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Gravimetric and Electrochemical Evaluation of 1-allyl-1*H*-indole-2,3-dione of Carbon Steel Corrosion in Hydrochloric Acid

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The present paper brings report on a newly observed effect of corrosion inhibition of 1-allyl- 1H-indole-2,3-dione (Ind1) against carbon steel corrosion, in hydrochloric acid using gravimetric and electrochemical measurements. Ind1 inhibited the corrosion of carbon steel in 1.0 M HCl solution and the inhibition efficiency increased with increasing concentration of this inhibitor but decreased with increasing temperature. Polarization measurements showed the mixed type behavior of this inhibitor. Changes in impedance parameters suggested the adsorption of Ind1 on the carbon steel surface, leading to the formation of protective films. The high inhibition efficiency was attributed to the blocking of active sites by adsorption of inhibitor molecules on the steel surface. It was shown that adsorption of 1-allyl- 1H-indole-2,3-dione (Ind1) on the steel surface is consistent with the Langmuir adsorption isotherm and the obtained standard free energy of adsorption (ΔG°_{ads}) values indicate that the corrosion inhibition of the carbon steel in 1.0 M HCl is depends on chemisorption.

Keywords: Indole, Steel, Corrosion inhibition, Polarization curves, EIS.

1. INTRODUCTION

Acid solutions are widely used in industry [1-5]. The corrosion of steel in acidic solution receives considerable concern. Corrosion inhibitors are used to reduce the corrosion rates of metallic materials in acidic media [5]. Organic compounds containing nitrogen, sulphur, and oxygen are usually used as inhibitors against the corrosion of metals in acidic media [6-23].

It is generally accepted that the primary step in the protecting action of an inhibitor in the acid metal corrosion is adsorption of the organic molecule onto the metal surface, which is usually oxide-free. The adsorption requires the existence of attractive forces between the metal surface (adsorbent) and the organic molecule (adsorbate). According to the type of forces, adsorption can be physisorption, chemisorptions or a combination of both [24,25]. Physisorption is weak undirected interaction and is due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of metal. A peculiarity of physisorption is that the ions or dipoles are non in direct physical contact with the metal. A layer of water molecules separates the metal from the ions or dipoles. Physisorption involves rapid interaction between adsorbent and adsorbate but it is also easily removed from surface with the temperature increase.

Chemisorption involves charge sharing or charge transfer from the adsorbate to adsorbent in order to form a coordinate type of bond. The adsorbent is in contact with the metal surface. It may take place in presence of heteroatoms (P, Se, S, N, O) with lone-pair electrons and/or π electrons due to the presence of multiple bonds or aromatic rings in the adsorbate. The organic inhibitors used generally have reactive functional groups which can be the sites for the chemisorption process. Chemical adsorption has a higher adsorption energy than physical adsorption and, hence, usually is irreversible. It takes place more slowly than physisorption and the temperature dependence shows higher inhibition efficiencies at higher temperatures [26-29]. Previous studies have shown that indole and some its derivatives display good inhibiting effects on steel corrosion in acid solutions [30-33].

Hence, in the present study 1-allyl- 1H-indole-2,3-dione (Ind1), is selected. The choice of this compound was based on the consideration that this compound contains many π-electrons and hetero atoms which induce greater adsorption of the inhibitor compared with other compounds organic.

By considering the remarks mentioned above, in the present work, the inhibition effect of Ind1 on the corrosion of carbon steel in 1.0 M HCl solution at 308-343K was studied using weight loss, potentiodynamic polarisation curves and electrochemical impedance spectroscopy (EIS) methods. The adsorption isotherm of inhibitor on steel surface was determined. Both standard thermodynamic parameters and kinetic parameters are calculated and discussed in detail. A probable inhibitive mechanism is presented from the viewpoint of adsorption. The chemical structure of the studied indole derivative is given in Fig 1.

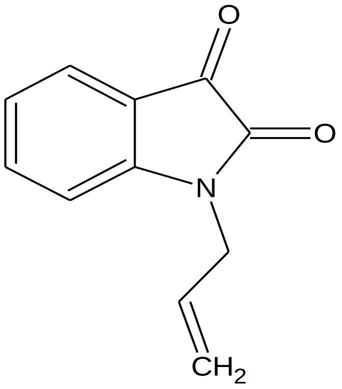

Figure 1. The chemical structure of the studied indole compound.

2. EXPERIMENTAL METHODS

2.1. Materials

The steel used in this study is a carbon steel (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe). The carbon steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600 and 1200); rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5 min, washed again with bidistilled water and then dried at room temperature before use. The acid solutions (1.0 M HCl) were prepared by dilution of an analytical reagent grade 37 % HCl with double-distilled water. The concentration range of Ind1 employed was 10^{-6} M to 10^{-3} M.

2.2. Measurements

2.2.1. Weight loss measurements

The steel sheets of 1.6 × 1.6 × 0.07 cm dimensions were abraded with different grades of emery papers, washed with distilled water, degreased with acetone, dried and kept in a desiccator. After weighing accurately by a digital balance with high sensitivity the specimens were immersed in solution containing 1.0 M HCl solution with and without various concentrations of the investigated inhibitor. At the end of the tests, the specimens were taken out, washed carefully in ethanol under ultrasound until the corrosion products on the surface of carbon steel specimens were removed thoroughly, and then dried, weighed accurately. Duplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed calculation of the mean corrosion rate in mg cm^{-2} h^{-1}.

2.2.2. Electrochemical measurements

The electrochemical measurements were carried out using Volta lab (Tacussel- Radiometer PGZ 100) potentiostate and controlled by Tacussel corrosion analysis software model (Voltamaster 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode of surface area of 1 cm^2. The working electrode was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 minutes to a establish steady state open circuit potential (E_{ocp}). After measuring the E_{ocp}, the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 308 K. The polarization curves were obtained in the potential range from -750 to -200 mV(SCE) with 1 mV s^{-1} scan rate. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit 0.1 Hz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the *x*-axis.

3. RESULTS AND DISCUSSION

3.1. Polarization curves

Fig. 2 shows Tafel polarization curves of carbon steel in hydrochloric acid in the absence and presence of different concentrations of Ind1 at 308K. The associated corrosion parameters such as E_{corr}, cathodic Tafel slopes (β_c) and corrosion current density (I_{corr}) are listed in Table 1. In this case, the inhibition efficiency is defined as follows:

$$IE_I(\%) = \frac{I_{\mathrm{corr}} - I_{\mathrm{corr(inh)}}}{I_{\mathrm{corr}}} \times 100 \tag{1}$$

where I_{corr} and $I_{\mathrm{corr(inh)}}$ are the corrosion current densities for steel electrode in the uninhibited and inhibited solutions, respectively.

It is clear that the addition of Ind1 causes a decrease in the corrosion rate, i.e. shifts the cathodic and anodic curves to lower values of current densities. Namely, both cathodic and anodic reactions of carbon steel electrode corrosion are inhibited by the inhibitor in acidic medium. This may be ascribed to adsorption of inhibitor over the corroded surface of carbon steel [34]. It follows from the date of Table 1 that the corrosion current, I_{corr} decreases, while IE_I (%) enhances with increase in inhibitor concentration. The decrease in the corrosion current density was observed for the Ind1, corresponding to a maximum efficiency of 94.9% at 1×10^{-3} M.

Further inspection of Table 1 reveals that the presence of Ind1 does not remarkably shift the E_{corr}, therefore, the selected compound can be described as mixed-type inhibitor for carbon steel corrosion in 1.0 M HCl, and the inhibition of the compound on carbon steel is caused by adsorption, namely, the inhibition effect results from the reduction of the reaction area on the surface of the carbon steel [35]. The value of β_c slight changed, indicates that the cathodic corrosion mechanism of steel does not change. As it is shown in Fig. 2, cathodic current–potential curves give rise to parallel Tafel lines, which indicate that oxygen reduction reaction is activation controlled and that the addition of the Ind1 does not modify the mechanism of this process [36]. The results demonstrate that the oxygen reduction is inhibited and that the inhibition efficiency increases with inhibitor concentration.

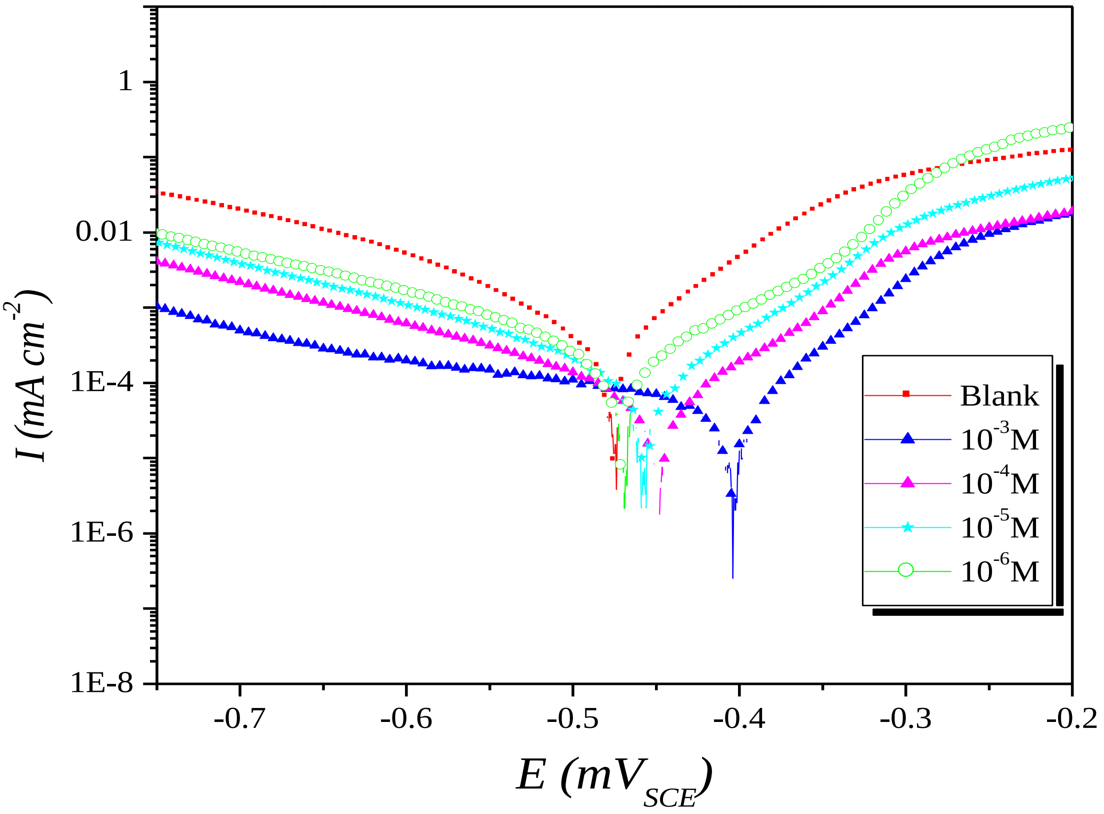

Figure 2. Polarisation curves of carbon steel in 1.0 M HCl for various concentrations of Ind1.

Table 1. Polarization data of carbon steel in 1.0 M HCl without and with addition of inhibitor at 308 K.

Inhibitor	Conc (M)	-E_{corr} (mV/SCE)	-β_c (mV dec^{-1})	I_{corr} (μA cm^{-2})	EI_I (%)
HCl	1	475.9	176.0	1077.8	-
Ind1	10^{-3}	402.5	220.3	55.1	94.9
	10^{-4}	449.4	192.8	78.6	92.7
	10^{-5}	458.5	169.9	161.5	85.0
	10^{-6}	469.8	157.3	271.1	74.9

3.2. Electrochemical impedance spectroscopy

The impedance diagrams obtained after 0.5 h of exposure of the samples at 308K in inhibited and uninhibited 1.0 M HCl containing various concentrations of Ind1 are shown in Fig. 3. All the obtained plots show only one capacitive loop and the diameter of the semicircle increases with increasing the inhibitor concentration suggesting that the formed inhibitive film was strengthened by the addition of inhibitor [37]. The above Nyquist plots contain depressed semicircles with the center under the real axis, such behavior characteristic for solid electrodes and often referred to as frequency dispersion has been attributed to different physical phenomena such as roughness and inhomogeneities of the solid surfaces [38], impurities, dislocations, grain boundaries [39], fractality [40], distribution of the active sites, adsorption of inhibitors [41].

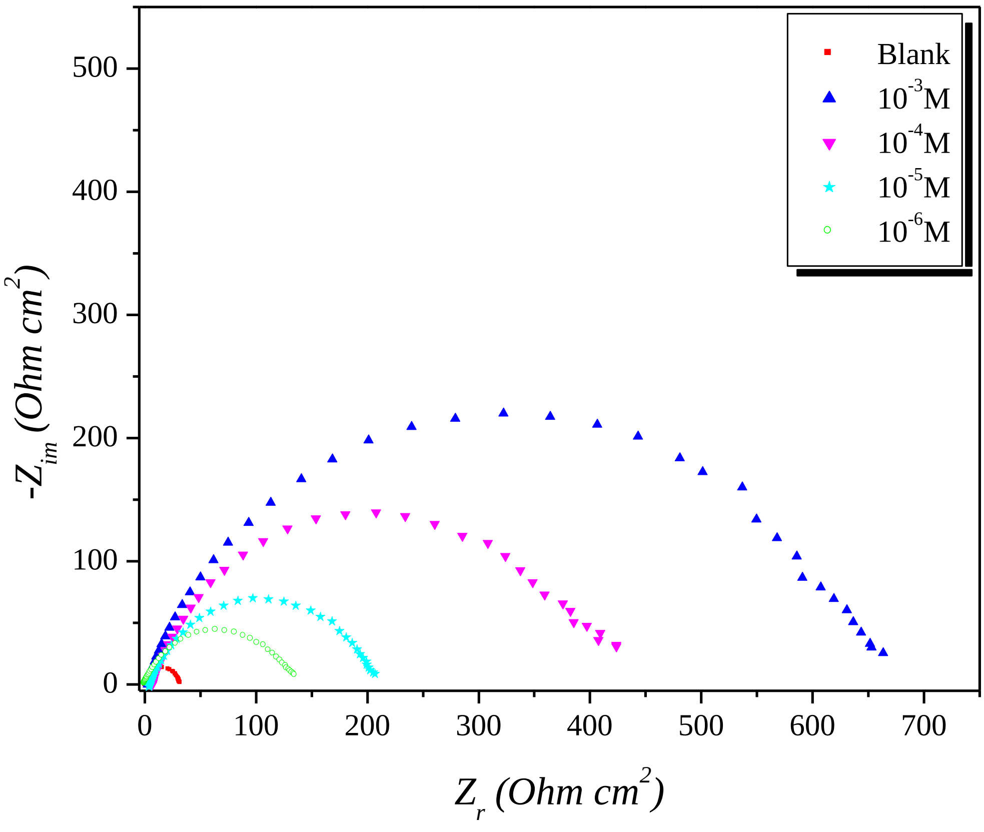

Figure 3. Nyquist diagrams for carbon steel in 1.0 M HCl containing different concentrations of Ind1 at 308 K.

Therefore, a constant phase element (CPE) instead of a capacitive element is used to get amore accurate fit of experimental data set. The impedance function of a CPE is defined by the mathematical expression given below [42]:

$$Z_{CPE} = A^{-1} (i\,\omega)^{-n} \qquad (2)$$

where A is the CPE constant (in Ω^{-1} S^n cm^{-2}), ω is the sine wave modulation angular frequency (in rad s^{-1}), $i^2 = -1$ is the imaginary number, and n is an empirical exponent ($0 \leq n \leq 1$) which measures the deviation from the ideal capacitive bahaviour [43].

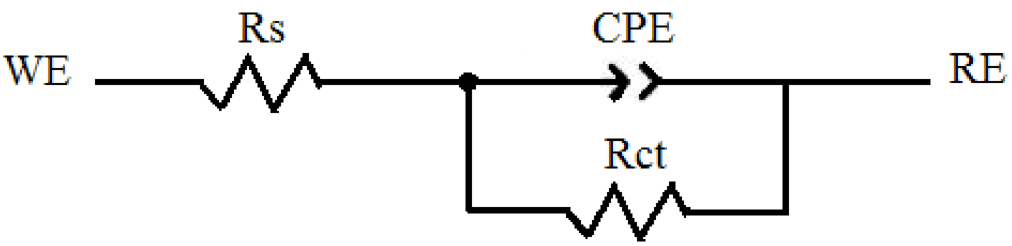

Figure 4. The electrochemical equivalent circuit used to fit the impedance measurements.

The impedance parameters such as the double layer capacitance (C_{dl}), the charge-transfer resistance (R_{ct}), the solution resistance (R_s), the constant phase element (A) and the exponent (n) derived from Nyquist diagrams are given in Table 2. These parameters were calculated from the non-linear least square fit of the equivalent circuit shown in Fig. 4, which has been previously used to evaluate the inhibitor mechanism of organic inhibitor for carbon steel in 1.0 M HCl [44].

Table 2. Impedance parameters for corrosion of steel in 1.0 M HCl in the absence and presence of different concentrations of Ind1 at 308 K.

Conc (M)	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	n	A×10^{-4} ($s^n\ \Omega^{-1}cm^{-2}$)	C_{dl} (μF cm^{-2})	IE_{Rct} (%)
Blank	1.67	29.66	0.91	0.14612	85.31	-----
10^{-3}	3.13	624.5	0.82	0.34890	15.06	95.2
10^{-4}	6.41	400.6	0.79	0.95070	39.88	92.6
10^{-5}	2.08	201.8	0.79	1.45760	57.09	85.3
10^{-6}	0.41	133.5	0.74	2.72170	84.91	77.8

Simulation of bode plot with above model shows excellent agreement with experimental data (Fig. 5, representative example). It means that the suggested equivalent circuit model, presented in Fig. 4, could reasonably represent the charge-transfer and metal/solution interface features related to the corrosion process of carbon steel in 1.0 M HCl solution containing Ind1. In Table 2 the calculated C_{dl} derived from the CPE are also presented, by using the following equation [45]:

$$C_{dl} = (AR_{ct}^{1-n})^{1/n} \qquad (3)$$

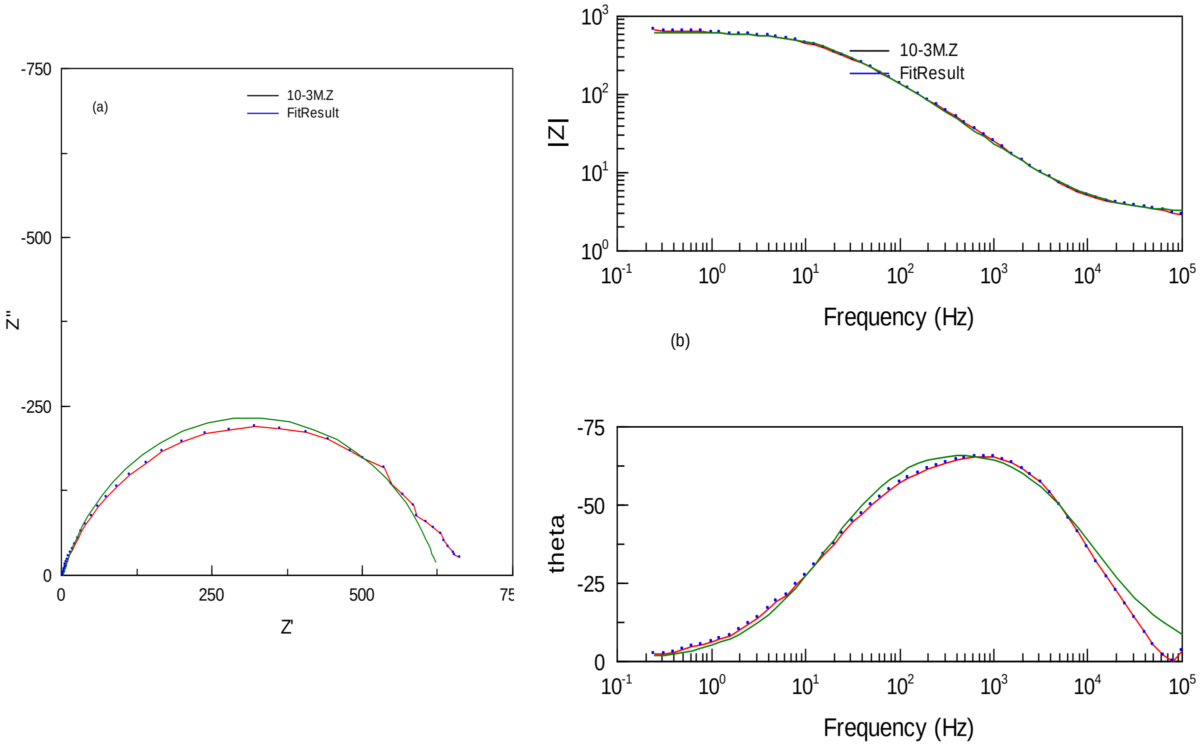

Figure 5. EIS Nyquist (a) and Bode (b) plots for carbon steel/1.0 M HCl + 10^{-3}M Ind1 interface: dotted lines experimental data; dashed line calculated.

Data in Table 2 shows that additional Ind1 inhibits the corrosion of carbon steel in 1.0 M HCl. The inhibition efficiency increased by increasing the concentration of the studied inhibitor. The inhibition efficiency is calculated using charge transfer resistance from equation [38]:

$$IE_{Rct}(\%) = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \qquad (4)$$

where R_{ct} and $R_{ct(inh)}$ are the charge transfer resistance values in absence and presence of inhibitor for carbon steel in 1.0 M HCl, respectively.

By increasing the inhibitor concentration the R_{ct} values increase but C_{dl} values decrease. The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The decrease in the C_{dl} value is due to the adsorption of the inhibitor on the steel surface, which displace the water molecule and others ions originally adsorbed on the surface [46]. The adsorption of the inhibitor on carbon steel surface can occur either directly on the basis of donor–acceptor interaction between the π electrons (of the double bonds, pyrrolidine ring and benzene ring) and the vacant d orbitals of steel surface atoms or interaction of them with already adsorbed chloride ions as proposed [47]. The inhibition efficiencies calculated from ac impedance results show the same trend as those obtained from polarization curves.

3.3. Gravimetric study

3.3.1. Effect of concentration inhibitor

The corrosion rate of carbon steel specimens after exposure to 1.0 M HCl solution with and without the addition of various concentrations of inhibitor was calculated in mg cm^{-2} h^{-1} and the data obtained are given in Table 3. The corrosion rate, ρ_{WL} (mg cm^{-2} h^{-1}), IE_{WL} of each concentration were calculated using the following equations.

$$\rho_{WL} = \left[\frac{w_1 - w_2}{At_\infty}\right] \qquad (5)$$

$$IE_{WL}\% = \left[1 - \frac{\rho_{WL}}{\overset{\circ}{\rho}_{WL}}\right] \times 100 \qquad (6)$$

where w_1 is the weight of the specimen before corrosion, w_2 is the weight of the specimen after corrosion (mg), A is the surface area of the specimen (cm^2) and t_∞ is the final immersion time (h), $\overset{\circ}{\rho}_{WL}$ and ρ_{WL} are the corrosion rates in absence and presence of inhibitor. The corrosion rate values (in g m^{-2} h^{-1}) decrease as the inhibitor concentrations increase, i.e. the corrosion inhibition enhances with the inhibitor concentration. This result may be due to the fact that the adsorption amount and the coverage of inhibitor on the carbon steel increase with the inhibitor concentration, which shields the carbon steel surface efficiently from the medium [48]. Table 3 indicates that the IE_{WL}% values obtained from the weight loss measurements were slightly higher than those obtained based on other techniques. This indicates that the adsorption of Ind1 is not strongly dependent on the potential, in contrast to the results obtained through the polarization resistance. On the other hand, the high $IE_{WL}\%$ values found indicate a strong adsorption favored by the long duration of the experiments. Therefore, the weight loss experiments confirmed the electrochemical results regarding the adsorption of this compound on the carbon steel surface forming a protective film barrier.

Table 3. Corrosion parameters obtained from weight loss measurements for carbon steel in 1.0 M HCl containing various concentration of inhibitor at 308 K.

Inhibitor	Conc (M)	ρ_{WL} (mg/cm^2 h)	IE_{WL} (%)	θ
Blank	1	1.070	-----	-----
Ind1	1×10^{-3}	0.030	97.2	0.972
	5×10^{-4}	0.045	95.8	0.958
	1×10^{-4}	0.074	93.1	0.931
	1×10^{-5}	0.149	86.1	0.861
	1×10^{-6}	0.248	76.8	0.768

3.3.2. Effect of temperature

To evaluate the adsorption of Ind1 and activation parameters of the corrosion processes of steel in acidic media, weight loss measurements are investigated in the absence and presence of inhibitor and also in the range of temperature 308-343K (see Table 4). In the studied temperature range, the corrosion rates were found to increase with the increase in the temperature for both inhibited and uninhibited acid solutions while they decreased with the increase of inhibitor concentration for a given temperature. The temperature dependence of the corrosion rate (ρ_{WL}) can be expressed by Arrhenius equation:

$$\rho_{WL} = A\exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

where ρ_{WL} is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature, and A is the frequency factor. The fractional surface coverage θ can be easily determined from weight loss measurements by the ratio IE_{WL}% / 100 if one assumes that the values of IE_{WL}% do no differ substantially from θ.

Table 4. Various corrosion parameters for carbon steel in 1.0 M HCl in the absence and the presence of optimum concentration of Ind1 at different temperatures after 1h.

Temp (K)	Inhibitor	ρ_{WL} (mg cm^{-2} h^{-1})	IE_{WL} (%)	θ
	Blank	1.070	-----	-----
308	Ind1	0.030	97.2	0.972
	Blank	1.490	-----	-----
313	Ind1	0.070	95.3	0.953
	Blank	2.870	-----	-----
323	Ind1	0.238	91.7	0.917
	Blank	5.210	-----	-----
333	Ind1	0.844	83.8	0.838
	Blank	10.02	-----	-----
343	Ind1	2.796	72.1	0.721

The apparent activation energie (E_a) for carbon steel in 1.0 M HCl with inhibitor and in the absence of inhibitor was by using the linear regression between Ln (ρ_{WL}) and 1/*T* (Fig. 6), and also the results listed in Table 5. The linear regression coefficients are close to one, indicating that the carbon steel corrosion in HCl can be elucidated using the kinetic model.

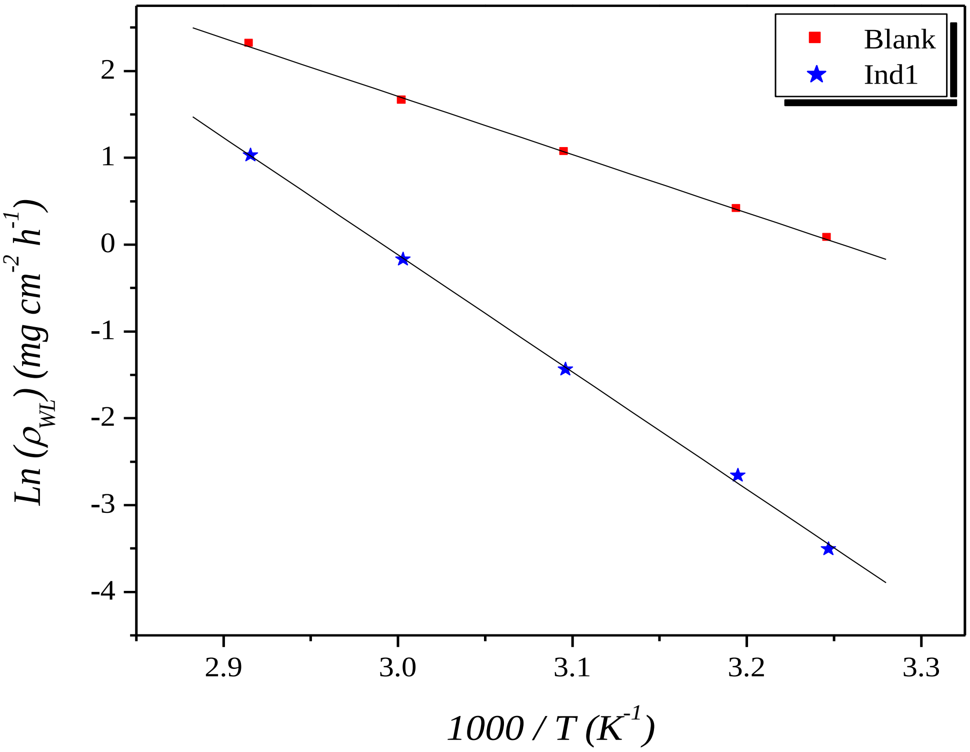

Figure 6. Arrhenius plots of Ln (ρ_{WL}) vs. 1/T for steel in 1.0 M HCl in the absence and the presence of Ind1 at optimum concentration.

Table 5. Activation parameters for the steel dissolution in 1.0 M HCl in the absence and the presence of Ind1 at optimum concentration.

Inhibitor	*A* (mg cm^{-2} h^{-1})	Linear regression coefficient (r)	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J/mol K)
Blank	3.0066×10^{9}	0.99961	55.75	53.05	-72.49
Ind1	3.3934×10^{17}	0.99955	112.19	109.49	81.66

The calculated values of the apparent activation corrosion energies in the absence and presence of the inhibitor are 55.75 and 112.19 kJ mol^{-1}, respectively. The higher activation energy value in the presence of Ind1 supports the results obtained from the weight loss indicates the higher inhibition efficiency of the inhibitor [49]. The increase in activation energy after the addition of the inhibitor to the 1.0 M HCl solution indicates that physical adsorption (electrostatic) occurs in the first stage [50]. On the other hand, the adsorption phenomenon of an organic molecule is not considered only as a physical or as chemical adsorption phenomenon. A wide spectrum of conditions, ranging from the dominance of chemisorption or electrostatic effects arises from other adsorption experimental data

[51]. The higher E_a value in the inhibited solution can be correlated with the increased thickness of the double layer, which enhances the activation energy of the corrosion process [50].

An alternative formulation of Arrhenius equation is [52]:

$$\rho_{WL} = \frac{RT}{Nh}\exp\left(\frac{\Delta S_{\mathrm{a}}}{R}\right)\exp\left(-\frac{\Delta H_{\mathrm{a}}}{RT}\right) \tag{7}$$

where ρ_{WL} is the corrosion rate, h is the Planck's constant (6.626176 × 10^{-34} Js), N is the Avogadro's number (6.02252 × 1023 mol^{-1}), R is the universal gas constant and T is the absolute temperature, ΔH_a the enthalpy of activation, and ΔS_a entropy of activation. Fig. 7 shows a plot of Ln (ρ_{WL}/T) against 1/T. Straight lines were obtained with a slope is equal to (ΔH_a /R) and intercept is equal to (Ln (R/Nh + ΔS_a /R))), from which the values of ΔH_a and ΔS_a were calculated and listed in Table 5. The positive signs of ΔH_a reflect the endothermic nature of the carbon steel dissolution process [53]. As seen in Table 3, the values of ΔH_a were the same, and the values of E_a increased for the corrosion of carbon steel in the presence of inhibitor, indicating that the energy barrier for the corrosion reaction increased in the presence of inhibitor without changing the dissolution mechanism [54,55].

The large negative value of ΔS_a for carbon steel in 1.0 M HCl implies that the activated complex is the rate-determining step, rather than the dissociation step. In the presence of the inhibitor, the value of ΔS_a increases and is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes [56]. The positive values of ΔS_a reflect the fact that the adsorption process is accompanied by an increase in entropy, which is the driving force for the adsorption of the inhibitor onto the steel surface.

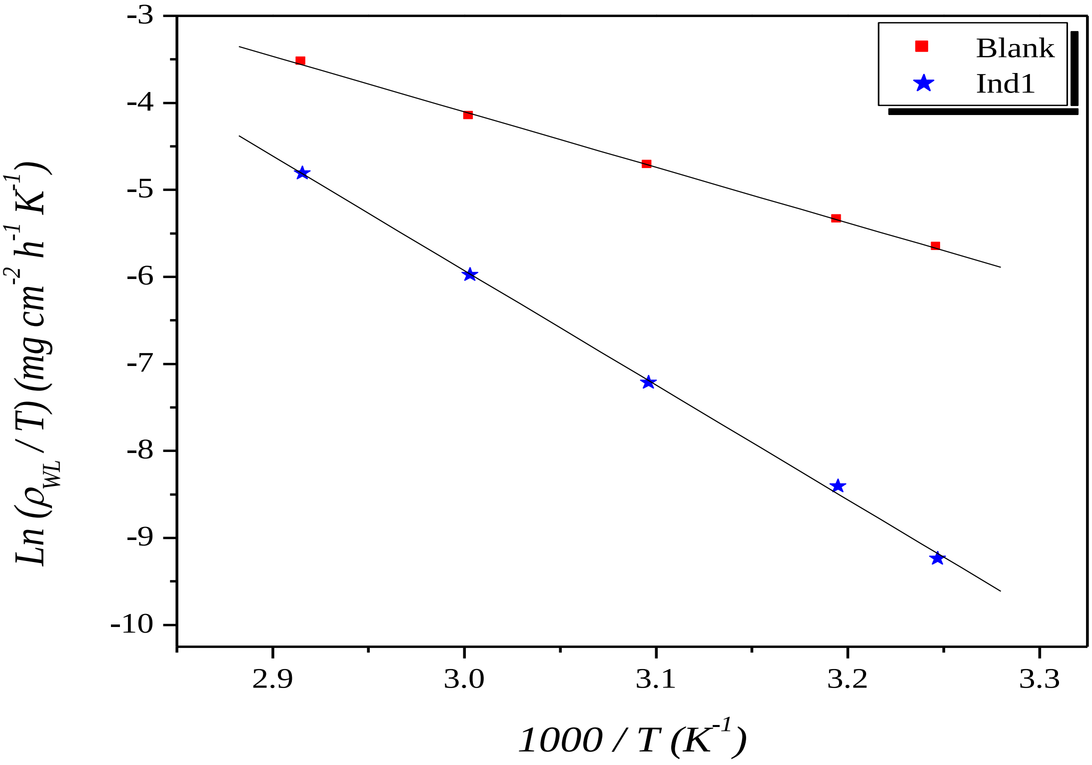

Figure 7. Arrhenius plots of Ln (ρ_{WL}/T) vs. 1/T for steel in 1.0 M HCl in the absence and the presence of Ind1 at optimum concentration.

3.3.3. Adsorption and thermodynamic considerations

The extent of corrosion inhibition depends on the surface conditions and the mode of adsorption of the inhibitors [57]. Under the assumptions that the corrosion of the covered parts of the surface is equal to zero and that corrosion takes place only on the uncovered parts of the surface (i.e., inhibitor efficiency is due mainly to the blocking effect of the adsorbed species), the degree of surface coverage θ has been estimated from the weight loss techniques employed in this study as follows: $\theta = IE_{WL}\% / 100$ (assuming a direct relationship between surface coverage and inhibition efficiency) [57-59].

The adsorption on the corroding surfaces never reaches the real equilibrium and tends to reach an adsorption steady state. However, when the corrosion rate is sufficiently small, the adsorption steady state has a tendency to become a quasi-equilibrium state. In this case, it is reasonable to consider the quasi-equilibrium adsorption in thermodynamic way using the appropriate equilibrium adsorption isotherms [60].

Basic information on the interaction between the inhibitor and the carbon steel surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the linear relation between the values of θ and the inhibitor concentration (C_{inh}) must be found. Attempts were made to fit the θ values to various isotherms including Langmuir, Hill de Boer, Parsons, Temkin, Flory-Huggins, Dahar-Flory-Huggins and Bockris-Swinkel. By far the best fit is obtained with Langmuir isotherm. According to this isotherm, θ is related to C_{inh} by:

$$\frac{C_{\mathrm{inh}}}{\theta} = \frac{1}{K_{\mathrm{ads}}} + C_{\mathrm{inh}} \qquad (8)$$

where K_{ads} is the adsorption constant, C_{inh} is the concentration of the inhibitor and surface coverage values (θ) are obtained from the weight loss measurements for various concentrations.

Fig. 8 shows the relationship between C_{inh} / θ and C_{inh} for the indole derivative at 308K. The correlation coefficient (R^2) was used to choose the isotherm that best fit experimental data (Table 3). The linear correlation coefficient (R^2) is almost equal to one. The slope of the straight line for this inhibitor was close to unity. Data illustrated in Fig. 8 indicated that the adsorption process obeyed Langmuir adsorption isotherm. Longmuir's isotherm assumes that there is no interaction between the adsorbed molecules, the energy of adsorption is independent on the surface coverage (θ), the solid surface contains a fixed number of adsorption sites, and each site holds one adsorbed species.

Moreover, the essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless separation factor, K_L [61] which describe the type of isotherm and is defined by

$$K_L = \frac{1}{1 + K_{ads} C_{inh}} \qquad (12)$$

If
$K_L > 1$ unfavourable;
$K_L = 1$ linear
$0 < K_L < 1$ favourable;
KL = 0 irreversible;

Table 6. The values of dimensionless separation factor, K_L, for Ind1 at various concentrations.

C_{inh} (M)	K_L
1×10^{-3}	0.0028
5×10^{-4}	0.0058
1×10^{-4}	0.0273
1×10^{-5}	0.2190
1×10^{-6}	0.7371

Table 6 gives the estimated K_L values for Ind1 at different concentrations. It was found that all K_L values are less than unity confirming that the adsorption process is favourable.

The equilibrium constant for adsorption process is related to the free energy of adsorption, ΔG°_{ads}, and is expressed by following equation:

$$K_{ads} = (\frac{1}{55.5})\exp(-\frac{\Delta G^{\circ}_{ads}}{RT}) \tag{9}$$

Where R is gas constant and T is absolute temperature of experiment and the constant value of 55.5 is the concentration of water in solution in mol L^{-1}.

The thermodynamics parameters derived from Langmuir adsorption isotherm for the studied compound, are given in Table 7. The negative value of ΔG°_{ads} along with the high K_{ads} indicate a spontaneous adsorption process [62].

Table 7. Thermodynamic parameters for the adsorption of Ind1 in 1.0 M HCl on the carbon steel at 308K.

Inhibitor	Slope	K_{ads} (M^{-1})	R^2	ΔG°_{ads} (kJ/mol)
Ind1	1.03	356591.41	0.99997	-43.02

Generally, the energy values of -20 kJ mol^{-1}or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, physisorption; those of -40 kJ mol^{-1} or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond, chemisorption [63,64]. The value of ΔG°_{ads} is equal to -43.02 kJ mol^{-1}. The large value of ΔG°_{ads} and its negative sign is usually characteristic of strong interaction and a highly efficient adsorption [49]. The high value of ΔG°_{ads} shows that in the presence of 1.0 M HCl chemisorption of Ind1 may occur. The possible mechanisms for chemisorption can be attributed to the donation of π-electron in the aromatic rings, the presence of one nitrogen and two oxygen atoms in inhibitor molecule as reactive centers is an electrostatic adsorption of the protonated indole compound in acidic solution to adsorb on the metal surface.

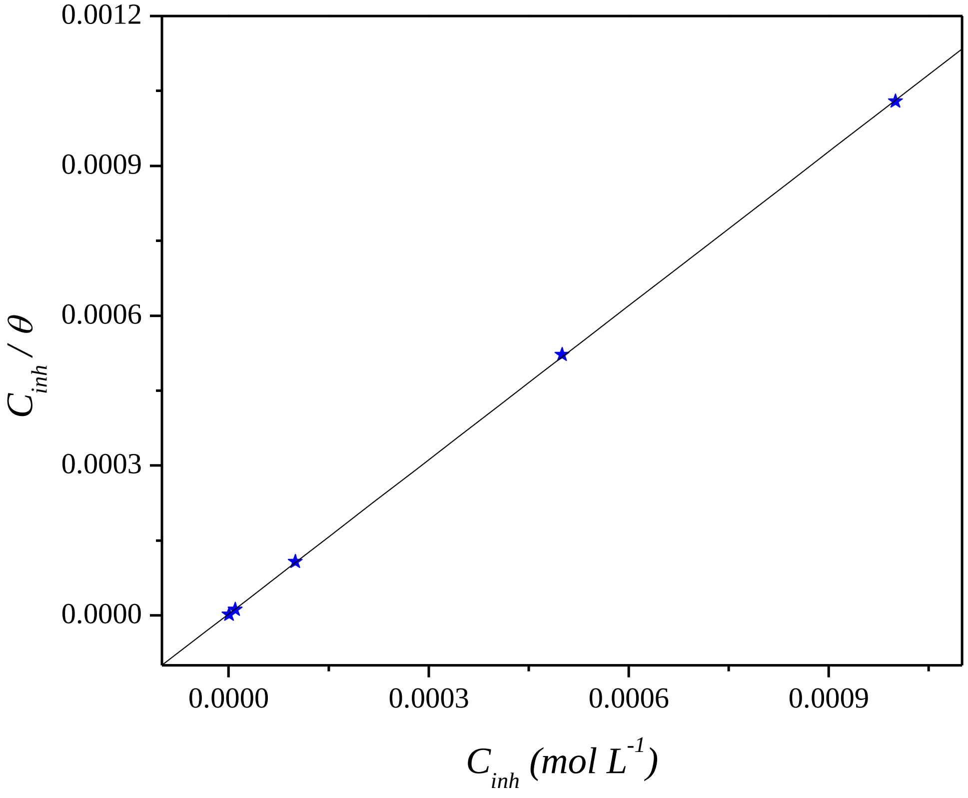

Figure 8. Langmuir adsorption of Ind1 on the carbon steel surface in 1.0 HCl solution.

The value of the heat of adsorption were evaluated from the kinetic thermodynamic model [65]

$$\left[\frac{\theta}{1-\theta}\right] = A.C.\exp\left(-Q_{ads} / RT\right) \tag{10}$$

where A is a constant, C is the inhibitor concentration, θ is the occupied and (1- θ) is the vacant site not occupied by inhibitor. In this equation a Q_{ads} is the heat of adsorption which is almost equal to enthalpy of adsorption process (ΔH°_{ads}). Plot of Ln [θ /(1- θ)] against 1/T of Ind1 at 10^{-3} M is shown in Fig. 9. The slope of the linear parts of the curves is equal to $-\Delta H^{\circ}_{ads}$/R from which the average heat of adsorption ΔH°_{ads} was calculated. The value derived from Figure 9 is -63.57 kJ mol^{-1}, the negative value of ΔH°_{ads} reflect the exothermic behavior of inhibitor on the carbon steel surface. Entropy of inhibitor adsorption (ΔS°_{ads}) can be calculated using the following equation [66, 67]:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \tag{11}$$

From this equation the value of ΔS°_{ads} is -66.72 J mol^{-1} K^{-1}. The negative value of ΔS°_{ads} might be explained as: before the adsorption of inhibitor onto the steel surface, inhibitor molecules might freely move in the bulk solution (the inhibitor molecules were chaotic), but with the progress in the adsorption, inhibitor molecules were orderly adsorbed onto the steel surface, as a result, a decrease in entropy [68]. Therefore negative value of ΔS°_{ads} in the present investigation support the higher adsorbability of organic compounds on the metal surface.

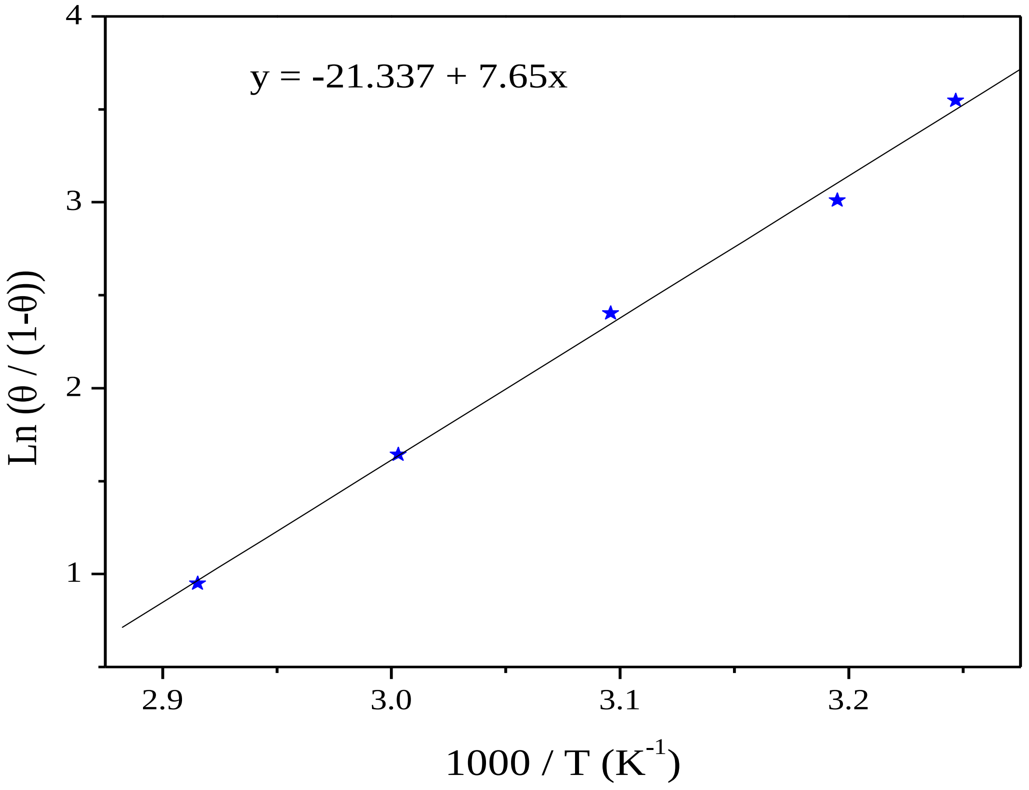

Figure 9. Ln (θ / (1- θ)) vs.1/T for adsorption of Ind1.

4. CONCLUSION

Ind1 acts as an excellent mixed type inhibitor for the corrosion of carbon steel in 1.0 M HCl solution. Inhibition efficiency increases with increase in concentration of Ind1 but decreases with rise temperature. The surface adsorption of the used inhibitor led to a reduction in the double layer capacitance as well as an increase in the charge transfer resistance. The inhibition efficiencies obtained from weight loss measurements are comparable with those obtained from polarization and electrochemical impedance measurements. The adsorption of Ind1 follows Langmuir adsorption isotherm. Inhibitive action is due to chemical adsorption of Ind1 on carbon steel surface and the adsorption process is a spontaneous and exothermic process.

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