Research Article

Adsorption Properties and Inhibition of C38 Steel Corrosion in Hydrochloric Solution by Some Indole Derivates: Temperature Effect, Activation Energies, and Thermodynamics of Adsorption

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The corrosion rates in the presence of some indole derivates, namely, 9H-pyrido[3,4-b]indole (norharmane) and 1-methyl-9H-pyrido[3,4-b]indole (harmane), as inhibitors of C38 steel corrosion inhibitor in 1M HCl solution, were measured by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques, in the range of temperatures from 25 to 55°C.

Results obtained revealed that the organic compounds investigated have inhibiting properties for all temperatures. The inhibition was assumed to occur via adsorption of the indole molecules on the metal surface. Adsorption of indole derivates was found to follow the Langmuir isotherm. The apparent activation energies, enthalpies, and entropies of the dissolution process and the free energies and enthalpies for the adsorption process were determined by potentiodynamic polarization and electrochemical impedance.

The fundamental thermodynamic functions were used to collect important information about indole inhibitory behaviour.

1. Introduction

The effect of temperature on the inhibited acid–metal reaction is highly complex, because many changes occur on the metal surface such as rapid etching and desorption of inhibitor and the inhibitor itself may undergo decomposition and/or rearrangement. Temperature effects on acidic corrosion and corrosion inhibition of iron and steel most often in HCl and H₂SO₄ solutions had been the object of a large number of investigations [1–12]. However, it was found that few inhibitors with acid-metal systems have specific reactions which are effective (or more) at high temperature as they are at low temperature [13–15]. Thermodynamic parameters such as adsorption heat, adsorption entropy, and adsorption free energy can be obtained from experimental data of the studies of the inhibition process at different temperatures. The kinetic data such as apparent activation energy and preexponential factor at different inhibitor concentrations are calculated, and the effects of the activation energy and preexponential factor on the corrosion rate of steel were discussed [16–20].

Our earlier results obtained for 9H-pyrido[3,4-b]indole (norharmane) and 1-methyl-9H-pyrido[3,4-b]indole (harmane) as corrosion inhibitors of C38 steel demonstrated that correlation exists between the inhibition efficiency and the chemical structure [21]. It was found that these compounds are good inhibitors in acidic solutions and the inhibition efficiency of these indole-type organic compounds may be explained in terms of electronic properties (the energy of the highest occupied molecular orbital ($E_{HOMO}$) and the energy of the lowest unoccupied molecular orbital ($E_{LUMO}$)). The aim of this paper is to extend these investigations in order to obtain a better understanding of the mode of inhibitory action of the harmane and norharmane by calculating thermodynamic parameters for both C38 steel dissolution and inhibitor adsorption process in hydrochloric acid solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2. Experimental

Electrode and Solution. Corrosion tests have been carried out on electrodes cut from sheets of C38 steel. Steel strips contained 0.36 wt% C, 0.66 wt% Mn, 0.27 wt% Si, 0.02 wt% S, 0.015 wt% P, 0.21 wt% Cr, 0.02 wt% Mo, 0.22 wt% Cu, 0.06 wt% Al, and the remainder iron. The specimens were embedded in epoxy resin leaving a working area of 0.78 cm².
Table 1: Corrosion parameters obtained from electrochemical measurements of C38 steel in 1 M HCl containing various concentrations of indole derivatives at 25\(^\circ\)C.

| Inhibitor | Polarisation curves | EIS |
|-----------|---------------------|-----|
|           | \(E_{\text{corr}}\) versus SCE (mV) | \(I_{\text{corr}}\) (\(\mu\)A cm\(^{-2}\)) | IE (%) | \(R_{\text{ct}}\) (\(\Omega\) cm\(^{2}\)) | \(C_{\text{dl}}\) (\(\mu\)F cm\(^{-2}\)) | IE (%) |
| 1 M HCl   | −529 | 284 | — | 49 ± 0.02 | 546 |
| Norharmane | 0.2 mM | −467 | 67 | 76 | 148 ± 0.91 | 183 | 67 |
|          | 0.4 mM | −476 | 61 | 79 | 238 ± 1.65 | 120 | 79 |
|          | 0.8 mM | −494 | 52 | 82 | 514 ± 1.18 | 55 | 90 |
|          | 1.2 mM | −455 | 28 | 90 | 641 ± 1.73 | 44 | 92 |
| Harmane   | 0.2 mM | −476 | 65 | 77 | 181 ± 0.10 | 330 | 73 |
|          | 0.4 mM | −489 | 55 | 81 | 321 ± 0.97 | 270 | 85 |
|          | 0.8 mM | −479 | 34 | 88 | 537 ± 0.17 | 188 | 91 |
|          | 1.2 mM | −492 | 24 | 91 | 736 ± 0.68 | 148 | 93 |

**Figure 1:** Chemical formulas of the tested inhibitors (a) norharmane and (b) harmane.

The working surface was subsequently ground with 180 and 1200 grit grinding papers, cleaned by distilled water and ethanol. The solutions (1 M HCl) were prepared by dilution of an analytical reagent grade 33% HCl with doubly distilled water. All the tests were performed in the range of temperatures from 25 to 55\(^\circ\)C. The tested inhibitors are 9H-pyrido[3,4-b]indole (norharmane) and 1-methyl-9H-pyrido[3,4-b]indole (harmane); their molecular structures are shown in Figure 1. The investigated compounds were commercial products: norharmane (Aldrich, P99%), harmane (Sigma, P98%), the concentration range of inhibitor employed was 0.2 mM to 1.2 mM. The concentration of inhibitor was determined in accordance with its solubility. Varela et al. reports the solubility of norharmane and harmane in water at 20\(^\circ\)C, at pH 7 and 13, using the absorbance at the maxima in the absorption spectra of saturated solutions [22]. The solubility of norharmane was 1.86 mM (pH = 7) and 1.81 mM (pH = 13). For harmane, the solubility was 1.61 mM (pH = 7) and 0.786 mM (pH = 13). At lower pH (Our experimental conditions, pH = 0), where the cationic form is the predominant species, all the compounds present a very high solubility, and it was not possible to obtain data with this technique at lower pH.

**Electrochemical Measurements.** Electrochemical measurements, including potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS), were performed in a three-electrode cell. C38 steel specimen was used as the working electrode, a platinum wire as the counter, and a saturated calomel electrode (SCE) as the reference. Before potentiodynamic test and EIS experiments, the electrode was allowed to corrode freely and its open circuit potential (OCP) was recorded as a function of time during 3 h, the time necessary to reach a quasi-stationary value for the open-circuit potential. This steady-state OCP corresponds to the corrosion potential (\(E_{\text{corr}}\)) of the working electrode. The anodic and cathodic polarization curves were recorded by a constant sweep rate of 20 mV min\(^{-1}\). Electrochemical impedance spectroscopy (EIS) measurements were carried out, using ac signals of amplitude 5 mV peak to peak in the frequency range of 100 kHz to 10 mHz. Electrochemical measurements were performed through a VSP electrochemical measurement system (Bio-Logic). The above procedures were repeated two times with success for each concentration of the two tested inhibitors. The Tafel fit and EIS data were analysed using graphing and analyzing impedance software, version EC-Lab V9.97.

3. Results and Discussion

3.1. Effect of Concentration. The corrosion rates of metals and alloys in aggressive solutions can be determined using different electrochemical methods. Electrochemical impedance spectroscopy and polarization curves were thus employed in the present work to study the effect of indole derivatives concentration. The percentages of inhibition efficiency and values of associated electrochemical parameters are listed in Table 1. Inspections of the obtained data reveal that the \(I_{\text{corr}}\) values decrease considerably in the presence of harmane and norharmane with increasing inhibitor concentration. The \(E_{\text{corr}}\) values shifted to more positive potentials in the presence of indole derivatives concentration, although there was not
3.2. Effect of Temperature

3.2.1. Potentiodynamic Polarisation. In order to get more information about the performance of indole derivates, the nature of adsorption isotherm, and thereafter to evaluate the adsorption and activation processes, the influence of temperature is studied by potentiodynamic polarisation. Some of the polarisation curves for C38 steel electrode in 1M HCl in the absence and in the presence of 0.2 mM of harmane in the temperature range 25–55°C are given in Figures 2, 3, and 4, respectively. As it can be seen, raising the temperature increases both anodic and cathodic reactions of C38 steel electrode both in the absence and in the presence of inhibitors. Polarisation curves of the C38 steel electrode in 1M HCl without and with addition of various concentrations of harmane at 45°C are shown in Figure 5, representative example. As it can be seen, the anodic and cathodic reactions are affected by the addition of inhibitor. Similar observations were found for all concentrations studied in the presence of both inhibitors. Accurate evaluation of Tafel slopes by Tafel extrapolation is often impossible, simply because an experimental polarization curve does not exhibit linear Tafel regions [24–27]. Our experimental polarization curves presented here do not display the expected log/linear Tafel behaviour with anodic branches exhibiting curvature over the complete applied potential range. The curvature of the anodic branch may be attributed to the deposition of the corrosion products or impurities in the steel (e.g., Fe5C) to form a nonpassive surface film [24]. The various electrochemical parameters were calculated from Tafel plots and summarized in Table 2. The inhibition efficiency and the surface coverage degree (θ) values for steel are also shown in the same table. The surface coverage θ was calculated from (1) [28]. It has been observed from Table 2, that the corrosion current density (Icorr) increased with increasing temperature in both uninhibited and inhibited solutions. The addition of norharmane or harmane to the HCl solution shifts the Ecorr towards more negative values at all of the studied temperatures, although there was not a specific relation between Ecorr and inhibitors concentration. The IE (%) values decrease with increasing temperature; a decrease in inhibition efficiencies with the increase in temperature might be due to weakening of physical adsorption. Consider

\[
\theta = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}},
\]

where \(I_{\text{corr}}\) and \(I_{\text{corr(inh)}}\) are the corrosion current density values in the absence and presence of indole derivates, respectively.
Table 2: Electrochemical parameters calculated from Tafel plots and the corresponding inhibition efficiencies at various temperatures studied of C38 steel in 1M HCl containing different concentrations of indole derivate.

| Temp. (°C) | Con. (mM) | $E_{corr}$ versus SCE (mV) | $I_{corr}$ (μA·cm$^{-2}$) | $b_a$ (mV·dec$^{-1}$) | $b_c$ (mV·dec$^{-1}$) | IE (%) | $E_{corr}$ versus SCE (mV) | $I_{corr}$ (μA·cm$^{-2}$) | $b_a$ (mV·dec$^{-1}$) | $b_c$ (mV·dec$^{-1}$) | IE (%) | θ |
|------------|-----------|-----------------------------|-----------------------------|------------------------|------------------------|--------|-----------------------------|-----------------------------|------------------------|------------------------|--------|----|
| 1 M HCl    | 0.2       | -460 | 232 | 106 | 89 | — | — | — | — | — | — | — | — |
|            | 0.4       | -476 | 61  | 116 | 122 | 79 | 0.7852 | -489 | 55 | 98 | 107 | 81 | 0.8063 |
|            | 0.8       | -494 | 52  | 97  | 118 | 82 | 0.8169 | -479 | 34 | 113 | 119 | 88 | 0.8803 |
| 25         | 1.2       | -455 | 28  | 93  | 112 | 90 | 0.9014 | -492 | 24 | 87 | 107 | 91 | 0.9155 |
| 1 M HCl    | 0.2       | -473 | 236 | 112 | 144 | 72 | 0.7200 | -465 | 212 | 118 | 133 | 75 | 0.7485 |
|            | 0.4       | -472 | 195 | 109 | 126 | 77 | 0.7687 | -470 | 182 | 116 | 136 | 78 | 0.7841 |
|            | 0.8       | -470 | 165 | 102 | 131 | 80 | 0.8043 | -456 | 154 | 109 | 128 | 82 | 0.8173 |
| 35         | 1.2       | -479 | 98  | 103 | 135 | 88 | 0.8837 | -464 | 101 | 103 | 118 | 88 | 0.8802 |
| 1 M HCl    | 0.2       | -501 | 1192 | 120 | 109 | — | — | — | — | — | — | — | — |
|            | 0.4       | -509 | 512 | 130 | 146 | 57 | 0.5705 | -496 | 413 | 117 | 134 | 65 | 0.6535 |
|            | 0.8       | -505 | 472 | 112 | 115 | 60 | 0.6040 | -488 | 389 | 112 | 125 | 67 | 0.6737 |
| 45         | 1.2       | -485 | 443 | 135 | 135 | 63 | 0.6284 | -487 | 335 | 113 | 126 | 72 | 0.7190 |
| 1 M HCl    | 0.2       | -525 | 1982 | 131 | 116 | — | — | — | — | — | — | — | — |
|            | 0.4       | -529 | 1023 | 142 | 150 | 48 | 0.4839 | -504 | 983 | 136 | 148 | 50 | 0.5040 |
|            | 0.8       | -566 | 954 | 114 | 156 | 52 | 0.5817 | -496 | 852 | 123 | 140 | 57 | 0.5701 |
| 55         | 1.2       | -504 | 867 | 117 | 127 | 56 | 0.5626 | -564 | 715 | 110 | 146 | 64 | 0.6393 |
|            | 1.2       | -504 | 651 | 109 | 139 | 67 | 0.6715 | -515 | 574 | 107 | 132 | 71 | 0.7104 |
containing indole deri v a t e s is also high er th an th at fo r uninhibited solution. The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage [29]. Moreover, the values obtained for norharmane are somewhat higher than those obtained for harmane and confirm the fact that the inhibitor efficiency of norharmane is slightly lower than that of harmane. Szauer and Brand explained that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the steel surface with increase in temperature [30]. Figure 7 showed a plot of ln \( \frac{I_{\text{corr}}}{T} \) versus 1/T with a slope of \(-\Delta H_a / R\) and an intercept (ln \( R/ Nh + \Delta S_a / R \)) from which the values of \( \Delta H_a \) and \( \Delta S_a \) were calculated, respectively.

### 3.2.2. Impedance Measurements

The corrosion behaviour of C38 steel in 1 M HCl solution in the presence of indole deri v a t e s was also investigated by EIS in the temperature range 25–55°C. The EIS of C38 steel electrode in 1 M HCl

\[ I_{\text{corr}} = K \exp \left( -\frac{E_a}{RT} \right) \]

\[ I_{\text{corr}} = \frac{RT}{Nh} \exp \left( \frac{\Delta S_a}{R} \right) \exp \left( -\frac{\Delta H_a}{RT} \right) \]

where \( I_{\text{corr}} \) is the corrosion current density, \( K \) the Arrhenius preexponential constant, \( E_a \) is the activation energy for the corrosion process, \( h \) is the Plank’s constant, \( N \) is the Avogadro’s number, the enthalpy of activation (\( \Delta H_a \)), and the entropy of activation (\( \Delta S_a \)).

Arrhenius plots for the corrosion density of C38 steel in the case of harmane are given in Figure 6, representative example. Similar plots are obtained in the case of norharmane. The apparent activation energies (\( E_a \)) at different concentrations of indole deri v a t e s were determined by linear regression between \( \ln I_{\text{corr}} \) and 1/T and the result is shown in Table 3. All the linear regression coefficients were close to 1, indicating that the C38 steel corrosion in hydrochloric acid can be elucidated using the kinetic model. Inspection of Table 3 showed that the values of \( E_a \) determined in 1 M HCl containing indole deri v a t e s are higher than that for uninhibited solution. The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage [29]. Moreover, the values obtained for norharmane are somewhat higher than those obtained for harmane and confirm the fact that the inhibitor efficiency of norharmane is slightly lower than that of harmane. Szauer and Brand explained that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the steel surface with increase in temperature [30]. Figure 7 showed a plot of ln \( \frac{I_{\text{corr}}}{T} \) versus 1/T with a slope of \(-\Delta H_a / R\) and an intercept (ln \( R/ Nh + \Delta S_a / R \)) from which the values of \( \Delta H_a \) and \( \Delta S_a \) were calculated, respectively. All estimated kinetic-thermodynamic parameters were tabulated also in Table 3. Inspection of these data revealed that the thermodynamic parameters (\( \Delta H_a \) and \( \Delta S_a \)) for dissolution reaction of C38 steel in 1 M HCl in the presence of both inhibitors are higher than that of in the absence of inhibitors.

The positive signs of \( \Delta S_a \) reflect the endothermic nature of the steel dissolution process suggesting that the dissolution of steel is slow in the presence of inhibitors [31]. Furthermore, the values obtained for norharmane are somewhat higher than those obtained for harmane and confirm the fact that the inhibitor efficiency of norharmane is slightly lower than that of harmane. One can notice that \( E_a \) and \( \Delta H_a \) values vary in the same way for both inhibitors (Table 3). The values of \( \Delta S_a \) were negative both in the absence and presence of inhibitors, implying that the activated complex represented the rate-determining step with respect to the association rather than the dissociation step. It means that a decrease in disorder occurred when proceeding from the reactants to the activated complex [30]. Also, the \( \Delta S_a \) shift can be explained as a result of the replacement process of water molecules during adsorption of organic inhibitor on the steel surface.

#### 3.2.2. Impedance Measurements

The corrosion behaviour of C38 steel in 1 M HCl solution in the presence of indole deri v a t e s was also investigated by EIS in the temperature range 25–55°C. The EIS of C38 steel electrode in 1 M HCl...
Table 3: Thermodynamic parameters calculated from Tafel plots for the adsorption of indole derivatives in 1 M HCl on the C38 steel at different temperatures.

| Concentration (mM) | Norharmane | Harmane |
|--------------------|------------|---------|
|                    | $E_a$ (kJ mol$^{-1}$) | $\Delta H_a$ (kJ mol$^{-1}$) | $\Delta S_a$ (J mol$^{-1}$ K$^{-1}$) | $E_a$ (kJ mol$^{-1}$) | $\Delta H_a$ (kJ mol$^{-1}$) | $\Delta S_a$ (J mol$^{-1}$ K$^{-1}$) |
| HCl                |             |         |                      |             |         |                      |
| 0.2                | 24.42       | 23.29   | $-119.48$            |             |         |                      |
| 0.4                | 31.73       | 30.60   | $-99.81$             | 31.20       | 30.07   | $-101.88$            |
| 0.8                | 33.40       | 32.27   | $-95.27$             | 35.18       | 34.05   | $-90.53$             |
| 1.2                | 37.99       | 36.85   | $-81.97$             | 36.89       | 35.76   | $-86.63$             |

Figure 8: Nyquist diagrams for C38 steel in 1 M HCl at different temperatures.

Figure 9: Nyquist diagrams for C38 steel in 1 M HCl containing 0.2 mM of norharmane at different temperatures.

Figure 10: Nyquist diagrams for C38 steel in 1 M HCl containing 0.2 mM of harmane at different temperatures.

Figure 11: Nyquist diagrams for C38 steel in 1 M HCl containing different concentrations of norharmane at 35$^\circ$C.

solution in the absence and in the presence of 0.2 mM of norharmane and harmane, at different temperatures, are shown in Figures 8, 9, and 10; representative example. Figure 11 shows the impedance plots of C38 steel electrode in 1 M HCl solution in the absence and presence of different concentrations of norharmane at 35$^\circ$C. It can be seen that, the size of the capacitive loop increased by increasing the concentration of norharmane. All the impedance spectra were measured at the corresponding open-circuit potentials. After analyzing the shape of the Nyquist plots, it is concluded that the curves obtained up to 45$^\circ$C approximated by a single capacitive semi-circles, showing that the corrosion process was mainly charge transfer controlled. The general shape of the curves is very similar for all concentrations studied. The diameter of Nyquist plots ($R_c$) decreases with increasing temperature for both inhibitors. For the most temperatures 45 and 55$^\circ$C, an inductive loop appeared at low-frequency
values. Similar observations were found for all concentrations studied. The presence of the LF inductive loop may be attributed to the relaxation process obtained by adsorption species like $\text{Cl}_{\text{ads}}$ and $\text{H}_{\text{ads}}^+$ on the electrode surface [32–35]. It may also be attributed to the adsorption of inhibitor on the electrode surface [36] or to the redissolution of the passivated surface at low frequencies [37]. The above impedance diagrams (Nyquist) contain depressed semicircles with the center under the real axis; such behaviors characteristic for solid electrodes and often referred to as frequency dispersion have been attributed to roughness and inhomogeneities of the solid surfaces, impurities [38–41]. Therefore, a constant phase element (CPE) instead of a capacitive element is used to get a more accurate fit of experimental data set. For analysis of the impedance spectra exhibiting one capacitive loop, the equivalent circuit (EC) given in Figure 12(a) was used to fit the experimental spectra while the EC shown in Figure 12(b) was used for the impedance spectra containing one capacitive loop and an inductive loop. Simulation of Nyquist plots with the above models shows excellent agreement with experimental loop and an inductive loop. Simulation of Nyquist plots with the experimental spectra while the EC shown in Figure 12(b) was used for the impedance spectra containing one capacitive loop and an inductive loop. Simulation of Nyquist plots with the above models shows excellent agreement with experimental data (Figures 12(a) and 12(b); representative example).

The parameters calculated with the application of these models are summarized in Tables 4 and 5. The values discussed show that the organic compounds investigated have inhibiting properties for all temperature values. This conclusion is based on the values of $R_{\text{ct}}$ in inhibitors presence. They are greater than those in 1 M HCl. The temperature rise leads to a decrease of $R_{\text{ct}}$ values. This is due, on one hand, to the increase of the rate of metal dissolution and, on the other hand, to the shift of the adsorption/desorption equilibrium towards the inhibitor’s desorption and hence to the decrease of surface coverage degree. The $n$ value almost decreases with temperature increase and this is interpreted as an evidence for surface inhomogeneity increase. The latter is attributed to the accelerated corrosion and the developed metal surface. At lower temperatures the inhibitors adsorb on the most active surface sites; this results in a decrease of surface inhomogeneity. The desorption, which is favored by high temperatures, will increase with this effect. The $C_{\text{dl}}$ value was calculated using (4) [42–44]:

$$C_{\text{dl}} = (A \cdot R_{\text{ct}}^{1-n})^{1/n}. \tag{4}$$

It is clear that the addition of harmene or norharmene causes a significant increase in $C_{\text{dl}}$ in the additive-free solution for all temperatures studied. As the double layer capacitance can be connected with the thickness of the layer of adsorbed inhibitor molecules at the interface and this dependence is of reverse proportionality; it follows that the thickness of the adsorption layer will decrease with temperature increase. Similar tendency was found for CPE constant ($A$) for all temperatures studied. It can be seen from Tables 2, 4, and 5 that the inhibition efficiencies calculated by both methods show the same trend. The IE (%) values decrease with increasing temperature and no difference of numerical values of inhibition efficiencies was observed at 25 and 35°C. However the results obtained at 45 and 55°C show a difference in numerical values obtained by both methods. This variation may be due to the difference between methods, which each method is realised differently with some conditions and assumptions.

To obtain the activation parameters from the impedance technique, values of $R_{\text{ct}}$ and those of $\beta_a$ and $\beta_c$ obtained at different temperatures were used to calculate values of $I_{\text{corr}}$ according to Stern-Geary [45] equation:

$$I_{\text{corr}} = \frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c) \left( \frac{1}{R_{\text{ct}}} \right)}. \tag{5}$$

Figures 13 and 14 show the Arrhenius plot for the results obtained in 1 M HCl solutions in the presence of harmene, representative example. Similar plots are obtained in the case of norharmene. The results are in good agreement with those obtained from polarization studies and show the same trend. The difference of numerical values of $\Delta S_a$ determined from the two techniques may be attributed to the different methods that have been used for the determination of the corrosion rates.
### Table 4: Values of the elements of equivalent circuit required for fitting the EIS for C38 steel immersed in the presence and absence of norharmane at different temperatures.

| Temp (°C) | $R_d$ (Ω cm$^2$) | $A10^4$ (Ω$^{-1}$ s$^6$ cm$^{-2}$) | $n$ | $C_{dl}$ (µF cm$^{-2}$) | $L$ (H cm$^{-2}$) | $R_t$ (Ω cm$^2$) | IE (%) | $\theta$ |
|-----------|-----------------|-------------------|-----|-----------------|---------------|----------------|--------|---------|
| Blank     |                 |                   |     |                 |               |               |        |         |
| 25        | 49 ± 0.02       | 9.5 ± 0.73        | 0.853 ± 0.014 | 546             | —             | —             | —      | —       |
| 35        | 17 ± 0.64       | 20.5 ± 4.21       | 0.795 ± 0.421 | 863             | 18 ± 1.87     | 6 ± 1.26      | —      | —       |
| 45        | 12 ± 0.94       | 43.5 ± 3.56       | 0.745 ± 0.362 | 1583            | 15 ± 2.35     | 3 ± 0.87      | —      | —       |
| 55        | 3 ± 0.96        | 72.8 ± 5.64       | 0.735 ± 0.093 | 1834            | 10 ± 8.54     | 2 ± 1.25      | —      | —       |
| 0.2 mM    |                 |                   |     |                 |               |               |        |         |
| 25        | 148 ± 0.91      | 2.91 ± 0.02       | 0.871 ± 0.008 | 183             | —             | —             | 67     | 0.6689  |
| 35        | 53 ± 0.43       | 4.37 ± 0.25       | 0.836 ± 0.053 | 209             | —             | —             | 60     | 0.6038  |
| 45        | 30 ± 0.35       | 10.88 ± 3.65      | 0.765 ± 0.059 | 380             | 25 ± 4.61     | 9 ± 1.78      | 50     | 0.5000  |
| 55        | 10 ± 0.65       | 13.35 ± 1.75      | 0.815 ± 0.120 | 501             | 2 ± 0.40      | 2 ± 1.37      | 50     | 0.5000  |
| 0.4 mM    |                 |                   |     |                 |               |               |        |         |
| 25        | 238 ± 1.65      | 1.89 ± 0.19       | 0.872 ± 0.005 | 120             | —             | —             | 79     | 0.7941  |
| 35        | 95 ± 0.89       | 3.53 ± 0.14       | 0.829 ± 0.052 | 175             | —             | —             | 78     | 0.7789  |
| 45        | 55 ± 3.04       | 6.19 ± 0.94       | 0.790 ± 0.032 | 252             | 10 ± 1.20     | 15 ± 1.60     | 73     | 0.7273  |
| 55        | 14 ± 0.93       | 8.84 ± 2.31       | 0.831 ± 0.054 | 362             | 3 ± 0.21      | 2 ± 0.32      | 64     | 0.6429  |
| 0.8 mM    |                 |                   |     |                 |               |               |        |         |
| 25        | 514 ± 1.18      | 0.84 ± 0.03       | 0.883 ± 0.012 | 55              | —             | —             | 90     | 0.9047  |
| 35        | 180 ± 1.04      | 3.18 ± 0.13       | 0.825 ± 0.045 | 173             | —             | —             | 82     | 0.8235  |
| 45        | 85 ± 1.56       | 5.01 ± 0.30       | 0.814 ± 0.023 | 244             | 7 ± 0.27      | 14 ± 0.90     | 79     | 0.7857  |
| 55        | 22 ± 1.55       | 7.13 ± 0.47       | 0.809 ± 0.251 | 267             | 6 ± 1.60      | 2 ± 1.10      | 77     | 0.7727  |
| 1.2 mM    |                 |                   |     |                 |               |               |        |         |
| 25        | 641 ± 1.73      | 0.66 ± 0.02       | 0.887 ± 0.010 | 44              | —             | —             | 92     | 0.9236  |
| 35        | 245 ± 0.55      | 2.3 ± 0.78        | 0.803 ± 0.072 | 114             | —             | —             | 91     | 0.9143  |
| 45        | 123 ± 0.81      | 2.9 ± 0.57        | 0.802 ± 0.140 | 127             | —             | —             | 88     | 0.8780  |
| 55        | 25 ± 0.41       | 4.46 ± 0.17       | 0.804 ± 0.023 | 149             | 6 ± 0.50      | 3 ± 1.43      | 80     | 0.8000  |

**Figure 13:** Arrhenius plots ln $I_{corr}$ versus $1/T$ of 1 M HCl and at different concentrations of harmane.

**Figure 14:** Arrhenius plots of corrosion ln($I_{corr}/T$) versus $1/T$ of 1 M HCl at different concentrations of harmane.

### 3.3. Adsorption Isotherm

Inhibition by organic compounds is, mainly, due to their ability to adsorb onto a metal surface to form a protective film. The establishment of isotherms that describe the adsorption behaviour of corrosion inhibitor is important as they provide important information about the nature of metal-inhibitor interaction. It has been reported that the adsorption of the inhibitor molecules depends on a variety of factors such as the presence of functional groups (either electron donating or withdrawing), charge distribution at the donor atom, the $\pi$ orbital character of donating electrons, the nature of substrate metal and the type of interaction between organic molecules and the metallic surface as well.

The most frequently used isotherms are Langmuir (6), Temkin (7), and Frumkin (8). All these isotherms are tested. In all cases, the degree of surface coverage ($\theta$) is plotted as a function of the inhibitor concentration ($C_{inh}$). In the present study, values of $\theta$ are obtained from $I_{corr}$ and $R_d$. The significance of the adsorption isotherm was obtained by calculating the correlation coefficients ($R^2$). As an example,
Table 5: Values of the elements of equivalent circuit required for fitting the EIS for C38 steel immersed in the presence and absence of harmamine at different temperatures.

| Temp (°C) | $R_c$ (Ω cm²) | $A10^4$ ($Ω^{-1}$ s⁰ cm⁻²) | $n$ | $C_{dl}$ (μF cm⁻²) | $L$ (H cm⁻²) | $R_L$ (Ω cm²) | IE (%) | $\theta$ |
|-----------|----------------|---------------------------|-----|-------------------|--------------|--------------|---------|----------|
| Blank     |                |                           |     |                   |              |              |         |          |
| 25        | 49 ± 0.02      | 9.5 ± 0.73                | 0.853 ± 0.014 | 546               | —            | —            | —       | —        |
| 35        | 17 ± 0.64      | 20.5 ± 4.21               | 0.795 ± 0.421 | 863               | 18 ± 1.87    | 6 ± 1.26    | —       | —        |
| 45        | 12 ± 0.94      | 43.5 ± 3.56               | 0.745 ± 0.362 | 1583              | 15 ± 2.35    | 3 ± 0.87    | —       | —        |
| 55        | 3 ± 0.96       | 72.8 ± 5.64               | 0.735 ± 0.093 | 1834              | 10 ± 8.54    | 2 ± 1.25    | —       | —        |
| 0.2 mM    |                |                           |     |                   |              |              |         |          |
| 25        | 181 ± 0.10     | 4.82 ± 0.19               | 0.866 ± 0.042 | 330               | —            | —            | 73      | 0.7293   |
| 35        | 73 ± 0.61      | 6.92 ± 0.44               | 0.816 ± 0.501 | 353               | —            | —            | 71      | 0.7123   |
| 45        | 50 ± 1.23      | 9.73 ± 0.27               | 0.805 ± 0.062 | 468               | 25 ± 8.41    | 8 ± 3.02    | 70      | 0.7000   |
| 55        | 16 ± 0.81      | 19.5 ± 4.03               | 0.719 ± 0.501 | 503               | 11 ± 0.34    | 3 ± 0.8    | 69      | 0.6875   |
| 0.4 mM    |                |                           |     |                   |              |              |         |          |
| 25        | 321 ± 0.97     | 3.71 ± 0.37               | 0.870 ± 0.036 | 270               | —            | —            | 85      | 0.8474   |
| 35        | 129 ± 0.65     | 5.29 ± 0.09               | 0.804 ± 0.074 | 275               | —            | —            | 84      | 0.8372   |
| 45        | 82 ± 1.54      | 7.95 ± 1.02               | 0.784 ± 0.128 | 375               | 25 ± 1.74    | 9 ± 1.5    | 82      | 0.8171   |
| 55        | 21 ± 2.31      | 10.31 ± 2.13              | 0.824 ± 0.054 | 455               | 21 ± 0.58    | 4 ± 1.3    | 76      | 0.7619   |
| 0.8 mM    |                |                           |     |                   |              |              |         |          |
| 25        | 537 ± 0.17     | 2.52 ± 0.27               | 0.873 ± 0.051 | 188               | —            | —            | 91      | 0.9088   |
| 35        | 218 ± 0.56     | 3.96 ± 0.72               | 0.795 ± 0.104 | 211               | —            | —            | 90      | 0.9037   |
| 45        | 136 ± 1.53     | 4.37 ± 0.73               | 0.811 ± 0.091 | 226               | —            | —            | 89      | 0.8897   |
| 55        | 27 ± 1.20      | 8.64 ± 2.03               | 0.780 ± 0.035 | 299               | 5 ± 0.12    | 2 ± 0.76   | 81      | 0.8148   |
| 1.2 mM    |                |                           |     |                   |              |              |         |          |
| 25        | 735 ± 0.68     | 1.92 ± 0.12               | 0.883 ± 0.036 | 148               | —            | —            | 93      | 0.9333   |
| 35        | 293 ± 0.54     | 3.28 ± 0.27               | 0.814 ± 0.037 | 192               | —            | —            | 93      | 0.9283   |
| 45        | 182 ± 0.53     | 4.33 ± 0.07               | 0.826 ± 0.051 | 254               | —            | —            | 92      | 0.9176   |
| 55        | 32 ± 0.66      | 7.36 ± 1.91               | 0.783 ± 0.102 | 260               | 11 ± 1.54   | 5 ± 0.8    | 84      | 0.8438   |

Figure 15: Langmuir adsorption plots for C38 steel in 1M HCl containing different concentrations of norharmamine at 55°C.

Figures 15, 16, and 17 represent fitting of impedance and polarization data obtained for C38 electrode in 1M HCl containing various concentrations of norharmamine at 55°C to Langmuir, Temkin, and Frunkin isotherms. The best correlation between the experimental results, obtained from the three tested isotherm functions, was obtained using Langmuir isotherm (the strong correlation $R^2 = 0.999$ for both methods). Similar observations were found for all temperatures studied. The simplest, being the Langmuir isotherm, is based on assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites being occupied or not [46]. Consider

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \quad \text{(Langmuir isotherm),} \quad (6)$$

$$\left( \frac{\theta}{1-\theta} \right) \exp(-2a\theta) = KC_{inh} \quad \text{(Frumkin isotherm),} \quad (7)$$

$$\exp(-2a\theta) = KC_{inh} \quad \text{(Temkin isotherm),} \quad (8)$$
where \( K \) is the binding constant of the adsorption reaction and \( \alpha \) is the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the surface.

The well known thermodynamic adsorption parameters are the standard free energy of adsorption \( (\Delta G_{\text{ads}}^0) \), the heat of adsorption \( (\Delta H_{\text{ads}}^0) \), and the standard entropy of adsorption \( (\Delta S_{\text{ads}}^0) \). These quantities can be calculated depending on the estimated values of \( K \) from adsorption isotherms at different temperatures.

The constant of adsorption, \( K \), is related to the standard free energy of adsorption, \( \Delta G_{\text{ads}}^0 \), with the following equation:

\[
K = \frac{1}{55.5} \exp \left( \frac{-\Delta G_{\text{ads}}^0}{RT} \right).
\]

The value 55.5 in the above equation is the concentration of water in solution in \text{mol L}^{-1} \ [47]. The \( \Delta G_{\text{ads}}^0 \) values at all studied temperatures can be calculated. Then, the obtained \( \Delta G_{\text{ads}}^0 \) values plotted versus \( T \) (Figures 18 and 19) gave the heat of adsorption \( \Delta H_{\text{ads}}^0 \) and the standard adsorption entropy \( \Delta S_{\text{ads}}^0 \) in accordance with the basic equation:

\[
\Delta G_{\text{ads}}^0 = \Delta H_{\text{ads}}^0 - T\Delta S_{\text{ads}}^0.
\]  \( \text{(10)} \)

All thermodynamic adsorption parameters estimated from both methods for indole derivatives on C38 steel from 1 M of HCl solution are listed in Tables 6, 7, and 8. The entire values of thermodynamic adsorption obtained by both methods are in good agreement and follow the same trend. The negative values of \( \Delta G_{\text{ads}}^0 \) ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface. The calculated \( \Delta G_{\text{ads}}^0 \) values indicate the physical nature of adsorption of norharmane and harmane. The dependence of \( \Delta G_{\text{ads}}^0 \) on experimental temperature can be summarized in two cases as follows.

(a) Value of \( \Delta G_{\text{ads}}^0 \) becomes less negative with increasing temperature indicating the occurrence of exothermic process at which adsorption was unfavourable with increasing reaction temperature as the result of the inhibitor desorption from the steel surface \[48\].

(b) Value of \( \Delta G_{\text{ads}}^0 \) becomes more negative with increasing temperature indicating the occurrence of endothermic process at which increasing temperature facilitates inhibitor adsorption.

The first case (a) is observed for the adsorption of the studied inhibitor species on C38 steel surface from HCl solution depending on the applied temperature range (Tables 7 and 8), indicating the occurrence of exothermic adsorption processes. Also, it is noteworthy feature that the calculated value of \( \Delta G_{\text{ads}}^0 \) at 25°C in the case of harmane is greater than that in the case of norharmane, which means that the electrostatic interaction between the harmane and the steel surface is stronger. This is in good agreement with the range of the inhibition efficiency values obtained at 25°C from both impedance and polarisation measurements. However in the temperature range 35–55°C, there is an observable contradiction between the results of inhibition efficiency values and the finding of the calculated value of \( \Delta G_{\text{ads}}^0 \). The negative sign of \( \Delta H_{\text{ads}}^0 \) reveals that the adsorption of inhibitor molecules is
Table 6: Thermodynamic parameters calculated from IES for the adsorption of indole derivatives in 1M HCl on the C38 steel at different temperatures.

| Temp. (°C) | Norharmane | Harmame |
|------------|------------|----------|
| HCl        |            |          |
| 25         | 28.00      | 26.87    | -131.04   | -120.35   | -105.77  |
| 35         | 32.78      | 31.65    | -105.35   | 32.82     | -131.67  |
| 45         | 33.34      | 32.22    | -116.44   | 34.05     | -121.55  |
| 55         | 38.00      | 36.87    | -104.36   | 37.05     | -119.20  |

Table 7: Thermodynamic parameters calculated from IES for the adsorption of indole derivatives on C38 steel in 1M HCl at different temperatures.

| Temp. (°C) | Norharmane | Harmame |
|------------|------------|----------|
| 25         | -18.00     | -14.63   |
| 35         | -14.46     | -8.18    | 20.2      | -15.03    |
| 45         | -14.50     | -15.44   |
| 55         | -14.90     | -15.69   |

Table 8: Thermodynamic parameters calculated from LP for the adsorption of indole derivatives on C38 steel in 1M HCl at different temperatures.

| Temp. (°C) | Norharmane | Harmame |
|------------|------------|----------|
| 25         | -14.59     | -14.71   |
| 35         | -14.84     | -8.45    | 20.7      | -15.04    |
| 45         | -15.06     | -15.23   |
| 55         | -15.21     | -15.46   |

It is an exothermic process. Generally, an exothermic adsorption process suggests either physisorption or chemisorption while endothermic process is attributed to chemisorption [17]. Moreover, the values obtained for harmame are somewhat higher than those obtained for norharmane. This result indicated that harmame is more strongly adsorbed on the steel surface. This is in good agreement with the results obtained from impedance and polarization measurements. The results show a great difference between the value of $\Delta H^0_{\text{ads}}$ for harmame obtained from EIS ($-3.88 \text{ kJ mol}^{-1}$) and from LP ($-7.40 \text{ kJ mol}^{-1}$). This difference may be due to the accuracy of linear regression between $\Delta G^0_{\text{ads}}$ and $T$, where the linear regression coefficient ($R^2$) obtained from EIS is 0.9905 and from LP is 0.9254. The $\Delta S^0_{\text{ads}}$ values in the presence of indole derivatives are large and positive, meaning that an increasing in disordering takes place in going from reactants to the metal-adsorbed species reaction complex [49].

The integrated version of the Van’t Hoff equation expressed by (11) can be also deduced the $\Delta H^0_{\text{ads}}$ value [50]:

$$\ln K = \frac{-\Delta H^0_{\text{ads}}}{RT} + \text{constant.}$$

(11)

Figures 20 and 21 show the plot of ln $K$ versus $1/T$ from both methods which gives straight lines with slopes of $(-\Delta H^0_{\text{ads}}/R)$ and intercepts of $(-\Delta S^0_{\text{ads}}/R + \ln1/55.5)$. The calculated $\Delta H^0_{\text{ads}}$ using the Van’t Hoff equation are $-8.25$ (from IES) and $-8.41$ (from LP) kJ mol$^{-1}$ for norharmane. For harmame, the calculated $\Delta H^0_{\text{ads}}$ are $-3.88$ (from IES) and $-7.40$ (from LP) kJ mol$^{-1}$. These results confirm the exothermic behaviour of the adsorption of the inhibitors on the steel surface, therefore, the physisorption process. Values of
The structural parameters calculated show decrease of the dispersed capacitance. For the most temperatures 45 and 293 ∘C, an inductive loop appeared at low-frequency values. The structural parameters calculated show decrease of the resistance $R_a$ and increase of the capacitance. The inhibition is attributed to physisorption of the heterocyclic compound on the steel surface and blocking its active sites. The activation parameters of corrosion process such as activation energy, $E_a$, activation enthalpy, $\Delta H_a$, and activation entropy, $\Delta S_a$, were calculated from the dependence of corrosion rates on the temperature from polarization and impedance measurements. Also, the thermodynamic adsorption parameters were calculated and commented on from polarization and impedance measurements. The adsorption of indole derivatives on the mild steel surface in 1M HCl obeyed the Langmuir adsorption isotherm model at all studied temperatures.

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