISI 304 stainless steel in 2.5-7.5M HCl and concluded that aliphatic substitution of N atom generally gave a better inhibition than an aromatic substitution and that liberation of H_2S in acidic solution did not impair that inhibition.

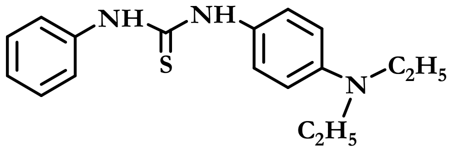

Figure 1 : Molecular structure of DAPPTU

In the present investigation, experiments have been performed to assess the inhibitive action of N-(4-diethylaminophenyl)-N'-phenylthiourea (DAPPTU) towards the corrosion inhibition of carbon steel in 0.5M H_2SO_4. The choice of this inhibitor is based on the fact that it can be synthesized conveniently from relatively cheap raw materials. The effect of temperature on the inhibition efficiency has also been examined.

EXPERIMENTAL

Inhibitor was synthesised according to previously reported experimental procedure[13] from condensation reaction phenylisothiocyanate and N,N'-diethyl-1,4-phenylene-diamine in ethanol media. Figure 1 shows the molecular structure of DAPPTU.

The aggressive solutions used were made of analytical reagent grade 98% H_2SO_4. Appropriate concentrations of acid were prepared using double-distilled water.

For the weight loss measurements, the experiments were carried out in solution of 0.5M H_2SO_4 (uninhibited and inhibited)on carbon steel, classified as 1038, with the composition(in wt. %) C 0.35-0.4; Si 0.1-0.4; Mn 0.5-0.8; Fe balance. Specimens in the form of discs with a diameter of 17 mm and a thickness of 1 mm were used for the test work. The samples were polished successively with different grades of emery paper up 1200 grade. Each experiment was carried out in a glass vessel containing 100 ml of fresh test solution. A clean weighed carbon steel sample was immersed completely at an inclined position in the vessel. The temperature was thermostatically controlled at 30±0.1^{0}C. After 2 hours of immersion in acid with and without addition of inhibitor at different concentrations, the specimen was withdrawn, rinsed with double-distilled water, washed with acetone, dried and weighted. Duplicate experiments were performed in each case and the mean value of the weight loss has been reported. The weight loss was used to calculate the corrosion rate in milligrams per square centimetre per hour.

Electrochemical experiments were carried out in a glass cell(CEC/TH-Radiometer) with a capacity of 500ml. A platinum electrode and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode. The working electrode(WE) was in the form of a disc cut from mild steel under investigation and was embedded in a Teflon rod with an exposed area of 0.5cm^2.

Electrochemical impedance spectroscopy(EIS), potentiodynamic and linear polarisation were conducted in an electrochemical measurement system(VoltaLab40) which comprises a PGZ301 potentiostat, a personal computer and VoltaMaster 4 software.

The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -700 to-200mV with scanning rate of 0.5mV s^{-1}. The polarisation resistance measure ments were performed by applying a controlled potential scan over a small range typically ±15mV with respect to E_{corr}. The resulting current is linearly plotted versus potential, the slope of this plot at E_{corr} being the polarisation resistance(R_p). All experiments were carried out in freshly prepared solution at constant temperatures, 30^{0}C, 40^{0}C, 50 and 60^{0}C± 0.1^{0}C using a thermostat.

The a.c. impedance measurements were performed at corrosion potentials(E_{corr}) over a frequency range of 10kHz-20mHz, with a signal amplitude perturbation of 10 mV. Nyquist plots were obtained. The impedance parameters were calculated using software Z-View, version 2.80, 2002, Scribner Associates Inc.

All tests were performed in non de-aerated solutions under unstirred conditions.

RESULTS AND DISCUSSION

Gravimetric measurements

TABLE 1 : Corrosion rate(W) of carbon steel and inhibition efficiency(P_W) for different concentrations of DAPPTU for the corrosion of carbon steel in 0.5M H_2SO_4

Concentration/M	W/mg cm^{-2}h^{-1}	P_W/%
Blank	0.860	-----
1×10^{-5}	0.125	85.5
1×10^{-4}	0.060	93.0
4×10^{-4}	0.038	95.6
8×10^{-4}	0.025	97.1
1.6×10^{-3}	0.020	97.7

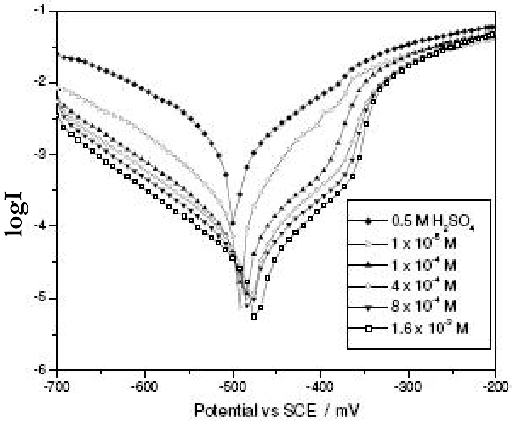

Figure 2 : Potentiodynamic polarisation curves for carbon steel in 0.5M H_2SO_4 containing different concentrations of DAPPTU at 30^{0}C.

TABLE 1 shows the results for carbon steel in 0.5M H_2SO_4 at 30^{0}C both in the absence and the presence of DAPPTU. The percentage inhibition efficiencies (P_W %) were calculated in the classical way as follows:

$$P_W\ \% = \frac{W_0 - W_{inh}}{W_0} \times 100 \qquad (1)$$

where W_0 and W_{inh} are the corrosion rate observed in the absence and the presence of inhibitor, respectively.

It can be seen from TABLE 1 that the inhibitor efficiency increased with increasing DAPPTU concentration in the test solution. We remark that the inhibition efficiency increases with inhibitor concentration reaching a maximum value at 1.6× 10^{-3}M.

Tafel polarisation

Figure 2 shows cathodic and anodic Tafel plots for carbon steel in 0.5M H_2SO_4 with and without different concentrations of DAPPTU. It is clear that

TABLE 2 : Electrochemical parameters and the corresponding corrosion inhibition efficiencies for the corrosion of carbon steel in 0.5 MH_2SO_4 containing different concentrations of DAPPTU

	Conc./M	$-E_{corr}$ /mV/SCE	I_{corr} /mAcm^{-2}	b_c/mV dec^{-1}	R_p/ Ωcm^2	P_I/ %	P_{Rp}/ %
0.5 M H_2SO_4	-	501	1.930	150	18	-	-
DAPPTU	1×10^{-5}	496	0.218	115	126	88.7	85.7
	1×10^{-4}	490	0.088	118	231	95.4	92.2
	4×10^{-4}	483	0.066	119	402	96.6	95.5
	8×10^{-4}	483	0.048	119	618	97.5	97.1
	1.6×10^{-3}	476	0.029	120	793	98.5	97.7

the current density decreases with addition of DAPPTU and comparison of curves showed that DAPPTU acts as mixed type inhibitor, i.e. both the cathodic and anodic curves of steel are affected by the presence of the inhibitor. Corrosion current densities, I_{corr}, were obtained from the polarisation curves by linear extrapolation of the cathodic Tafel curves at points 60mV more negative than E_{corr}, the corrosion potential.

TABLE 2 presents values of I_{corr}, the corrosion potential(E_{corr}), the cathodic Tafel slopes (b_c) and the corrosion inhibition efficiency(P_I%) as function of DAPPTU concentration. P_I% is given by:

$$P_I\,\% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \qquad (2)$$

Where I_{corr} and $I_{corr(inh)}$ are the corrosion current densities for the uninhibited and inhibited solutions, respectively.

Analysis of these data shows that the addition of DAPPTU hindered the attack on the steel electrode i.e. I_{corr} decreased with addition of DAPPTU in 0.5M H_2SO_4, due to increase in the blocked fraction of the electrode surface by adsorption. The adsorption of DAPPTU on the metal surface can occur either directly on the basis of donor-acceptor interactions between the π-electrons of the phenyl groups and vacant d-orbital of steel surface atoms[14] or by an interaction of protonated species with already adsorbed sulphate ions[15].

As it is shown in figure 2, the cathodic current potential curves give rise to parallel Tafel lines, which indicated that hydrogen evolution reaction was activation controlled and that the presence of the DAPPTU did not modify the mechanism of this process.

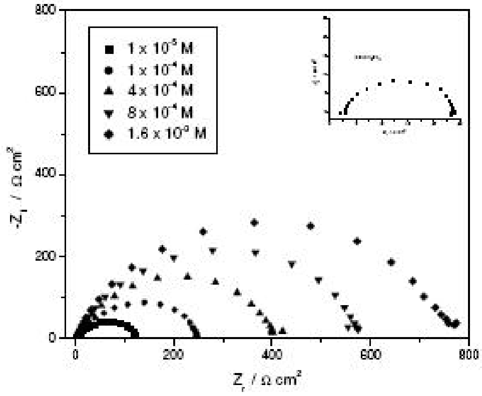

Figure 3 : Nyquist plots for carbon steel in 0.5M H_2SO_4 containing different concentrations of DAPPTU at 30^{0}C

Linear polarisation technique was performed in 0.5M H_2SO_4 with different concentrations of DAPPTU. The corresponding polarisation resistance (R_p) values of the carbon steel in the absence and in the presence of various inhibitor concentrations are also given in TABLE 2, which shows that R_p increased with increasing inhibitor concentration in acid solutions. The percentage inhibition efficiency, P_{Rp}(%), calculated from R_p values are also presented in this TABLE. P_{Rp} (%) is calculated as follows:

$$P_{Rp}\,(\%) = \frac{R_{P(inh)} - R_P}{R_{P(inh)}} \times 100 \qquad (3)$$

where R_p and $R_{p(inh)}$ are the resistance values without and with inhibitor, respectively.

We remark that P_{Rp} (%) increased with inhibitor concentrations reaching maximum values of 97.7 % at 1.6×10^{-3}M in 0.5M H_2SO_4.

Electrochemical impedance spectroscopy (EIS)

The corrosion behaviour of carbon steel in 0.5M H_2SO_4 in the absence and in the presence of DAPPTU was investigated by EIS at 30^{0}C after immersion of 1h. Impedance spectra for carbon steel in the presence of all concentrations of the compound are similar in shape. Figure 3, depict the Nyquist plots that exhibit one semicircle, which centre lies under the abscissa. To describe the observed depression of the capacitive semicircle it is necessary to replace the capacitor by some

TABLE 3 : Impedance parameters and inhibition efficiency for the corrosion of carbon steel in 0.5M H_2SO_4 containing different concentrations of DAPPTU

	Conc./M	R_t/Ω cm²	Q x 10^{-4} /$\Omega^{-1}cm^{-2}s^n$	n	C_{dl}/μF cm^{-2}	P_{Rt}/ %
0.5 M H_2SO_4	-	21	10.60	0.85	541.61	-
DAPPTU	1×10^{-5}	125	02.87	0.72	78.67	83.2
	1×10^{-4}	257	02.21	0.74	80.67	91.8
	4×10^{-4}	406	02.39	0.80	133.4	94.8
	8×10^{-4}	586	01.39	0.79	71.37	96.4
	1.6×10^{-3}	767	01.04	0.80	55.27	97.3

element, which has frequency dispersion like the constant phase element (CPE). This element is a generalised tool, which can reflect exponential distribution of the parameters of the electrochemical reaction related to energetic barrier at charge and mass transfer, as well as impedance behaviour caused by fractal surface structure. The introduction of such a CPE is often used to interpret data for rough solid electrodes[16]. The impedance of the CPE is[17-19]:

$$Z_{CPE} = Q^{-1}(j\omega)^{-n} \tag{4}$$

where Q is a proportionality coefficient and n an exponent related to the phase shift. For whole numbers of n=1,0,-1, CPE is reduced to the classical lumped elements capacitor(C), resistance(R) and inductance(L), respectively. The value of n=0.5 corresponds to Warburg impedance(W). Values of n can serve as a measure of the surface heterogeneity[17, 20-21]. Thus the equivalent circuit model employed for these systems is presented in figure 4.

The resistance R_s is the resistance of the solution, R_t reflects the charge transfer resistance and CPE has the meaning of a frequency distributed double-layer capacitance.

The impedance parameters for the corrosion of carbon steel in 0.5M H_2SO_4 without and with addition of various concentrations of DAPPTU are given in TABLE 3.

It can be seen that as DAPPTU concentration increased the R_t values increased as well, but the C_{dl} values tended to decrease. The greatest effect was observed at a concentration of 1.6×10^{-3} M, which produced R_t values of 767Ωcm² in 0.5M H_2SO_4. The decrease in C_{dl} values was due to the adsorption of DAPPTU on the metal surface. The decrease of the values of n when compared with blank and with concentration can be explained by some increase of surface heterogeneity, due to the adsorption of the inhibitor on the most active desorption sites[20]. On the other hand, the excellent behaviour of DAPPTU previously evidenced in the potentiodynamic polarisation measurements was again confirmed.

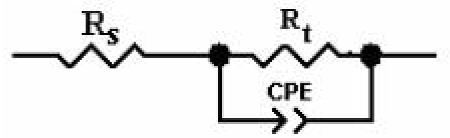

Figure 4 : Equivalent circuit used to represent the impedance result without and with inhibitor

Note that the capacitances were calculated from Q and R_t using the equation[22, 23]:

$$Q = \frac{(C \times R_t)^n}{R_t} \tag{5}$$

Adsorption consideration

The establishment of isotherms, which describe the adsorption behaviour of a corrosion inhibitor, is very important for the understanding of the mechanism of the metal-inhibitor interaction.

The degree of surface coverage θ of different concentrations of DAPPTU in 0.5M H_2SO_4 has been evaluated from the arithmetic average P of the values procured by the four methods used in this work (P_w, P_z, P_I, P_{Rp}), where θ is the ration P%/100.

TABLE 4 summarises corrosion inhibition efficiencies obtained through weight loss, electrochemical impedance, Tafel and resistance polarisation measurements. Very good agreement is found between the different methods.

TABLE 4 : Corrosion inhibition efficiencies obtained through weight loss (P_W), electrochemical impedance (P_{Rt}), Tafel (P_I) and resistance polarisation measurements (P_{Rp})

Concentration/M	P_W/%	P_I /%	P_{Rp}/%	P_{Rt}/ %	P/ %
1×10^{-5}	85.5	88.7	85.7	83.2	85.8
1×10^{-4}	93.0	95.4	92.2	91.8	93.1
4×10^{-4}	95.6	96.6	95.5	94.8	95.6
8×10^{-4}	97.1	97.5	97.1	96.4	97.0
1.6×10^{-3}	97.7	98.5	97.7	97.3	97.8

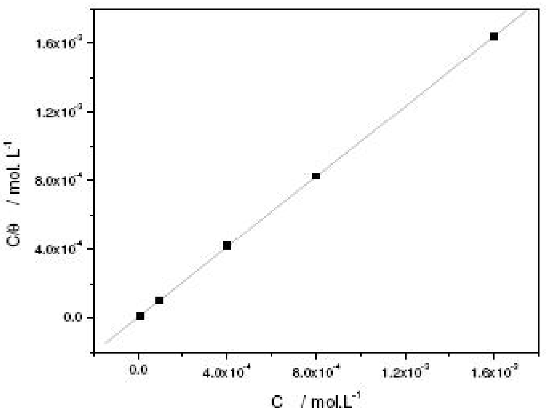

Figure 5 : Langmuir isotherm adsorption model of DAPPTU on the surface of carbon steel in 0.5M H_2SO_4

The straight lines obtained by the plot of C/θ versus C where C is the inhibitor concentration (Figure 5) indicated that DAPPTU adsorbed on the steel surface according to the Langmuir isotherm model:

$$\frac{C}{\theta} = C + \frac{1}{K} \qquad (6)$$

With

$$K = \left(\frac{1}{55.5}\right)\exp\left(-\frac{\Delta G_{ads}}{RT}\right) \qquad (7)$$

where ΔG_{ads} is the standard free energy of adsorption.

The value of the equilibrium constant(K) for carbon steel as calculated from the Langmuir type adsorption isotherm in 0.5M H_2SO_4 is 1.78×10^5.

The free value of the free energy of adsorption as calculated from equation(7) is -40.57kJ mol^{-1}. The largest negative values of ΔG_{ads} indicate that DAPPTU is strongly adsorbed on the carbon steel surface[24]. Moreover, it is well known that values of $-\Delta G_{ads}$ of the order of 20kJ mol^{-1} or lower indicate a physisorption; those of order of 40 kJ mol^{-1} or higher involve charge sharing or a transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond[25, 26].

The ΔG_{ads} value obtained here shows that in the presence of 0.5M H_2SO_4, chemisorption of DAPPTU may occur. Thus, DAPPTU may be adsorbed in the form of neutral molecules involving replacement of water molecules from the metal surface and sharing of electrons between the "N" and "S" atoms of the inhibitor molecule and metal surface. Adsorption of DAPPTU can occur through π electron interactions between the phenyl groups structure of the molecule and the metal surface and can also occur by the electrostatic interaction between the positively charges part of the molecule and already adsorbed sulphate ions. Moreover, despite the fact that the S atom, which has a great nucleophilic character compared to that of N atoms, is involved in the chemical reactivity of thiourea derivatives with the metal surface[13], the π-bond of the aromatic ring is considered as the principal centre for adsorption process[27, 28], in which the great adsorption of some organic compounds is attributed to the interaction of the π-electrons with surface atoms of the adsorbent. Consequently, it can be concluded that the adsorption of the DAPPTU molecules onto the carbon steel surface is principally arisen by two anchoring sites that are the π-bond of the phenyl rings.

Effect of temperature

It is known that the temperature has a great effect on the corrosion phenomenon. In case of corrosion in acid media, the corrosion rate increases exponentially with temperature increase because the hydrogen evolution overpotential decreases[29]. We have studied the effect of temperature on the inhibition efficiency of DAPPTU in 0.5M. For this purpose, we made potentiodynamic polarization measurements at temperatures of 30,40,50 and 60°C, in the absence and the presence of DAPPTU in 0.5M H_2SO_4. The values of corrosion current density (I_{corr}) were determined for uninhibited and inhibited acid solutions containing 4×10^{-4}M of DAPPTU at various temperatures and are given in TABLE 5. The change of inhibition efficiency (P%) with temperature variation are also given in the same TABLE. From this TABLE, we remark that the I_{corr} value increased

TABLE 5 : Inhibition efficiency(P_I%) and corrosion current density(I_{corr}) for uninhibited and inhibited acid solutions containing 4 x 10^{-4} M of DAPPTU at various temperatures

	0.5M H_2SO_4	(0.5M H_2SO_4+4×10^{-4}M DAPPTU)	
Temperature/K	I_{corr}/mAcm^{-2}	I_{corr}/mAcm^{-2}	P_I/ %
303	1.93	0.066	96.6
313	3.16	0.100	96.8
323	6.45	0.144	97.7
333	8.71	0.190	97.8

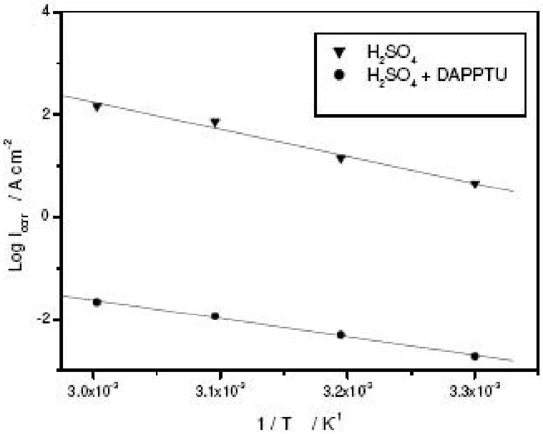

Figure 6 : Arrhenius plots for both the blank and the inhibitor

both in the presence and the absence of the inhibitor by increasing the temperature of the system. Moreover, we notice that the inhibition efficiency of DAPPTU at 4×10^{-4}M increases slightly with the rise of temperature. The fact that P% increases with increasing temperature is explained by Ammar and El-Khorafi[30], as the likely specific interaction between the iron surface and inhibitor.

The corrosion reaction can be regarded as an Arrhenius-type process, the rate of which is given by:

$$I_{corr} = k \exp\left(-\frac{E_a}{RT}\right) \qquad (8)$$

where I_{corr} is the corrosion current density, E_a is the apparent activation corrosion energy, T is the absolute temperature, k is the Arrhenius pre-exponential constant and R is the universal gas constant.

The values of E_a were determined using Arrhenius plots of Log I_{corr} versus 1/T given in figure 6 for the corrosion current density(I_{corr}) of carbon steel in 0.5M H_2SO_4 and inhibited acidic solutions containing 4 x 10^{-4}M of DAPPTU with correlation coefficient r^2 higher to 0.99. The calculated value of the apparent activation corrosion energy in 0.5M H_2SO_4 and (0.5M H_2SO_4+4 x 10^{-4}M DAPPTU) are 43.98 and 29.72kJmol^{-1}, respectively. The reduction in activation energy in the presence of DAPPTU may be attributed to the chimisorption of this inhibitor on steel [31-33].

Note that the relationships between the temperature dependence of inhibition efficiency (P%) of an inhibitor and apparent activation energy found in its presence was given as follows[29].

Inhibitors whose P% decreases with temperature increase. The value of E_a found is greater than that in the uninhibited solution.

Inhibitor whose P% does not change with temperature variation. The activation energy(E_a) does not change with the presence or absence of inhibitors.

Inhibitors whose P% increases with temperature increase. The value of activation energy(E_a) found is less than that in the uninhibited solution.

Thus, the smaller value of E_a in the presence of DAPPTU compared to that in its absence is attributed to the chemisorption of the inhibitor and the increase of P% with temperature increase can be interpreted as a confirmation of chemical adsorption of DAPPTU on the carbon steel surface. The protective effect of DAPPTU in 0.5M H_2SO_4 is great at all temperatures studied. This can be attributed to a strong adsorption bond, which can be found as a result of chemisorption[34].

CONCLUSIONS

From the overall studies the following conclusions can be deduced:

- DAPPTU is found to affect both the anodic and cathodic processes and its inhibition efficiency increases with inhibitor concentration in acidic media.
- The gravimetric technique and electrochemical measurements are in very good agreement.
- P(%) of DAPPTU increases slightly with the rise in temperature and its addition leads to a decrease of the apparent activation corrosion energy.
- Adsorption of the inhibitor on the carbon steel in 0.5M H_2SO_4 solutions fits a Langmuir isotherm model.
- The analysis of the experimental data leads to the suggestion of chemisorption of the inhibitor on the metal surface. In fact, the higher values of the free energy of adsorption and the decrease of the apparent activation corrosion energy verify the chemisorptive character of the adsorption.

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