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Use of *Prosopis Laevigata* as a Corrosion Inhibitor for Al in H_2SO_4

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The possibility of using *Prosopis laevigata* extract as a corrosion inhibitor for Al in 0.5 M H_2SO_4 has been evaluated by using weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy techniques. Inhibitor concentrations were included within the range between 0 and 200 ppm at 20, 40 and 60°C. Results have shown that P*rosopis laevigata* is a good corrosion inhibitor, acting as a cathodic type of inhibitor, with its efficiency increasing with increasing its concentration, reaching its highest efficiency at 200 ppm, but decreases with an increase in the temperature. It was found that the inhibitory effect is due to the presence of prosopine and prosopinine, on this extract which form a protective layer by reacting with Al^{3+} ions, which are chemisorbed onto the metal surface following a Tempkin type of adsorption isotherm and decreases the corrosion reaction energy barrier.

Keywords: Acidic corrosion, green inhibitor, electrochemical techniques.

1. INTRODUCTION

Metallic surface corrosion can be reduced or controlled by the addition of an inhibitor, which decreases the rate of anodic oxidation, cathodic reduction or both [1]. The inhibitors form a protective film on the surface of the metal by physical (electrostatic) adsorption or chemisorption [2]. Green inhibitors receive attention for the replacement of synthesized inorganic inhibitors which are often toxic, expensive and environmentally unfriendly [3-4]. Extracts from leaves, seeds, fruits and roots contain compounds with nitrogen, sulfur and oxygen described as efficient corrosion inhibitors indifferent aggressive environments [5-6] Some examples of natural products used as corrosion inhibitors include *Parthenium hysterophorus* [7], *Capsicum annuum* [8], *Lawsonia* [9], O*puntia* [10], *Swertia aungustifolia* [11], *Ficus religeosa* [12], *heena* [13], *Datura stramonium* [14], *calotropis* [15], *Prosopis cineraria* [16], *Sansevieria trifasciata* [17], *Pachylobus edulis* [18] and *Dacroydes edulia* [19]. These studies have shown that organic compounds containing N, S and O have high corrosion inhibitors. Most of these organic inhibitors are adsorbed on the metal surface [20]. These green corrosion inhibitors contain, for instance, tanines, saponines, proteins, flavonoids among others.

Prosopis spp. is a tree which fixes nitrogen, reaching heights between 5-10 m, and there are around 44 different species in the world, and 10 of them exist in Mexico [21-23]. This tree contains tannins, fibers and pigments and it is used as natural medicine for eyes, skin and stomach [24-26]. The tannins contain is between 6-20% and between 0.4-3.6% of flavonoids [27]. Two different alkaloids found in Prosopis spp. have been identified, namely Prosopine and Prosopinine [28-36] with chemical structures given in Fig. 1.

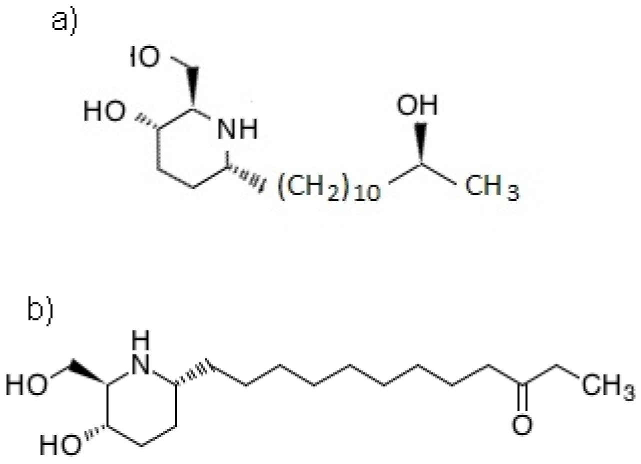

Figure 1. Chemical structure of a) Prosopine and b) Prosopinine

Prosopine is used as a weak stimulant for nervous system whereas Prosopinine has some local anesthetic effects three times stronger than cocaine [37]. Thus, the goal of the present work is to evaluate the use of *Prosopis laevigata* as a green corrosion inhibitor of aluminum in acidic environment.

2. EXPERIMENTAL PROCEDURE

Dried *Prosopis laevigata* leaves were soaked in methanol during 24 h and used as a stock solution and used then for preparation of the desired concentrations by dilution, i.e. 0, 5, 10, 25, 50 and 100 ppm. The resulting extract was used as a stock solution and characyerized by FTIR and UV-VIS techniques**.** Weight loss experiments were carried out with aluminium rods 2.5 cm length and 0.6 cm diameter abraded with fine emery paper until 1200 grade, rinsed with acetone, and exposed to the aggressive solution during 72 h. After a total time of exposition of 72 hours, specimens were taken out, washed with distilled water, degreased with acetone, dried and weighed accurately. Aggressive solution, 0.5 M H_2SO_4 was prepared by dilution of analytical grade H_2SO_4 with double distilled water.Tests were performed by triplicate at room temperature (25 °C), 40 and 60 °C by using a hot plate. Corrosion rates, in terms of weight loss measurements, ΔW, were calculated as follows:

$$\Delta W = (m_1 - m_2) / A \qquad (1)$$

were m_1 is the mass of the specimen before corrosion, m_2 the mass of the specimen after corrosion, and A the exposed area of the specimen. For the weight loss tests, inhibitor efficiency, *IE*, was calculated as follows:

$$IE\ (\%) = 100\ (\Delta W_1 - \Delta W_2) / \Delta W_1 \qquad (2)$$

were ΔW_1 is the weight loss without inhibitor, and ΔW_2 the weight loss with inhibitor. Specimens were removed, rinsed in water and in acetone, dried in warm air and stored in a dissicator. Specimens were weighed in an analytical balance with a precision of 0.1 mg. Electrochemical techniques employed included potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements, EIS. In all experiments, the carbon steel electrode was allowed to reach a stable open circuit potential value, E_{corr}. Polarization curves were recorded at a constant sweep rate of 1 mV/s at the interval from -500 to +800 mV respect to the E_{corr} value. Measurements were obtained by using a conventional three electrodes glass cell with two graphite electrodes symmetrically distributed and a saturated calomel electrode (SCE) as reference with a Lugging capillary bridge. Corrosion current density values, I_{corr}, were obtained by using Tafel extrapolation. Electrochemical impedance spectroscopy tests were carried out at E_{corr} by using a signal with amplitude of 10 mV in a frequency interval of 100 mHz-100 KHz. An ACM potentiostat controlled by a desk top computer was used for the polarization curves, whereas for the EIS measurements, a model PC4 300 Gamry potentiostat was used.

3. RESULTS AND DISCUSSION

The effect of *Prosopis laevigata* concentration in the weight loss for Al in 0.5M H_2SO_4 0.5 M at 20, 40 and 60 °C is shown in Fig. 2, where it can be seen that, generally speaking, the weight loss decreases as the inhibitor concentration increases from 0 to 200 ppm, except at 150 ppm, where a slight increase in the weight loss is observed respect to that value at 100 ppm. In all cases, the lowest corrosion rate is observed at 200 ppm, and it can be seen also that, at a fixed inhibitor concentration, the corrosion rate increases with an increase in the working temperature.

Table 1. Effect of *Prosopis laevigata* concentration in the inhibitor efficiency for Al in 0.5M H_2SO_4 at 20, 40 and 60 °C

C_{inh} (ppm)	*IE* (%)		
	20 °C	40 °C	60°C
0	-	-	-
50	- 45.02	24.78	36.62
100	8.41	54.53	54.95
150	3.67	49.25	31.75
200	40.49	81.37	93.53

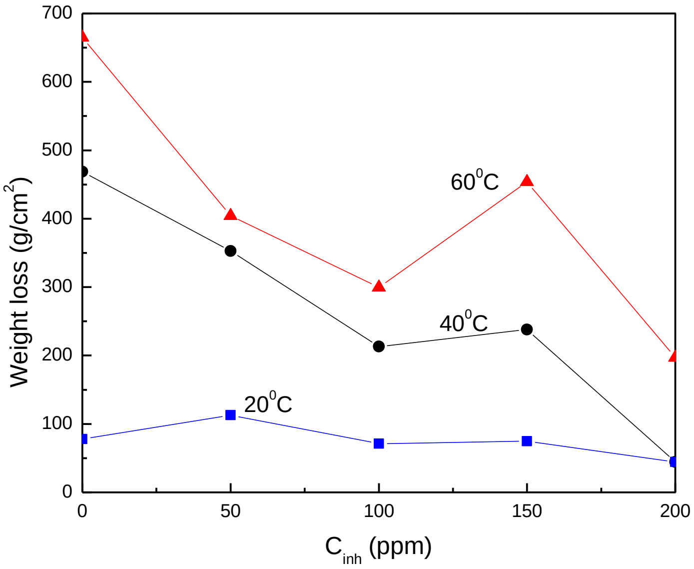

Figure 2. Effect of *Prosopis laevigata* concentration in the weight loss results for Al in 0.5M H_2SO_4 at 20, 40 and 60 °C

Table 1 shows that the inhibitor efficiency increases with an increase in its concentration but it decreases by increasing the temperature. This is due to the fact that *Prosopis laevigata* adsorbs on the metal surface, which form a barrier between the metal surface and corrosive surroundings and retard the corrosion reaction by hindering reduction/oxidation reactions that take place on the metal surface. At this point, it should be mentioned that, for the physisorption of species on the metal surface, there must be interactions between metal surface and species through relatively weak interactions, e.g. dipole–dipole interactions. On the other hand, chemisorption requires the sharing of charges or electrons of species and metals or the transfer of charges/electrons from the species to metal surface.

In order to evaluate the adsorption process of Buddleia perfoliata on the 1018 carbon steel surface, Langmuir, Temkin and Frumkin adsorption isotherms were obtained according to the following equations:

$$\text{Langmuir: } \theta/1\text{-}\theta = KC_{inh} \quad (3)$$

$$\text{Temkin: } \log\theta/C_{inh} = \log K - g\theta \quad (4)$$

$$\text{Frumkin: } \log \theta C_{inh}/(1\text{-}\theta) = \log K + g\theta \quad (5)$$

where θ is the surface coverage, K the adsorption-desorption equilibrium constant, C_{inh} the inhibitor concentration anf g the adsorbate interaction parameter.

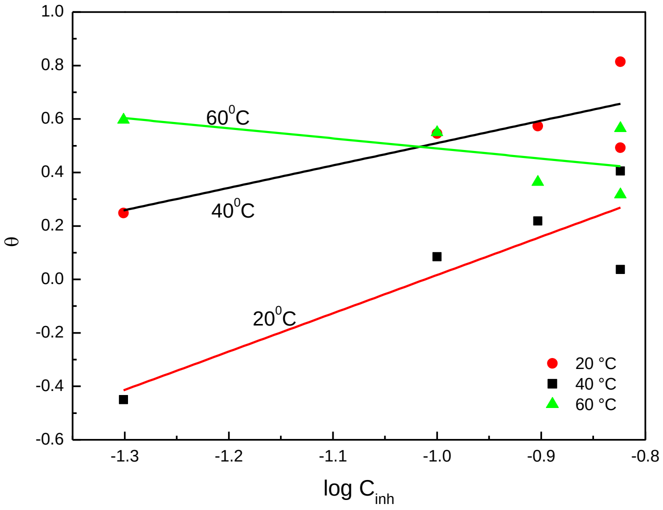

Figure 3. Tempkin adsorption isotherm for Al in in 0.5 M H_2SO_4 at 25 °C with the addition of *Prosopis laevigata*.

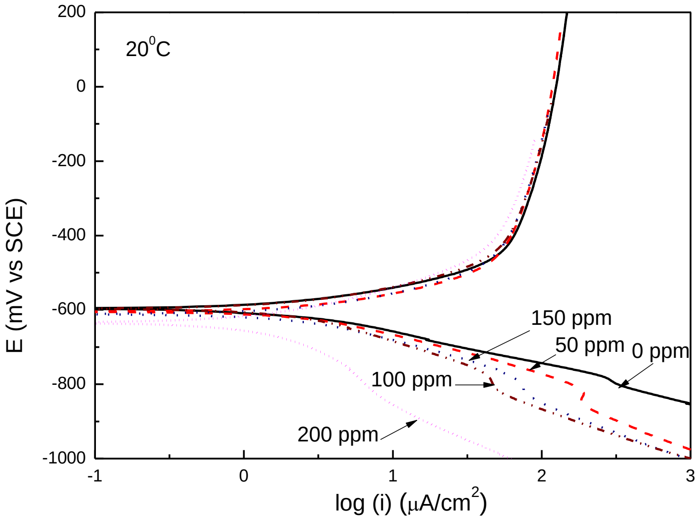

Figure 4. Effect of *Prosopis laevigata* concentration in the polarization curves for Al in 0.5 M H_2SO_4 a 20 °C

The three isotherms tested fitted well the data obtained, as can be seen in the Fig. 3 indicating that *Prosopis laevigata* adsorbed onto Al surface. However, the isotherm which had the best R^2 value, was that for the Tempkin one and the negative value of the slope indicates the existance of a repulsive lateral interaction in the adsorption layer [26]. Generally, values of the adsorption free-energy much less than -40 kJ/mol have typically been correlated with the electrostatic interactions between organic molecules and charged metal surface (physisorption) whilst those values in the order of -40 kJ/mol are associated with charge sharing or transfer from the organic molecules to the metal surface (chemisorption) to form a co-ordinate type of bond [26].The negative value of the free-energy of adsorption value means that the adsorption process is spontaneous, while the value around -40 kJ/mol indicates that *Prosopis laevigata* was chemically adsorbed on the steel surface.

The effect of *Prosopis laevigata* concentration on the polarization curves for aluminium in 0.5M H_2SO_4 at 20^0C using the are shown in Fig. 4, which indicates that the E_{corr} value shifts towards more cathodic values as the inhibitor concentrations increases, and at 200 ppm of inhibitor the lowest E_{corr} value was obtained; additionally, the I_{corr} value decreases as the inhibitor concentration increases up to 200 ppm were the lowest value is obtained. In the anodic branch of the curves, the current density values were very similar and a limit current density, or passive region, could be observed regardless of the inhibitor concentration without evidence of a passive film breakdown. Anodic Tafel slope was practically unaffected but the cathodic one was greatly affected, therefore this inhibitor acts as a cathodic one. In addition, the decreasing slopes of the cathodic branches suggest that the inhibitors make the corrosion reaction slow down, which is probably due to the barrier formation of inhibitor that makes the ion diffusion difficult.

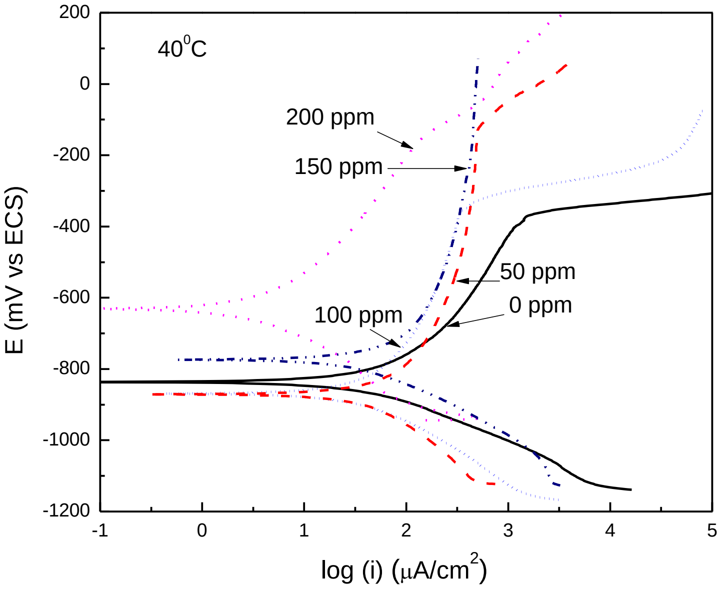

Figure 5. Effect of *Prosopis laevigata* concentration in the polarization curves for Al in 0.5 M H_2SO_4 a 40 °C.

At 40^0C, Fig. 5, aluminum showed an active-passive behavior with a pitting potential close to -400 mV for the uninhibited solution and with the addition of either 50 or 100 ppm of inhibitor. The addition of *Prosopis laevigata* shifted the E_{corr} value, in general terms, towards more active values and decreased the I_{corr} values, except when 150 ppm of inhibitor were added, reaching its lowest value with the addition of 200 ppm of inhibitor.

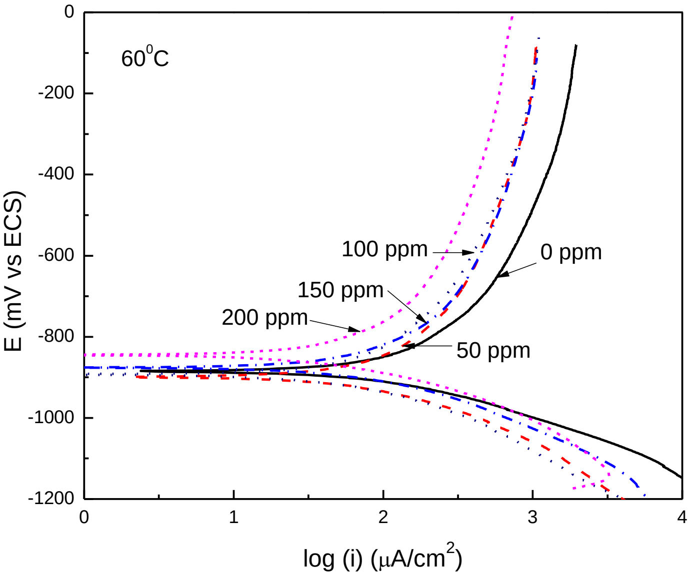

Figure 6. Effect of *Prosopis laevigata* concentration in the polarization curves for Al in 0.5 M H_2SO_4 a 60 °C

Table 2. Electrochemical parameters obtained from the polarization curves for Al in 0.5 M H_2SO_4 at 20, 40 and 60 °C.

T (°C)	C_{inh} (ppm)	I_{corr} (□A/cm^2)	E_{corr} (mV)	□□□□□ (%)
20	0	50.1	-598	-
	50	42.6	-602	16
	100	39.8	-609	20
	150	41	-595	18
	200	33.8	-635	34
40	0	110	-841	-
	50	107	-870	2.7
	100	52.4	-633	52
	150	91.2	-773	17.2
	200	7	-877	93.6
60	0	263	-881	-
	50	204	-908	22.4
	100	151	-894	42.5
	150	177	-878	32.7
	200	118	-844	55.1

Finally, at 60^0C, Fig. 6, metal described only an active behavior without evidence of a passive layer, with the lowest corrosion rate obtained with the addition of 200 ppm of *Prosopis laevigata.*

Table 2 summarizes the results obtained from the polarization curved, where it is shown that generally speaking the inhibitor efficiency increases with the increase in the inhibitor concentration reaching its highest value with the addition of 200 ppm.

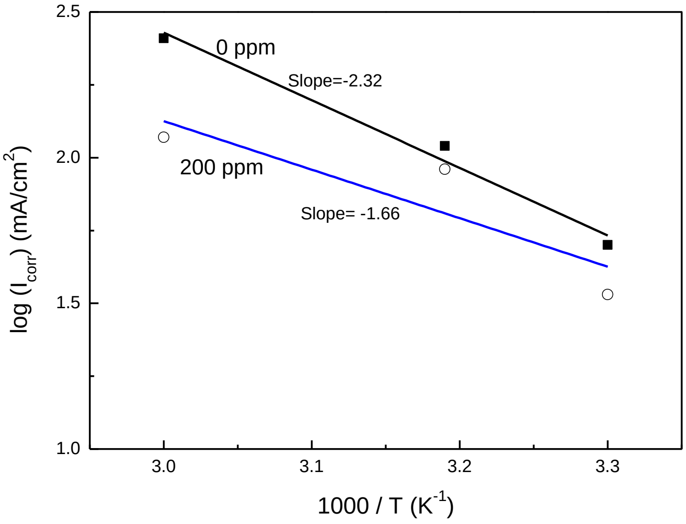

Figure 7. Arrhernius plots for log I_{corr} vs.1000/T for Al corroded in 0.5 M H_2SO_4 wihout and with 200 ppm of *Prosopis laevigata*.

It was found that the corrosion rates of Al in both uninhibited and inhibited solutions increase as the temperature was increased. However, the extent of the rate increment in the inhibited solution was higher in the uninhibited than in the inhibited solution. This suggests that the corrosion inhibition might be caused by the inhibitor adsorption onto the metal surface from the acidic solution, and higher temperatures might cause a stronger adsorption of the inhibitor on the steel surface. The apparent activation energy, E_a, associated with Al in uninhibited and inhibited acid solution was determined by using an Arrhenius-type plot according to the following equation:

$$\log I_{corr} = -E_a / 2.303RT + \log F \quad (6)$$

where I_{corr} is the corrosion current density value, R is the molar gas constant, T is the absolute temperature and F is the frequency factor. Arrhenius plots of log I_{corr} against T^{-1} for Al in 0.5 M H_2SO_4 in absence and presence of *Prosopis laevigata* is shown in Fig. 7. The apparent activation energy obtained for the corrosion process in the free acid solution was found to be 63.5 and 43.9 kJ/mol in presence of the inhibitor. Notably, the energy barrier of the corrosion reaction decreased in the presence of the inhibitor, which can be due to the chemisorption of the inhibitor on the steel surface. According to Popova et al. [38] lower E_a values in solutions in the presence of *Prosopis laevigata* indicate a specific type of adsorption of the inhibitor, while Szauer and Brandt [39] associate this behavior with the chemisorption of the inhibitor to the metal surface. Taking into consideration these references and the E_a value calculated from the Arrhenius plots, tha action of *Prosopis laevigata* as a corrosion inhibitor for Al in acid solution can be attributed to a strong type of chemisorption of the inhibitor onto the metal surface.

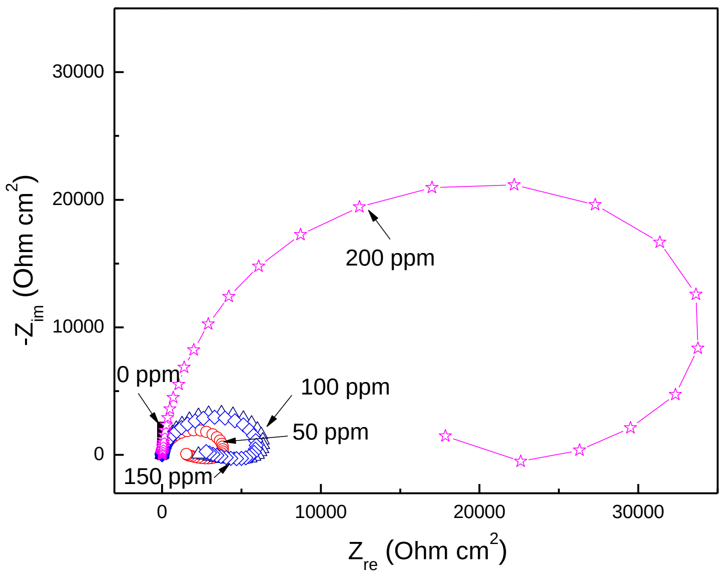

Figure 8. Effect of *Prosopis laevigata* concentration in the Nyquist curves for Al in 0.5 M H_2SO_4 a 20 °C

Nyquist plots for Al immersed in 0.5M H_2SO_4 containing different concentrations of *Prosopis laevigata* at 20°C are shown in Fig. 8. Nyquist plots show a depressed, capacitive loop in a high frequency range and an inductive loop in the low frequency range. At this point, it should be mentioned that the capacitive loop in the high frequency range is related with adsorption processes including charge transfer reaction, time constant of electrical double layer, or structural or interfacial heterogeneity [33] and that the inductive loop is related to the relaxation of the materials adsorbed on the electrode surface [34,35]. It is seen in Fig. 8 that the semicircle diameter of the Nyquist plot increases significantly with increasing amount of inhibitor, reaching a maximum value with 200 ppm of inhibitor, indicating the more densely packed monolayer of inhibitors on the metal surface.

This results in lower double-layer capacitance (C_{dl}) and higher charge transfer resistance (R_{ct}). The corrosion reaction is strictly controlled by electron transfer, and, thus the increasing R_{ct} is related to corrosion inhibition, and the decrease in the C_{dl} value is due to both the decrease in local dielectric constant and the increase in the thickness of electric double-layer, table 2, which indicates that *Prosopis laevigata* displaces the water molecules and other ions on the metal surface and adsorb at the metal/solution interface [13].

Table 2. Parameters obtained from the EIS data for Al in 0.5 M H_2SO_4 at different concentrations at 20, 40 and 60 °C.

T (°C)	C_{inh} (ppm)	R_s (Ohm cm^2)	R_{ct} (Ohm cm^2)	CPE (□F/cm^2)	η (%)
20	0	2.72	2372.32	1.84	-
	50	4.44	3840.89	1.16	38.96
	100	2.79	6384.95	1.78	62.09
	150	2.76	5930.65	1.79	60.65
	200	8.39	33809.59	0.62	92.97
40	0	3.75	264.92	1.28	-
	50	12.90	486.36	1.11	45.79
	100	4.86	598.75	1.09	55.85
	150	8.43	453.32	0.63	41.24
	200	4.65	2312.19	1.13	88.54
60	0	7.46	84.58	1.91	-
	50	2.80	119.41	1.82	30.02
	100	24.41	136.5	0.12	37.57
	150	2.06	123.63	2.44	30.64
	200	1.91	268.42	0.66	68.16

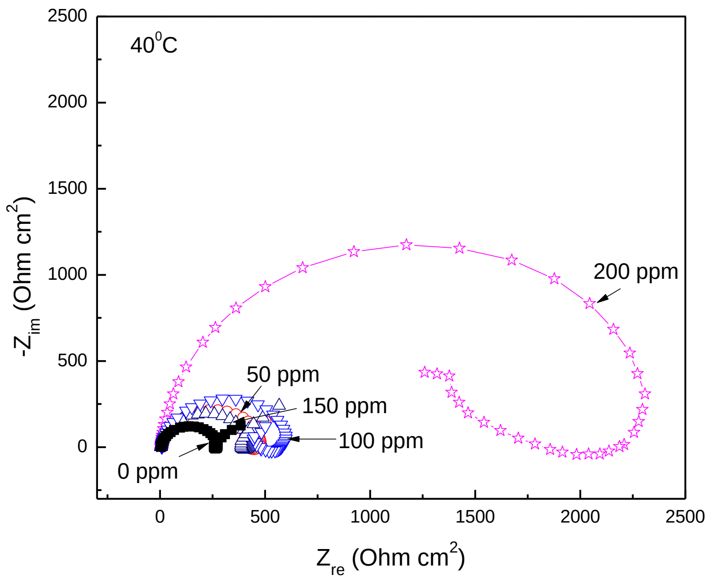

Figure 9. Effect of *Prosopis laevigata* concentration in the Nyquist curves for Al in 0.5 M H_2SO_4 a 40 °C

This causes the formation of a protective layer on the metal surface and the significant inhibition of corrosion of mild steel surface [36]. In addition, an increase in the R_{ct} value indicates that the metal corrosion involves a charge-transfer process. At 40 and 60°C, Figs. 9-10, Nyquist data describe a capacitive loop at high and intermediate frequency values and an inductive loop at lower frequency values, indicating that the corrosion process is controlled by the adsorption of some species or corrosion products on the metal surface.

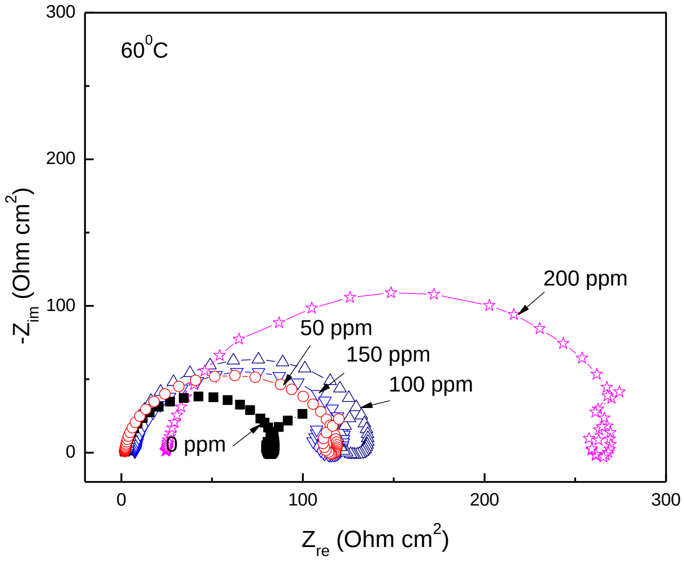

Figure 10. Effect of *Prosopis laevigata* concentration in the Nyquist curves for Al in 0.5 M H_2SO_4 a 60 °C

The semicircle diameter increases with the increase in the inhibitor concentration reaching its highest value at 200 ppm of inhibitor but decreases with an increase in the temperature, indicating an increase in the corrosion rate.

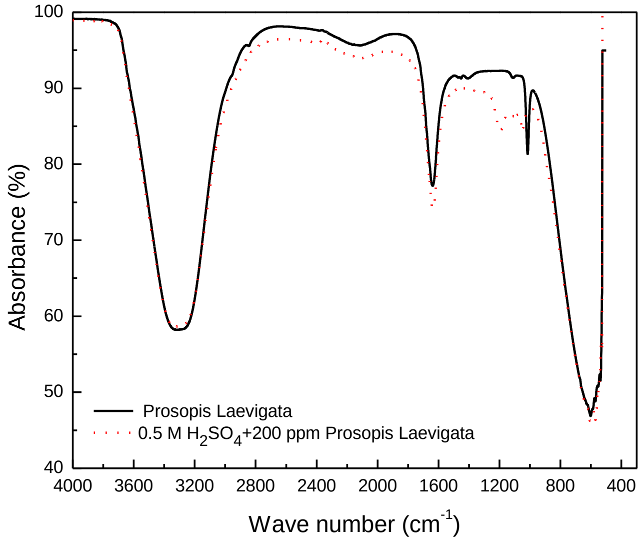

Figure 11. FTIR spectra for *Prosopis laevigata* extract.

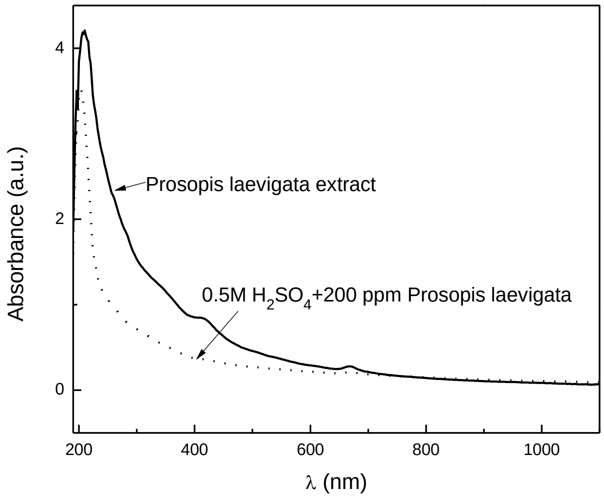

Figure 12. UV-vis spectra for Prosopis laevigata extract.

IR spectra for *Prosopis leavigata* with and without the addition of 0.5 M H_2SO_4 is shown in Fig.11; the main bands found for the pure extract are 3324 $cm^{-1,}$ assigned to the vibration of O–H, indicating the presence of the hydroxyl group; 1636 cm^{-1}, assigned to the vibration of a carbonile group, C=O; 1016 cm^{-1}, due to a single C–O group; and 599 cm^{-1} due to the vibration of the C–H group. These signals show the presence of organic compounds which contain the mentioned groups. Both prosopine and prosopinine contain these groups so it is very likely that the main compounds found here are prosopine and prosopinine. The signals corresponding to secondary amine could be overlapped and the signals due to the vibration of N-H and N-O are so weak that they could not be observed. In the UV-Vis spectra shown in Fig. 12, the highest intensity observed at 210 nm corresponds to the amine group present in both prosopine and prosopinine, which shows that these alkaloids are the responsible for the inhibitive properties of *Prosopis laevigata* in the corrosion of pure Al in acidic environment.

4. CONCLUSIONES

A study on the use of P*rosopis laevigata* as a corrosion inhibitor for Al in 0.5 M H_2SO_4 has been carried out in the concentration range from 0 to 200 ppm at 20, 40 and 60°C. It was found that P*rosopis laevigata* showed to be a good corrosion inhibitor, acting as a cathodic type of inhibitor, with its efficiency increasing with the concentration, reaching its highest efficiency at 200 ppm, but decreasing with an increase in the temperature. It was found that the inhibitory effect is due to the presence of prosopine and prosopinine, on this extract which form a protective layer by reacting with Al^{3+} ions, which are chemisorbed onto the metal surface following a Tempkin type of adsorption isotherm and decreases the corrosion reaction energy barrier.

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