

Corrosion Studies of C38 Steel by Alkaloids Extract of a Tropical Plant Type

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Received: 5 July 2011 / Accepted: 14 August 2011 / Published: 1 September 2011

Alkaloids extract of *Aspidosperma album* was tested as corrosion inhibitor for C38 steel in 1 M HCl by using polarization and electrochemical impedance spectroscopy (EIS). Potentiodynamic polarization curves indicated that the plant extract behaves as mixed-type inhibitors. Impedance measurements showed that the double-layer capacitance decreased and charge-transfer resistance increased with increase in the inhibitors concentration and hence increasing in inhibition efficiency. The effect of temperature on the corrosion behavior of C38 steel in 1 M HCl with and without addition of plant extract was studied in the temperature range 25 – 55 °C. The adsorption of the inhibitor molecules was in accordance with the Langmuir adsorption isotherm. The results obtained show that this plant extract could serve as an effective inhibitor for the corrosion of C38 steel in hydrochloric acid.

Keywords: C38 steel; acidic media; corrosion inhibitor; plant extract.

1. INTRODUCTION

Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric and sulphuric acids are widely used in the pickling processes of metals. Several methods are present for corrosion prevention. Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent metal dissolution and acid consumption [1]. Most effective inhibitors are organic compounds containing electronegative functional groups and π electrons in triple or conjugated double bonds [2-6]. These compounds also have heteroatoms (such as N, P, O, and S) and aromatic rings in their structure, which are the major adsorption centers [7-11]. In view of this, several inhibitors have been synthesized and used successfully to inhibit corrosion of metals in acid media. However, the major problem associated with most of synthetic compounds is that they are highly toxic to both human beings and cause severe

environmental hazards. The toxic effects of most synthetic corrosion inhibitors have led to use of natural products which are eco-friendly and harmless. There are numerous naturally occurring substances like henna [12], *Nypa fructicans* [13], natural honey [14], *Opuntia* [15], *jojoba oil* [16], and isolated alkaloids like berberine [17] which have been reported to have an anticorrosion effect in acid media. All these inhibitors are extracted from aromatic species, herbs, and medicinal plants. The use of natural products as corrosion inhibitors is well documented [18-29]. But studies on the use of alkaloid extract of *Aspidosperma album* as an inhibitor for the corrosion of C38 steel is unknown. *Aspidosperma album* belongs to the *Apocynaceae* family, it's a medicinal plant found in South America. The choice of this plant is based on widespread distribution and a frequent occurrence in French Guiana [30].

In the present work, the behavior of alkaloids extracts from *Aspidosperma album* have been studied as possible corrosion inhibitor for C38 steel in 1 M hydrochloric acid at various concentrations of extract by using electrochemical techniques.

2. EXPERIMENTAL

2.1. Electrode and solution

Corrosion tests have been carried out on electrodes cut from sheets of C38 steel. Steel strips containing 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. 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 at ambient temperature (25 °C).

2.2. Preparation of plant extract

Aspidosperma album Bark was collected in Roura, French Guiana. The typical alkaloid extractions were performed according to a previously described experimental procedure [31]. Air-dried plant material (100 g) was grounded and treated with aqueous NH₄OH (5%, 100 mL). The alkalized raw material was extracted under reflux (10 min) with dichloromethane (3x200 mL). The extract was collected by filtration and the combined dichloromethane fractions were washed with water (2x200 mL). Then, the organic layer was extracted with aqueous 3% HCl (3x100 mL). The combined aqueous fractions were washed with dichloromethane (3x80 mL) and the pH of the aqueous solution was then adjusted to 9 with aqueous 25% NH₄OH. This aqueous layer was extracted with dichloromethane (3x100 mL) and the combined organic layers were washed with distilled water (2x100 mL), dried over Na₂SO₄ and collected by filtration. Evaporation of the solvent yielded the desired alkaloids extract (0.27 % w/w). Four concentrations of the plant extracts (10, 25, 50 and 100 mg/L) were made by dissolving the known quantity of the resultant extract in acidic media.

2.3. Electrochemical measurements

Electrochemical measurements, including potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) were performed in a three-electrode cell. The C38 steel specimen was used as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Before each Tafel 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_{corr}) of the working electrode.

The anodic and cathodic polarisation 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 at different conditions 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 for each concentration of the two tested inhibitors. The Tafel and EIS data were analysed using graphing and analyzing impedance software, version EC-Lab V9.97.

3. RESULTS AND DISCUSSION

3.1. Linear polarization measurements

Linear polarization method was used to evaluate the corrosion rate of the C38 steel sample in the presence and absence of alkaloid extracts. Linear polarization curves of the C38 steel in 1 M HCl solution with and without addition of various concentrations of alkaloids extract of *Aspidosperma album* are shown in fig. 1. This figure shows that the anodic and cathodic reactions are affected by the alkaloids extract. Meaning that, the addition of alkaloids extract to HCl solution reduces the anodic dissolution of steel and also retards the cathodic hydrogen evolution reaction. These results indicated that this inhibitor (extract) exhibits cathodic and anodic inhibition effects. Based on the shift of E_{corr} and the increase of the anodic with a less extent of the cathodic polarisation, one can conclude that the alkaloids extract of *Aspidosperma album* is mixed-type inhibitor with predominant anodic action. The electrochemical parameters: corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel constant (b_a) and cathodic Tafel constant (b_c) are presented in Table 1. The inhibition efficiency was calculated, using the following equation:

$$IE(\%) = [(I_{\text{corr}}^0 - I_{\text{corr(inh)}}^0) / I_{\text{corr}}^0] \times 100 \quad (1)$$

where I_{corr}^0 and $I_{\text{corr(inh)}}^0$ are the corrosion current density values in the absence and presence of alkaloids extract, respectively. It is clear from Table 1 that increasing alkaloids extract concentration decrease the corrosion current density. The polarization resistance (R_p) values were obtained by using linear $I - E$ plots in the potential range $\pm 25 \text{ mV}$ from the corrosion potential. The corresponding R_p values of steel in 1 M HCl in the presence and absence of different concentrations of the extract are also given in Table 1. According to the obtained results, polarization resistance increases with

increasing concentration of extract. Corrosion potential values was shifted to the positive potentials in the presence of alkaloids extract, but has not been changed significantly with respect to inhibitor concentrations. The anodic Tafel slope (b_a) and the cathodic Tafel slope (b_c) of alkaloids extract changed with inhibitor concentration. This observation suggests that the inhibitor molecules controlled both of the reactions and adsorbed on the metal surface by blocking the active sites on the metal surface, retarding the corrosion reaction. $IE(\%)$, calculated by both methods, increases with extract concentrations, reaching a maximum value at 100 mg L^{-1} . The higher inhibition efficiency obtained at these concentrations suggests that the extract of *Aspidosperma album* could serve as effective corrosion inhibitor.

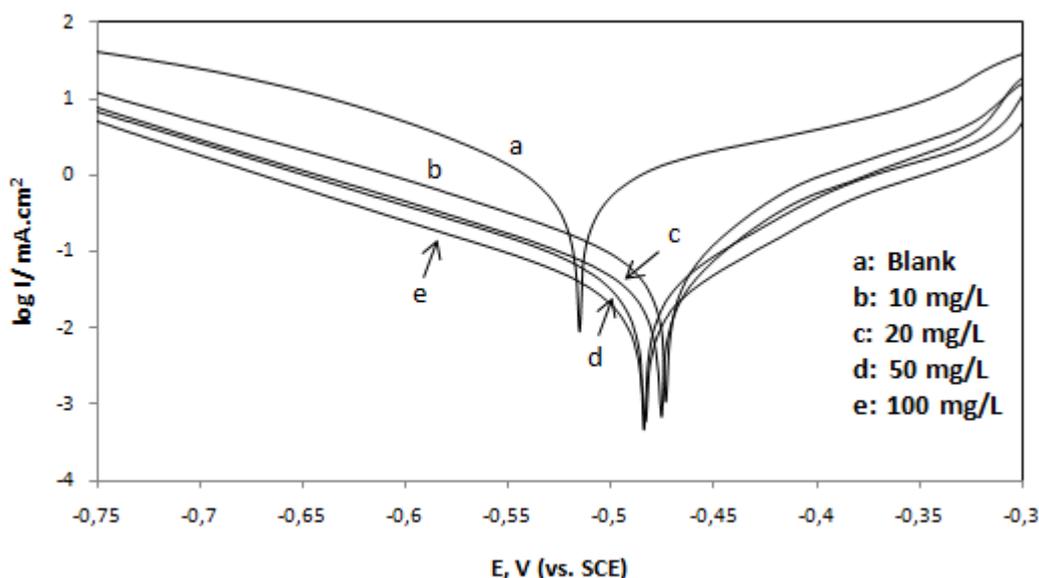


Figure 1. Polarisation curves for C38 steel in 1 M HCl containing different concentrations of *Aspidosperma album* extract.

Table 1. Polarization parameters and the corresponding inhibition efficiency for the corrosion of C38 steel in 1 M HCl containing different concentrations of *Aspidosperma album* extract at 25 °C.

Concentration mg L^{-1}	E_{corr} vs SCE	I_{corr}	b_a	b_c	R_p	$IE_{I_{corr}}$	IE_{R_p}
	(mV)	($\mu\text{A cm}^{-2}$)	(mV dec^{-1})	(mV dec^{-1})	($\Omega \text{ cm}^2$)	(%)	(%)
1 M HCl	-470	256	116	87	66	—	—
<i>Aspidosperma album</i>							
10	-473	72	82	132	355	72	81
25	-472	43	61	130	462	83	86
50	-484	37	76	115	495	86	87
100	-489	26	73	120	564	90	88

3.2. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a well-established and powerful tool in the study of corrosion. Surface properties, electrode kinetics, and mechanistic information can be obtained from the impedance diagrams [32]. In this work, the influence of concentration on the surface coverage was carried out also by electrochemical impedance spectroscopy. Fig. 2 shows the Nyquist plot obtained at the open-circuit potential after 3 hours of immersion, while Fig. 3 represents the Bode-phase diagrams, representative example. It is clear from the impedance diagrams of uninhibited and inhibited solutions containing different concentrations of alkaloids extract that Nyquist plots consists of a large capacitive loop (Fig. 2) with one capacitive time constant in the Bode-phase diagrams (Fig. 3). The shape of the capacitive loops suggests that the charge-transfer controls the corrosion of C38 steel at E_{corr} . It is also clear that the Nyquist plots are significantly changed after the addition of alkaloids extract and the capacitive loop enlarges as the concentration of inhibitor. It means that the inhibition efficiency is proportional to the concentration of inhibitor. All experimental Nyquist plots consist of a “depressed” semicircle with one capacitive loop and depressed semicircle has a centre under the real axis, such behaviour is characteristic for solid electrodes and often referred to as frequency dispersion which has been attributed to roughness and other inhomogeneities of solid surface [33-37]. The Nyquist impedance plots were analyzed by fitting the experimental data to a simple equivalent circuit model, fig. 4, that include the solution resistance R_s and the constant phase element (CPE) which is placed in parallel to charge transfer resistance element, R_{ct} . Often a CPE is used in a model in place of a capacitor to compensate for non-homogeneity in the system [20]. Excellent fit with this model was obtained for all experimental data (Fig. 4, representative example); with the measured and simulated data fit very well. The CPE impedance is defined by two values, A and n , and is described by the equation [38,39]:

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

Where A is the CPE constant, ω is the angular frequency in rad. S^{-1} , $\omega = 2\pi f$, and f is the frequency in Hz. $i^2 = -1$ is the imaginary number and n is a CPE exponent which can be used as a gauge of the heterogeneity or roughness of the surface [36,37].

Table 2 summarizes the impedance data extracted from EIS experiments carried out both in the absence and presence of increasing concentrations of alkaloids extract using the equivalent circuit model. In the same Table are shown also the calculated “double layer capacitance” values (C_{dl}), using the equation [40-42]:

$$C_{\text{dl}} = (A.R_{\text{ct}}^{1-n})^{1/n} \quad (3)$$

It is clear that the addition of alkaloid extracts decreases the double layer capacitance and increases the charge transfer resistance; as consequence a larger diameter of the semicircle is observed in Nyquist plots. The decrease in C_{dl} could be attributed to the adsorption of the inhibitors on the electrode surface

forming protective adsorption layers [43]. As, the impedance spectra show one capacitive loop, adsorption of alkaloids extract occurs by simple surface coverage and extract acts as a primary interface inhibitor [44]. The double layer formed at the electrode-solution interface is considered as an electric capacitor, whose capacitance decreases due to the displacement of water molecules and other ions originally adsorbed on the electrode by the alkaloid molecules, forming a protective layer which decrease the number of actives sites necessary for the corrosion reaction [43]. Indeed, increasing the coefficient n with increase in alkaloids extract concentration reflects a decreased heterogeneity of the steel surface as a result of adsorption of alkaloid molecules.

The relaxation time constants were calculated using the equation [41,45]:

$$\tau = C_{dl} R_{ct} \tag{4}$$

The time constants τ are almost dependent of the concentration of the *Aspidosperma album* extract, as τ shows a marked tendency to increase with concentration and its values are much higher than in the uninhibited acidic solutions which means slow adsorption process [46,47]. The R_{ct} values were used to calculate the IE (%), according to the following equation:

$$IE(\%) = [(R_{ct} - R_{ct}^0) / R_{ct}] \times 100 \tag{5}$$

where R_{ct}^0 and R_{ct} are respectively the charge transfer resistance in the absence and presence of alkaloid extracts. The results obtained are shown in Table 2. It can be clearly seen that the R_{ct} value increases with the inhibitor concentration, leading to an increase in the corrosion inhibition efficiency. The $IE(\%)$ values calculated from Ac impedance study are in complete agreement with those obtained from polarization measurements.

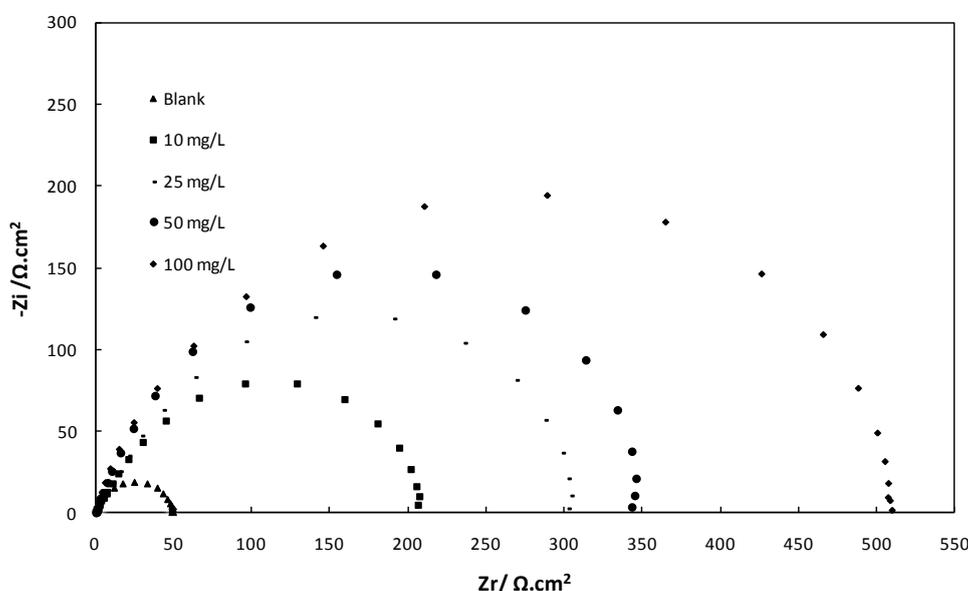


Figure 2. Nyquist plots for C38 steel in 1 M HCl in the absence and presence of different concentrations of *Aspidosperma album* extract

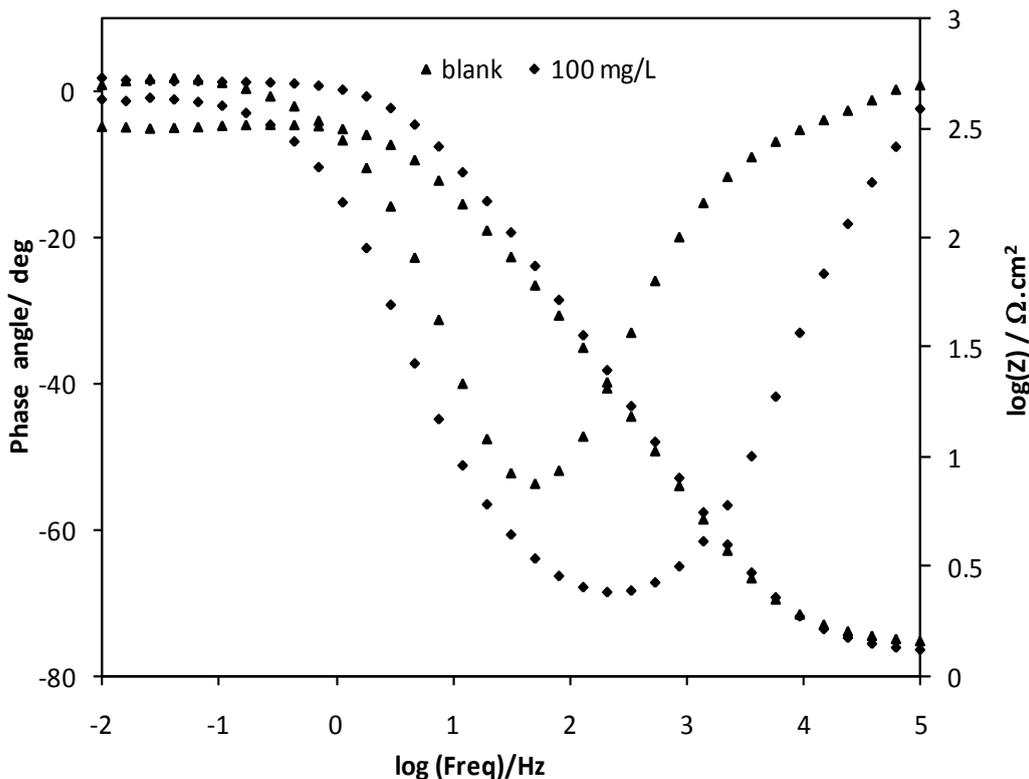


Figure 3. Bode plots for C38 steel in 1 M HCl in the absence and presence of 100 mg L⁻¹ of *Aspidosperma album* extract.

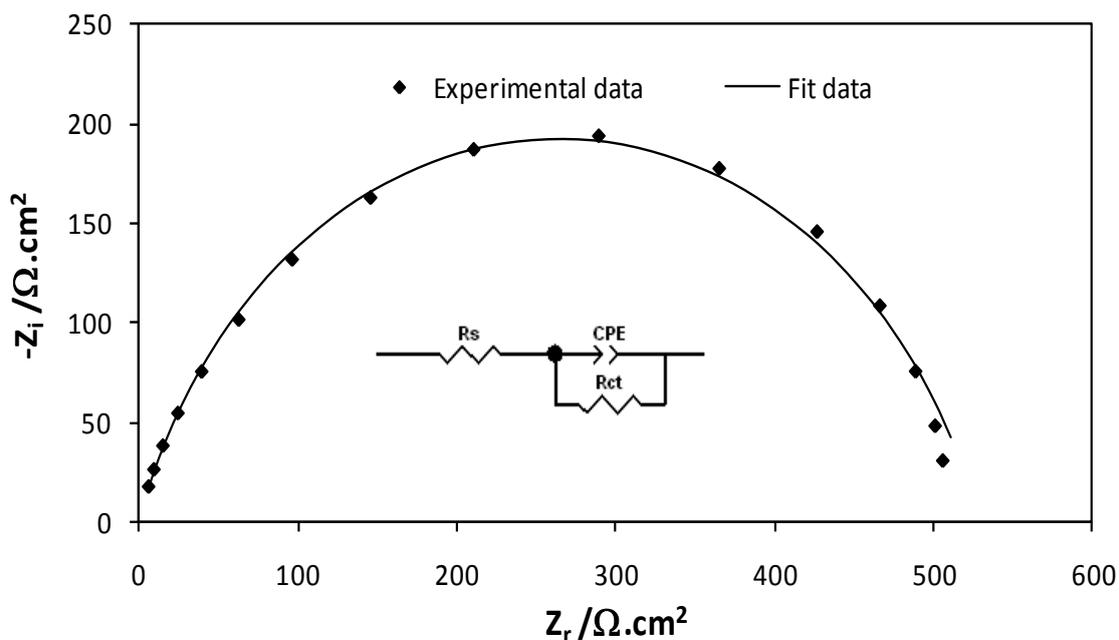


Figure 4. Nyquist plots, (♦) Experimental data and (—) Fit data, together with the equivalent circuit used to fit the impedance data, recorded for a C38 electrode in 1 M HCl solution + 100 mg L⁻¹ of *Aspidosperma album* extract.

Table 2. Values of the elements of equivalent circuit required for fitting the EIS for C38 steel in 1 M HCl in the absence and presence of different concentrations of *Aspidosperma album* extract and the corresponding inhibition efficiency.

Concentration (mg L ⁻¹)	R_{ct} (Ω cm ²)	$10^4 A$ (Ω^{-1} s ⁿ cm ⁻²)	n	C_{dl} (μ F cm ⁻²)	τ_d (s)	IE (%)
1 M HCl	49	9.5	0.851	555	0.0272	—
<i>Aspidosperma album</i>						
10	207	2.87	0.862	183	0.0378	76
25	301	1.98	0.866	128	0.0385	84
50	351	1.64	0.878	110	0.0387	86
100	505	0.95	0.838	66	0.0387	90

Table 3. Critical concentration and percentage inhibition efficiency for different plants extracts.

Natural Products	Optimum Concentration	Highest Inhibition Efficiency	Acidic Media	Metal Exposed
<i>Lupine</i> [48]	960 mg L ⁻¹	86.2%	1 M H ₂ SO ₄	steel
	640 mg L ⁻¹	86.2%	2 M HCl	steel
<i>Mango peel</i> [49]	600 mg L ⁻¹	91%	1 M HCl	carbon steel
<i>Orange peel</i> [49]	400 mg L ⁻¹	95%	1 M HCl	carbon steel
<i>Passion fruit peel</i> [49]	500 mg L ⁻¹	90%	1 M HCl	carbon steel
<i>Cashew peel</i> [49]	800 mg L ⁻¹	80%	1 M HCl	carbon steel
<i>Justicia gendarussa</i> [50]	150 ppm	93%	1 M HCl	mild steel
<i>Zenthoxylum alatum</i> [51]	2400 ppm	95%	5% HCl	mild steel
	2400 ppm	91%	15% HCl	mild steel
<i>Ricinus Communis leaves</i> [52]	2500 v/v	96.96%	1 M HCl	mild steel
<i>Chamaemelum mixtum L.</i> [53]	7.56 g L ⁻¹	90.2%	1 M H ₂ SO ₄	steel
<i>Lasianthera africana</i> [54]	0.5 g/L	94.23%	0.1 M H ₂ SO ₄	mild steel

Therefore, these results suggest, once again, that this plant extract could serve as effective corrosion inhibitors.

The use of the natural products such as extracted compounds from leaves or seeds as corrosion inhibitors have been widely reported by several authors [48–54]. As an example, Table 3 reports the percentage inhibition efficiency for some plants extracts used as corrosion inhibitors in various acidic media and their optimum concentrations. The data obtained by a lot of natural products (Table 3) and our results (Tables 1 and 2) suggests that the plant extracts could serve as effective corrosion inhibitors. Analyzing the efficiency obtained with the used concentrations, we can conclude that our extract is very effective compared with results of other authors, for the reason that we get almost the

same efficiency with a low concentration. In addition, plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature.

3.3. Effect of temperature

To ensure the effectiveness of *Aspidosperma album* extract under various conditions, tests were performed in 1 M HCl solution at different temperatures (25–55 °C). The concentration of *Aspidosperma album* extract which gave the highest *IE*% value in 1 M HCl solution at 25 °C (100 mg/L⁻¹) was chosen for further study.

3.3.1. EIS measurements

The effect of solution temperature on the impedance spectra recorded in the studied acid solutions without and with 100 mg/L⁻¹ of *Aspidosperma album* extract has been studied. In all cases, the charge transfer resistances are decreased with increasing the temperature. Nyquist plots obtained at different temperatures in 1 M HCl solution without and with *Aspidosperma album* extract are shown in Figs. 5 and 6, respectively. These spectra reveal that although values the charge transfer resistances are decreased with increasing the temperature, these values are higher in presence of extract than in its absence. The impedance spectra obtained are quite similar to those obtained in 1 M HCl in the absence and presence of different concentrations of *Aspidosperma album* extract at 25 °C. Except in HCl solution at 45 and 55 °C, an inductive loop appeared at low-frequency values. For analysis of the impedance spectra exhibiting one capacitive loop, the equivalent circuit (EC) given in Fig. 4 was used to fit the experimental spectra while the EC shown in Fig. 7 was used for the impedance spectra containing one capacitive loop and an inductive loop.

The various corrosion parameters obtained in 1 M HCl solution in absence and presence of 100 mg/L⁻¹ of *Aspidosperma album* extract are given in Table 4. Values of R_t obtained in presence and absence of extract are decreased with increasing the temperature and its values are much higher in the inhibited acidic solutions which means the corrosion inhibition process by the extract. Values of C_{dl} obtained in 1 M HCl solution drastically increased indicating the high corrosion rate of steel at elevated temperatures and then remain approximately unchanged. In presence of extract, values of C_{dl} are slightly increased with the rise of temperature and are still lower than those obtained in the pure medium.

This behavior indicates strong adsorption of extract on the steel surface. The decrease in the n values with increasing the temperature in presence and absence of extract may be a result of increasing surface heterogeneity. This was confirmed by the fact that the C_{dl} values increased over the temperature range. The influence of temperature on the inhibition efficiency of extract in the investigated acid solution is shown in Table 4. The maximum *IE* (91%) is obtained at 35 °C, further increase in temperature results in decrease in *IE*%. The decrease of *IE*% of the extract with increasing the temperature is a further evidence for the physical adsorption of the extract on the electrode surface.

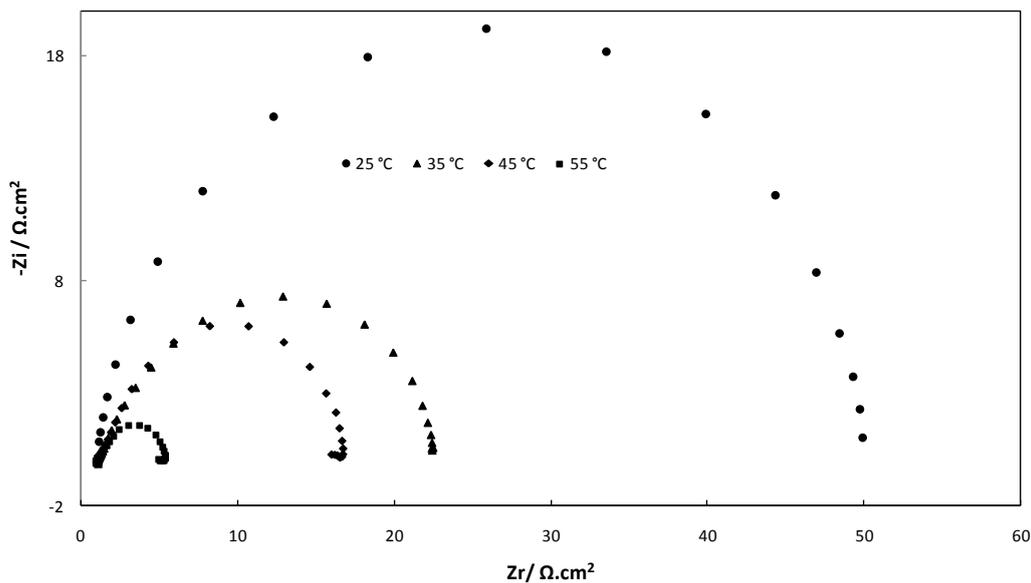


Figure 5. Nyquist diagrams for C38 steel in 1 M HCl at different temperatures.

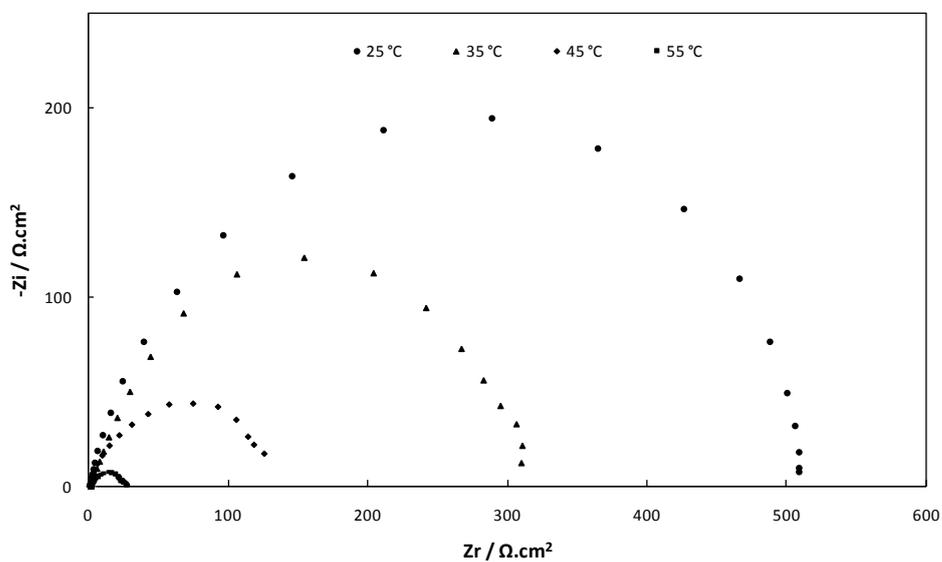


Figure 6. Nyquist diagrams for C38 steel in 1 M HCl + 100 mg L⁻¹ of *Aspidosperma album* extract at different temperatures.

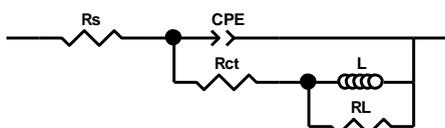


Figure 7. Equivalent circuit models which represent the C38 steel/1 M HCl (at 45-55 C°) interfaces.

Table 4. Values of the elements of equivalent circuit required for fitting the EIS for C38 steel in 1 M HCl in the absence and presence of 100 mg L⁻¹ of *Aspidosperma album* at different temperatures.

Temperature (C°)	R_{ct} ($\Omega \text{ cm}^2$)	$10^4 A$ ($\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$)	n	C_{dl} ($\mu\text{F cm}^{-2}$)	R_L	IE (%)
1 M HCl						
25	49	9.51	0.851	556	—	—
35	25	42.06	0.787	2286	—	—
45	18	57.52	0.761	2822	2	—
55	5	89.06	0.738	2951	1.5	—
<i>Aspidosperma album</i>						
25	505	0.95	0.838	66	—	90
35	307	1.98	0.826	112	—	91
45	135	3.82	0.801	126	—	85
55	26	7.75	0.793	150	—	75

3.3.2. LP measurements

The influence of temperature is also studied by potentiodynamic polarisation. The polarisation curves for C38 steel electrode in 1 M HCl in the absence and in the presence of 100 mg L⁻¹ of *Aspidosperma album* extract in the temperature range 25 – 55 °C are given in Figs. 8 and 9, respectively.

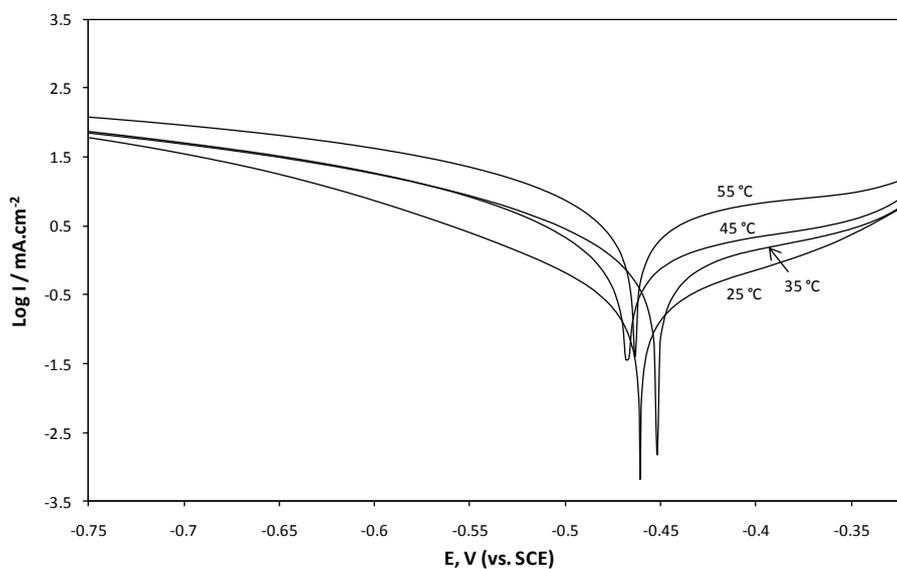


Figure 8. Polarisation curves for C38 steel in 1 M HCl at different temperatures.

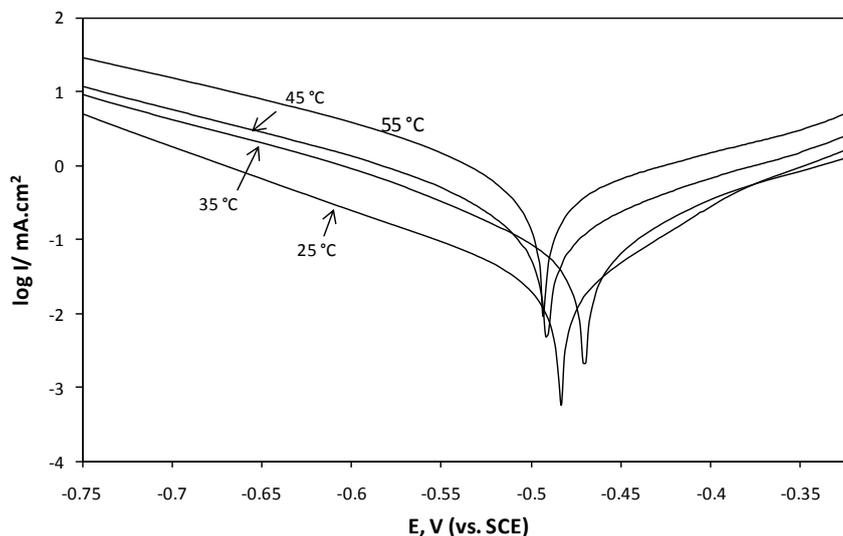


Figure 9. Polarisation curves for C38 steel in 1 M HCl containing 100 mg L⁻¹ of *Aspidosperma album* extract at different temperatures.

Table 5. Polarization parameters and the corresponding inhibition efficiency for C38 steel in 1 M HCl in the absence and presence of 100 mg L⁻¹ *Aspidosperma album* at different temperatures

Temperature (C°)	E_{corr} vs SCE (mV)	I_{corr} ($\mu\text{A cm}^{-2}$)	b_a (mV dec ⁻¹)	b_c (mV dec ⁻¹)	R_p ($\Omega \text{ cm}^2$)	$IE_{I_{corr}}$ (%)	IE_{R_p} (%)
1 M HCl							
25	-458	180	99	80	76	—	—
35	-451	823	106	92	25	—	—
45	-465	1029	208	94	20	—	—
55	-471	1947	135	46	6	—	—
<i>Aspidosperma album</i>							
25	-482	25	80	117	781	86	90
35	-470	83	118	128	337	90	92
45	-492	125	128	99	166	86	88
55	-502	698	173	103	27	64	78

The results deduced from the polarization curves are given in Table 5. As it can be seen, that raising the temperature increases both anodic and cathodic reactions of C38 steel electrode both in the absence and in the presence of extract. It is seen from Table 5 that the corrosion current density (I_{corr}) increased and the polarization resistance decreases with the increasing temperature, although the plant extract investigated have been inhibiting properties at all temperatures studied. The addition of extract to the HCl solution not affects the E_{corr} values; however there was not a specific relation between E_{corr}

and increasing temperature. The inhibition efficiency of extract reaches a maximum value (91%) at 35 °C, upon increasing the temperature, IE% is slightly decreased and the extract becomes less effective at 50 °C. This behavior shows again the physical nature of adsorption of extract in HCl solution. The inhibition efficiencies show the same trend as these obtained from ac impedance study.

3.3.3. Thermodynamic parameters

Activation parameters such as the activation energy, E_a , the enthalpy of activation, ΔH_a , and the entropy of activation, ΔS_a , for both corrosion and corrosion inhibition of C38 steel in 1 M HCl in the absence and presence of 100 mg L⁻¹ *Aspidosperma album* between 25 and 55 °C were calculated from an Arrhenius-type plot (Eq. (6)) and the transition state (Eq. (7)) [55,56]:

$$I_{\text{corr}} = K \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

where 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.

$$I_{\text{corr}} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right) \quad (7)$$

where h is Planck's constant, N is Avogadro's number, ΔS_a is the entropy of activation and ΔH_a is the enthalpy of activation.

The corrosion current density was calculated from polarisation measurement and EIS data according to Stern–Geary [57] equation:

$$I_{\text{corr}} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \left(\frac{1}{R_{\text{ct}}} \right) \quad (8)$$

Plots of $\ln(I_{\text{corr}})$ vs. $1000/T$ and $\ln(I_{\text{corr}}/T)$ vs. $1000/T$ gave straight lines with slopes of $-E_a/R$ and $-\Delta H_a/R$, respectively. The intercepts were A and $[\ln(R/Nh) + (\Delta S_a/R)]$ for the Arrhenius and transition state equations, respectively. Figs. 10 and 11 represent the data plots of $\ln(I_{\text{corr}})$ vs. $1000/T$ and $\ln(I_{\text{corr}}/T)$ vs. $1000/T$ in the absence and presence of 100 mg L⁻¹ *Aspidosperma album* extract, representative example.

The calculated values from both methods of the activation energy, E_a , the enthalpy of activation, ΔH_a , and the entropy of activation, ΔS_a , are tabulated in Table 6. Inspection of Table 6 shows that values of both E_a , ΔH_a obtained in presence of *Aspidosperma album* extract are higher than those obtained in the inhibitor-free solution. This observation further supports the proposed physical adsorption mechanism.

Table 6. Thermodynamic parameters for the adsorption of 100 mg L⁻¹ *Aspidosperma album* in 1 M HCl on the C38 steel at different temperatures

Corrosive medium	E_a (kJ mol ⁻¹)	ΔH_a (kJ mol ⁻¹)	ΔS_a (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	ΔH_a (kJ mol ⁻¹)	ΔS_a (J mol ⁻¹ K ⁻¹)
	From polarisation curves			From impedance measurements		
1 M HCl	26.21	25.08	-114.24	20.52	19.39	-156.20
<i>Aspidosperma album</i>	36.60	35.47	-87.72	37.00	35.87	-110.15

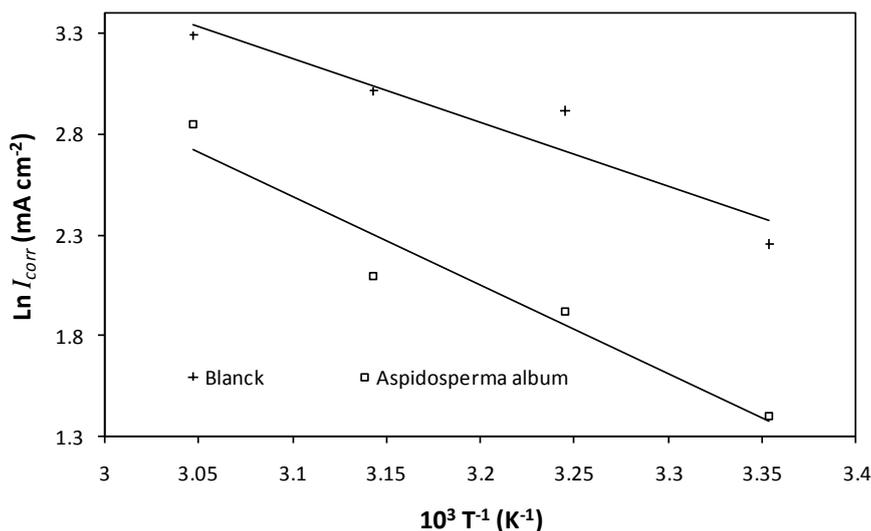


Figure 10. Arrhenius plots of corrosion $\ln I_{corr}$ vs. $1/T$ of 1 M HCl and 100 mg L⁻¹ *Aspidosperma album* extract obtained from LP.

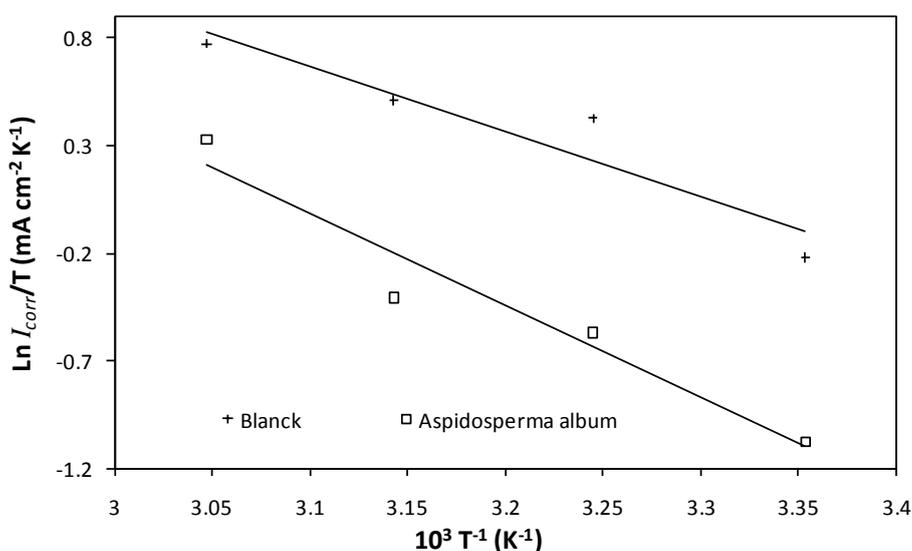


Figure 11. Arrhenius plots of corrosion $\ln(I_{corr}/T)$ vs. $1/T$ of 1 M HCl and 100 mg L⁻¹ *Aspidosperma album* extract obtained from LP.

Higher values of E_a in inhibited systems compared to the blank have been reported [2,22,24,58] to be indicative of physical adsorption mechanism, while lower values of E_a suggest a chemisorption mechanism. On the other hand, the positive sign of ΔH_a reflects the endothermic nature of the C38 steel dissolution process suggesting that the dissolution of C38 steel is slow [59] in the presence of inhibitor.

This behaviour can be explained as a result of the replacement process of water molecules during adsorption of *Aspidosperma album* extract on steel surface [60,61]. The results obtained from polarization and impedance studies are in good agreement and show the same trend.

3.3. Application of adsorption Isotherm

Adsorption isotherms are very important in understanding the mechanism of organo electrochemical reactions [62]. In order to obtain the isotherm, the fractional coverage values θ as a function of inhibitor concentration must be obtained.

The degree of surface coverage (θ) of the metal surface by an adsorbed plant extract is calculated using impedance and polarization data (equations 9 and 10):

$$\theta = (R_{ct} - R_{ct}^0) / R_{ct} \quad (9)$$

$$\theta = (I_{corr}^0 - I_{corr(inh)}) / I_{corr}^0 \quad (10)$$

The variations of surface coverage with concentration of *Aspidosperma album* extract are shown in Fig. 12.

These curves represent adsorption isotherm that are characterized by first sharp rising part followed by another gradual rising part (less significant than the first part), indicating formation of an adsorbated layer on the steel surface. On the other hand, the coverage values obtained by two methods show the same trend.

The data were tested graphically, see Figs. 13-15, by fitting to Langmuir and Frumkin isotherms which given by equations 11 and 12.

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \quad (11)$$

$$\left(\frac{\theta}{1-\theta} \right) \exp(-2a\theta) = KC_{inh} \quad (12)$$

where “ K ” is the binding constant of the adsorption reaction and “ a ” is the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the surface. The θ values are calculated using.

By far the best fit was obtained with the Langmuir isotherm (the strong correlation ($R^2 = 0.999$) for both methods). The plots of C_{inh}/θ vs. C_{inh} yield a straight line (Figs. 13 and 14). This confirms that these inhibitors (plant extracts) obeys Langmuir adsorption isotherm at 1 M HCl medium. It indicates that the adsorbing *Aspidosperma album* species occupies typical adsorption site at the metal/solution interface.

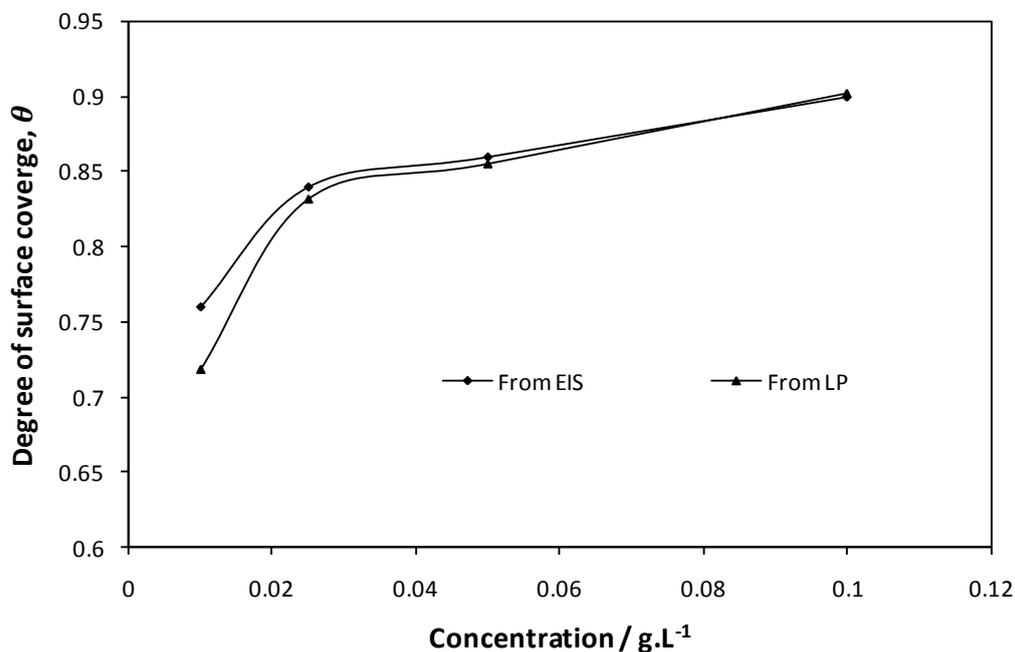


Figure 12. The variations of surface coverage, obtained from impedance and polarization data, with concentration of *Aspidosperma album* extract.

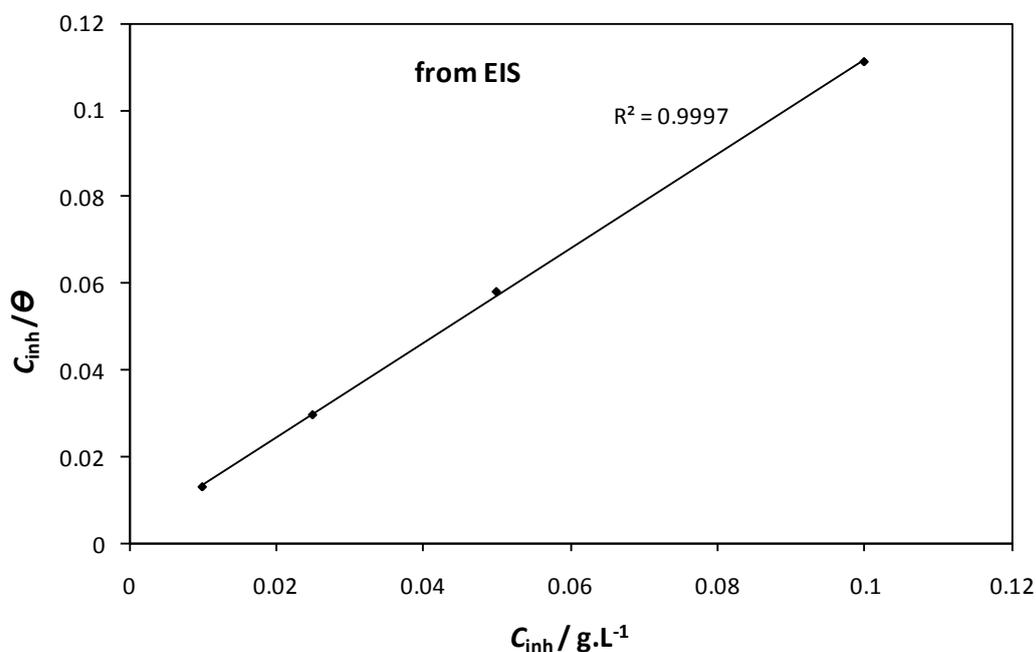


Figure 13. Langmuir adsorption plots obtained from EIS for C38 steel in 1 M HCl containing different concentrations of *Aspidosperma album* extract.

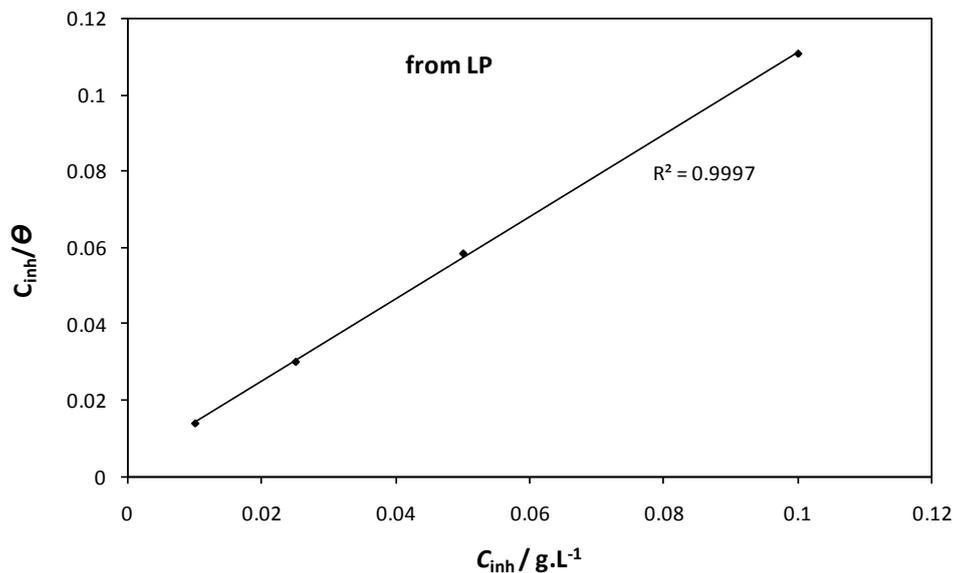


Figure 14. Langmuir adsorption plots obtained from LP for C38 steel in 1 M HCl containing different concentrations of *Aspidosperma album* extract.

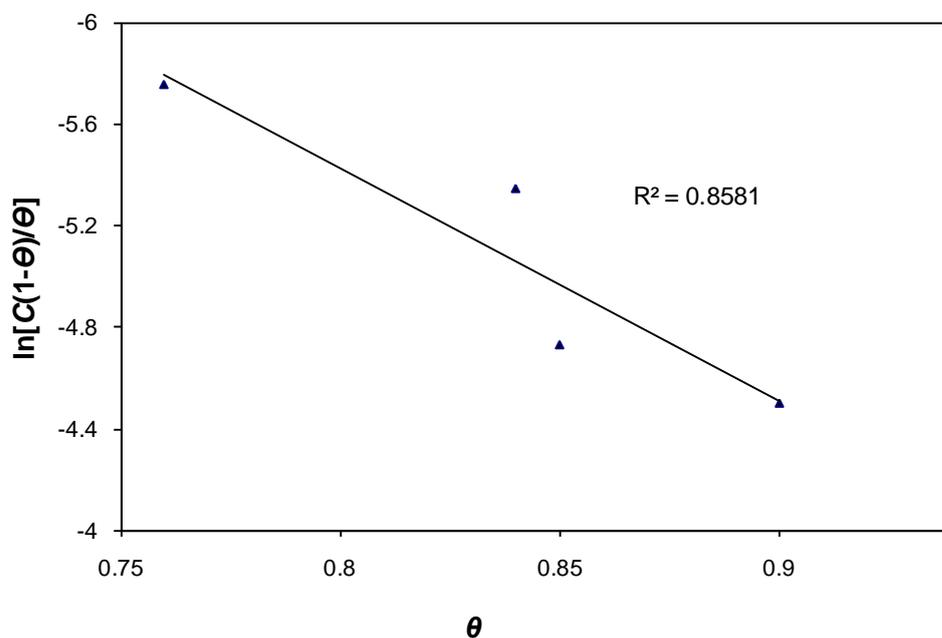


Figure 15. Frumkin adsorption plots obtained from LP for C38 steel in 1 M HCl containing different concentrations of *Aspidosperma album* extract.

4. CONCLUSION

The conclusions drawn from the study are:

- The alkaloids extract of *Aspidosperma album* behaved as a potent inhibitor to C38 steel in 1M HCl. The protection efficiency of the inhibitor was found to increase with increase in concentration of the inhibitor showing a maximum efficiency of 90% at 100 mg L⁻¹.

- The extract under study resists corrosion effectively even at higher temperature, further increase in temperature results in decrease in $IE\%$.
- The results obtained from the polarization studies reveal that the extract behaved as a mixed type of inhibitor.
- The thermodynamic parameters obtained from the study indicate that the spontaneous adsorption of inhibitor on the surface of the mild steel is endothermic in nature.
- The adsorption behavior of the extract is consistent with Langmuir adsorption model.

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