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Novel Corrosion Inhibitor for Steel in 0.5 M H_2SO_4 Containing Halide Ions

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Abstract Silene marmarica was studied as an environmentally friendly inhibitor for steel corrosion in 0.5 M H_2SO_4. The effect of iodide and chloride ions on the inhibition efficiency of Silene marmarica, were studied by using potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The results showed that Silene Marmarica inhibited the corrosion of steel in 0.5 M H_2SO_4, where the inhibition efficiency increased with the increasing concentration of Silene marmarica. The results also showed that the presence of iodide produced a synergistic effect on the inhibition efficiency while, the presence of chloride ion decreased the inhibition efficiency of Silene marmarica. The adsorption behavior of Silene marmarica in the absence and presence of iodide or chloride was studied and was found to fit both the Langumir adsorption isotherm and the Kinetic-Thermodynamic model.

Keywords Steel, Acidic, Inhibition, Adsorption, Iodide

1. Introduction

Mild steel is a widely used metal, that has many applications including the manufacturing of installations for petroleum, fertilizers, water treatment equipment [1-5], and different chemical industrial processes such as acid cleaning, acid descaling and pickling [6]. One of the most commonly used methods for protecting metals against corrosion, is using inhibitors [7, 8]. The common corrosion inhibitors are mostly organic compounds having hetero atoms in their aromatic ring or delocalized π – bonds [7-9]. Unfortunately, these compounds have toxic effects not only on living organisms but also on the environment [8]. Nowadays, the need for green corrosion inhibitors has become essential for the environment. This class of corrosion inhibitors is environmentally friendly and is extracted from natural products such as plant extracts [10]. Several authors carried out their studies on the inhibition of corrosion of metals by using plant extracts [11-17]. Ficus Nitida leaves was investigated as corrosion inhibitor towards general and pitting corrosion of steel, nickel and zinc in different aqueous solutions by using potentiostatic, potentiodynamic polarization and weight loss techniques [18]. Ficus Nitida leaves decreased the corrosion rates of the three tested metals in the three different corrosive media. Consequently, the inhibition efficiency of Ficus Nitida leaves increased as the extract concentration, increased. Zakvi and Mehta studied the corrosion behavior of steel in 0.1 N solutions of sulfuric acid, hydrochloric acid, nitric acid and phosphoric acid containing 0.5 g/L of Mahasudar shana Churna extract using the polarization resistance technique [19]. The inhibition efficiency of the plant extract in the previously mentioned acids was in the following order: phosphoric □ sulfuric □ hydrochloric □ nitric. The seeds of Brassica Negra (black mustard) was studied as a corrosion inhibitor for steel and 304 stainless steel by open circuit potential and potentiodynamic polarization techniques [20]. The potentiodynamic polarization measurements showed that 0.5% of final concentration of black mustard seeds has a passivating effect. Khamis *et al*. [21], investigated a new category of environmentally safe corrosion inhibitors (Thyme, Coriander, Hibiscus, Anise, Black Cumin and Garden Gress) for the corrosion of steel in 0.5 M sulfuric acid by using the potentiodynamic polarization and electrochemical impedance techniques. The inhibition efficiency of these plants was attributed to their chemical constituents which are volatile oils, hydrocarbons, aromatic phenyl ring and oxygenated compounds. Silene marmarica is a small herbaceous plant found in Meditranian basin countries. It has a soft texture and green color. It is one of the oldest plants used in ancient and modern medicine. It may be used as a sanitizer or antimicropial agent. It could also be used as a scented repellent.

The aim of this work is to evaluate Silene marmarica as an environmentally safe corrosion inhibitor for steel in 0.5 M sulfuric acid and to assess the effect of addition of halides on the inhibition efficiency.

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2. Experimental

2.1. Electrochemical Tests

Potentiodynamic polarization curves and Electrochemical impedance spectroscopy were achieved by using Gill ACM 604 Instrument. $0.01 \le f \le 3 \times 10^4$ Hz frequency range for EIS measurements with an applied potential range of ± 250 mV around the rest potential and a signal amplitude of 10 mV around the rest potential at a 20 mV/min. scan rate was used for polarization curves measurements. The data was obtained in a multi nicked cell in which graphite rod and saturated calomel electrode were used as counter and reference electrodes, respectively. Steel rods have the chemical composition (wt %): C 0.21; S 0.04; Mn 2.5; P 0.04; Si 0.35; balance Fe has been used as the working electrode. The steel samples were fixed in poly tetrafluoro ethylene (PTFE) rods by an epoxy resin in a manner that only one surface of area (0.28 cm^2) was left uncovered. The exposed area was mechanically polished with a series of emery papers of different grades, the samples were then washed thoroughly with distilled water followed by A.R. ethanol and finally with distilled water, just before insertion into the cell. Measurements were done at 30°C.

2.2. Preparation of Solution

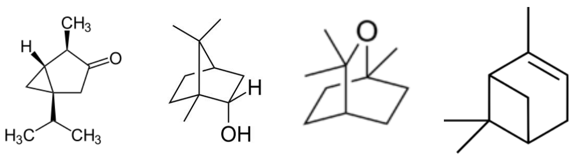

Figure 1. Chemical composition of Silene Marmarica

Silene marmarica is edible, its chemical composition, which is Thujon, Borneol, Cineol and Pinene, is given in Fig. 1. Raw Silene marmarica was used in this study as a whole. Stock solution of Silene marmarica was obtained by refluxing 10 g of dry plant in 100 mL of distilled water for 60 min. The refluxed solution was filtered off to remove any contaminants.

The concentration of the stock solution was determined by evaporating 10 mL of the filtrate and weighing the residue. The concentration of the stock solution was expressed in terms of ppm. The test solutions were prepared by diluting the stock solution and acid by using double distilled water to reach the required concentration.

3. Results and Discussion

3.1. Potentiodynamic Polarization Measurements

Tafel polarization curves for steel in 0.5 M H_2SO_4 in absence and presence of different concentrations of Silene marmarica are shown in Fig. 2. The cathodic and the anodic parts of Tafel lines were changed simultaneously, indicating that Silene marmarica acted as mixed type inhibitor and affects both the anodic dissolution and hydrogen evolution reactions.

The potentiodynamic polarization parameters and the inhibition efficiency were calculated and given in Table 1. The values of the inhibition efficiency were calculated according to the relation:

$$\% \text{ inh.} = [(i_{corr} - i_{corr}') / i_{corr}] \times 100 \qquad (1)$$

Where i_{corr} and i_{corr}' are the uninhibited and the inhibited corrosion current densities.

It is evident in the data in Table 1, that i_{corr} decreased in the presence of the extract this indicating that Silene marmarica acted as good inhibitor for steel in 0.5 M H_2SO_4. i_{corr} also, decreased with increasing the concentration of extract. Both the cathodic and anodic Tafel slopes (β_a and β_c) remained almost unchanged in presence of extract indicating that the inhibitor acted by adsorption on the metal surface and decreased the rate of both cathodic and anodic reactions. The values of the inhibition efficiency increase with increasing the concentration of the extract reaching a maximum value of 78.6%. Tafel polarization curves for steel in 0.5 M H_2SO_4 containing 700 ppm Silene marmarica in absence and presence of 0.01 M Iodide and Chloride are shown in Fig. 3.

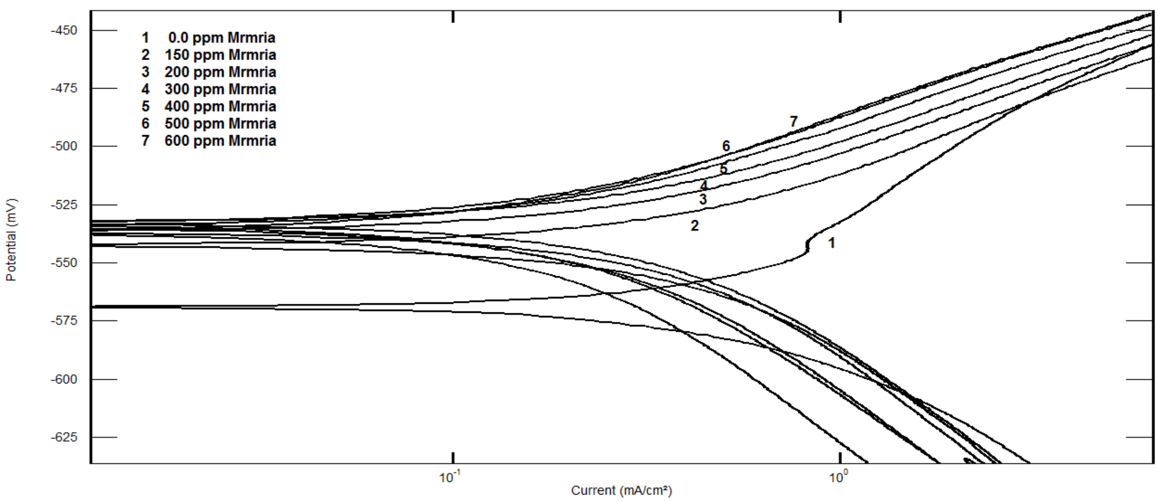

Figure 2. Potentiodynamic polarization curves for steel in 0.5 M H_2SO_4 containing different concentrations of Silene marmarica at 30°C

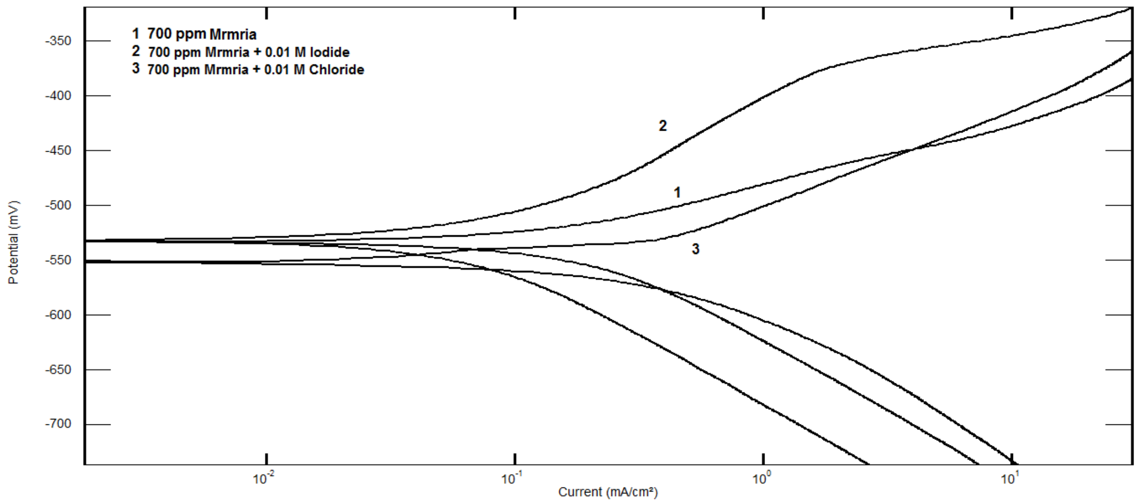

Figure 3. Potentiodynamic polarization curves for steel in 0.5 M H_2SO_4 containing 700 ppm Silene marmarica in absence and presence of 0.01 M chloride or iodide ions at 30°C

Table 1. Potentiodynamic polarization parameters for steel in 0.5 M H_2SO_4 in presence of different concentrations of Silene marmarica

Mrmria concn, ppm	β_a (V dec^{-1})	β_c (V dec^{-1})	-E_{corr} (mV)	I_{corr} (mA cm^{-2})	% Inhibition
0.0	102.3	107.2	555.9	0.56	----
150	60.2	127.3	534.8	0.39	30.4
200	59.4	119.0	532.5	0.33	41.1
300	55.3	118.7	525.8	0.30	46.4
400	51.1	123.3	522.5	0.22	60.7
500	63.0	110.9	531.2	0.21	62.5
600	52.6	119.5	528.0	0.15	73.2
700	59.9	119.8	528.6	0.16	71.4
800	63.4	102.5	533.6	0.13	76.7
900	67.3	97.1	547.6	0.12	78.6

Table 2. Potentiodynamic polarization parameters for steel in 0.5 M H_2SO_4 in presence of 700 ppm of Silene marmarica in absence and presence of 0.01 M chloride or iodide ions at 30 °C

Mrmria concn, ppm	β_a (V dec^{-1})	β_c (V dec^{-1})	-E_{corr} (mV)	I_{corr} (mA cm^{-2})	% Inhibition
700 ppm Mrmria	528.6	58.0	116.0	0.15	73.2
700 ppm Mrmria + I^-	541.9	115.9	118.6	0.07	87.5
700 ppm Mrmria + Cl^-	552.6	89.3	92.5	0.26	53.5

It is observed that the presence of chloride has acceleration effect while the presence of iodide shows positive effect. The potentiodynamic polarization parameters for steel in 0.5 M H_2SO_4 in presence of 700 ppm silene marmarica in absence and presence of iodide or chloride ions are calculated and given in Table 2.

It is clear that the presence of chloride ion increased i_{corr} while the presence of iodide decreased i_{corr}. This can be explained on the basis that the presence of iodide ion enhanced the adsorption of inhibitor due to the synergistic effect of iodide ions, while the chloride ion decreases the adsorption of the inhibitor.

3.2. Electrochemical Impedance Spectroscopy (EIS) Measurements

Nyquist plots for steel in 0.5 M H_2SO_4 for different concentrations of silene marmarica in absence and presence of 0.01 M of both iodide or chloride ions are shown in Figs. 4, 5 and 6, respectively. Nyquist plots showed only one capacitive depressed semicircle. It is clearly seen that the diameter of the semicircle increases with increasing the concentration of the inhibitor. The impedance spectra for different Nyquist plots were analyzed by fitting the experimental data using Zsimpwin program to a simple equivalent circuit model, Fig. 7. The equivalent circuit model includes the solution resistance R_s and the circuit includes capacitor C which is placed in parallel to charge transfer resistance element R_{ct}. The percentage of inhibition was calculated from the impedance measurements using the relation

$$\% \text{ inh.} = [(R_T - R_T0) / R_T] \times 100 \qquad (2)$$

The values of the electrochemical parameters obtained from EIS for steel in 0.5 M H_2SO_4 solution containing different extracts concentrations and the inhibition efficiency (% inh) are given in Table 3.

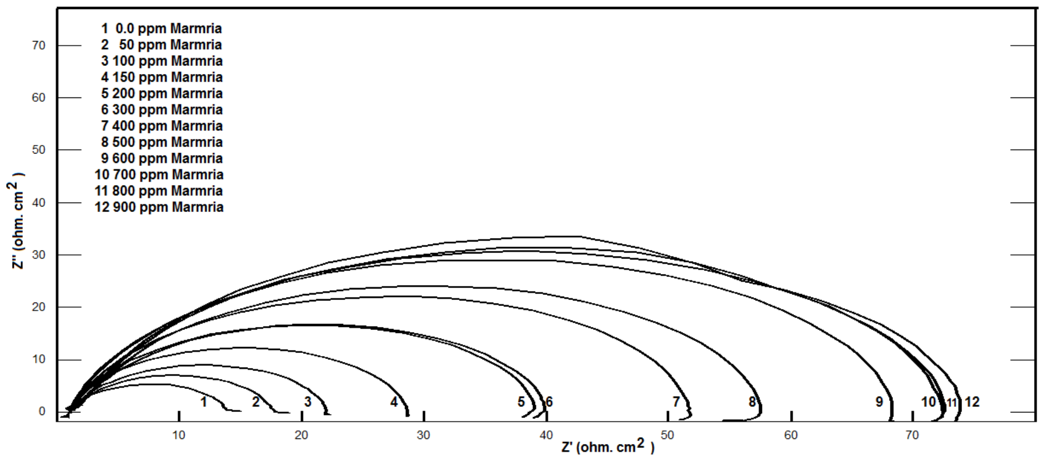

Figure 4. Nyquist plots for steel in 0.5 M H_2SO_4 containing various concentrations of Silene marmarica at 30°C

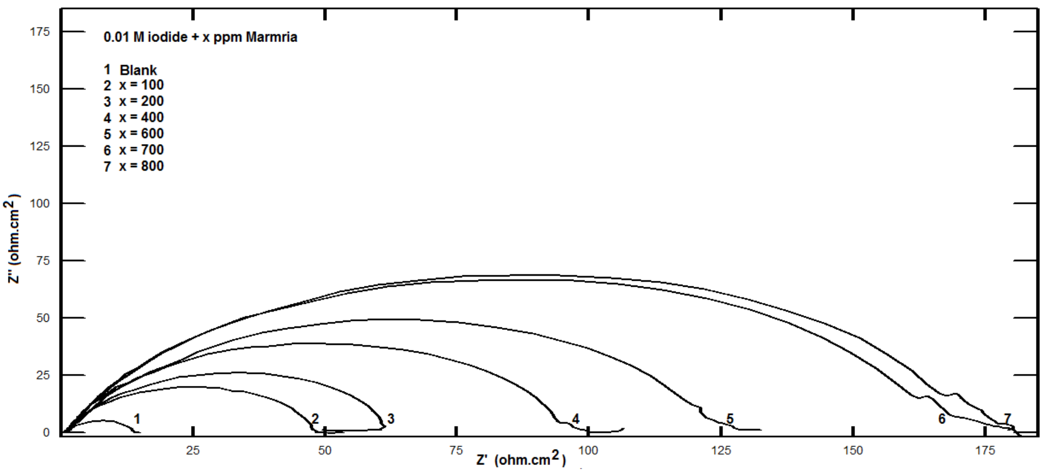

Figure 5. Nyquist plots for steel in 0.5 M H_2SO_4 containing various concentrations of Silene marmarica in presence of 0.01 M Iodide ion at 30°C

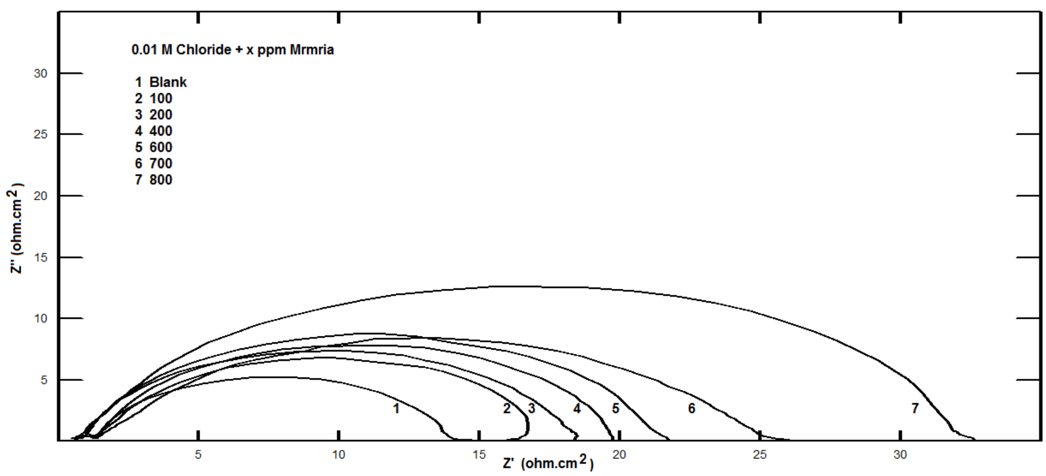

Figure 6. Nyquist plots for steel in 0.5 M H_2SO_4 containing various concentrations of Silene marmarica in presence of 0.01 M Chloride ion at 30°C

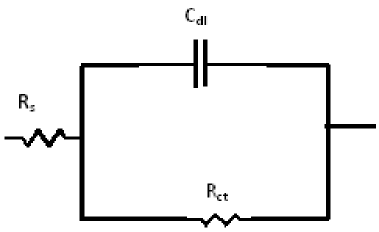

Figure 7. The equivalent circuit model

Table 3. EIS parameters for steel in 0.5 M H_2SO_4 in presence of different concentrations of Silene marmarica at 30°C

Concn (ppm)	Rs (ohm.cm^2)	Cdl (F.cm^{-2})	Rct (ohm.cm^2)	%Inh
0.0	1.04	3.97E-4	12.0	---
50	0.97	2.65E-4	16.9	28.9
100	1.01	3.04E-4	22.4	46.4
150	1.29	2.01E-4	27.0	55.5
200	0.79	1.30E-4	34.1	64.8
300	0.81	1.93E-4	39.7	69.7
400	1.06	1.23-4	51.6	76.7
500	1.17	1.41-4	57.8	79.2
600	1.14	8.30-5	68.1	82.3
700	1.11	9.10-5	72.2	83.3
800	0.88	1.10-4	72.5	83.4
900	1.00	6.20-5	72.7	83.5

From the impedance data in Table 3, it is clearly seen that the presence of Silene marmarica enhanced the values of R_{ct} and reduced the values of C_{dl}. The decrease in C_{dl} is due to the adsorption of the active ingredient of the extract on the metal surface, forming an adherent film, suggesting that the coverage of the metal surface with this film decreases the double layer thickness. The EIS parameters for steel in 0.5 M H_2SO_4 in presence of 700 ppm Silene marmarica in absence and presence of iodide and chloride ions are given in table 4.

Table 4. EIS parameters for steel in 0.5 M H_2SO_4 in presence of 700 ppm of Silene marmarica in absence and presence of 0.01 M chloride or iodide ions at 30 °C

Concentration	Rs (ohm. cm^2)	Cdl (F.cm^{-2})	Rct (ohm. cm^2)	%Inh
700 ppm Mrmria	1.11	9.00 x 10^{-5}	072.2	83.3
700 ppm Mrmria + I^-	0.93	1.23 x 10^{-4}	167.0	92.8
700 ppm Mrmria + Cl^-	1.01	3.50 x 10^{-4}	025.3	52.2

It is clear from table 4 that the values of R_{ct} and hence the inhibition efficiency increased in presence of iodide to 93% and decreased in presence of chloride. Fig. 8 represents the relation between the C_{dl} and the concentration of inhibitor in absence and presence of chloride and iodide ions. The higher values of C_{dl} was recorded in presence of chloride, indicating the displacement of the inhibitor molecules by the chloride ions which increased the thickness of the electrical double layer.

On the other hand, smaller values of C_{dl} in presence of iodide are observed in presence of iodide which are nearly similar to that obtained in presence of inhibitor indicating the co-adsorption of iodide ions and the inhibitor molecules which resulted in the formation of adherent film on the metal surface and suggests that the coverage of the metal surface with this film decreases the double layer thickness. Moreover, the inhibition efficiency of the extract increased, which was explained on the basis of the co-operative mechanism of adsorption by both the inhibitor and iodide [22].

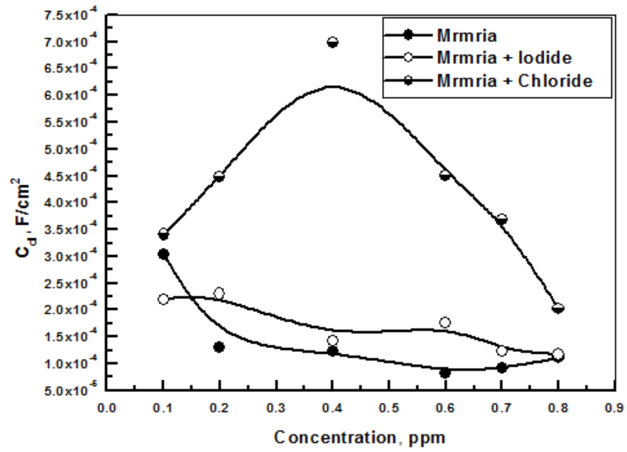

Figure 8. The variation of C_{dl} with the concentrations of Silene marmarica in presence of 0.01 M Chloride and 0.01 M Iodide ions at 30°C

3.3. Adsorption Characteristics

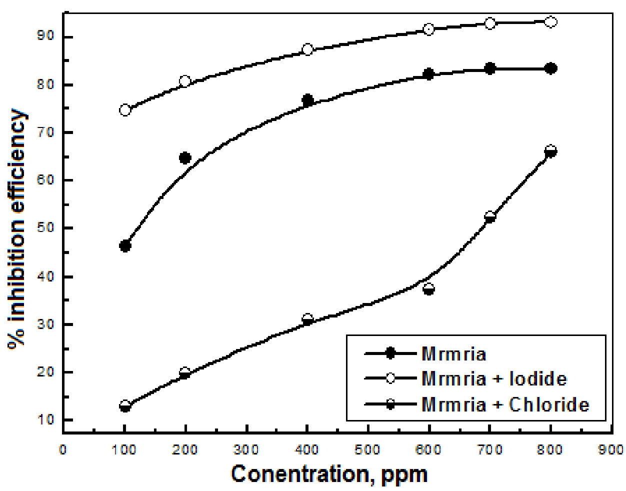

Figure 9. Variations of percentage inhibition of the corrosion of steel in 0.5 M H_2SO_4 with concentration of Silene marmarica extracts in absence and presence of chloride and iodide ions

In order to identify the nature of the adsorption between the inhibitor molecules and the metal surface; the application of different adsorption isotherm is essential. The relation between the percentage inhibition and the concentration of plant extract in absence and presence of iodide and chloride ions was shown in Fig. 9. The percentage inhibition was calculated from impedance measurements. These curves are characterized by an initial steeply rising part indicating the formation of a mono-layer adsorbate films on the steel surface until the saturation of metal surface is reached. It has been found that the presence of iodide increased the inhibition efficiency at all concentrations, in accordance with the results obtained from electrochemical measurements, while the presence of chloride decreased the inhibition efficiency at all concentrations. The experimental data was fitted to the Langumir adsorption isotherm and the Kinetic-Thermodynamic model in absence and presence of both chloride and iodide ions.

The following equation represents Langmuir adsorption isotherm [23]:

$$[C_{inh} / \theta] = [1 / K_{ads}] + C_{inh} \quad (3)$$

where K is the binding constant which represent the interaction between the additives and the metal surface and C represent the concentration of the additives.

The following equation represent the Kinetic - Thermodynamic model [24]:

$$\log [\theta /(1- \theta)]= \log K^{'} + y \log C \quad (4)$$

where; y represent the number of inhibitor molecules occupying one active site. K is called the binding constant and is given by:

$$K = K'^{\,(1/y)} \quad (5)$$

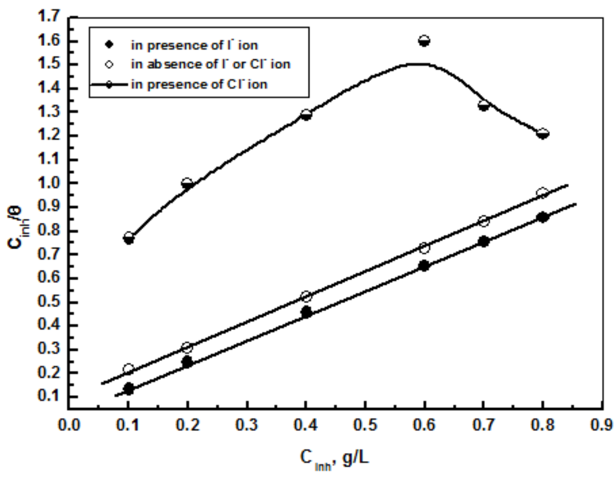

Figure 10. Application of Langmuir model to the results of adsorption of extract on steel surface in absence and presence of iodide ion

Figure 10, shows the application of the Langumir, model to the results of adsorption of the extract on steel surface in absence and presence of iodide or chloride ion. Fig. 11, shows the application of the Kinetic-Thermodynamic model to the results of adsorption of the extract on steel surface in absence and presence of iodide or chloride ion. The linear fitting parameters of Silene marmarica to the Langmuir and the Kinetic-Thermodynamic models are given in table 5. The validity of Langumir isotherm is confirmed from the linearity of C_{inh}/θ against vs C_{inh} having the slope value equal unity which represented ideal behavior of adsorption. The values of adsorption constant K_{ads} is calculated from the reciprocal of intercept of Langumir adsorption isotherm line and was found to be 9.9 in absence of iodide or chloride, 25.6 in presence of iodide and 0.05 in presence of chloride. It is clear that the Kinetic - Thermodynamic model fit the data obtained in absence and in presence of iodide or chloride ions.

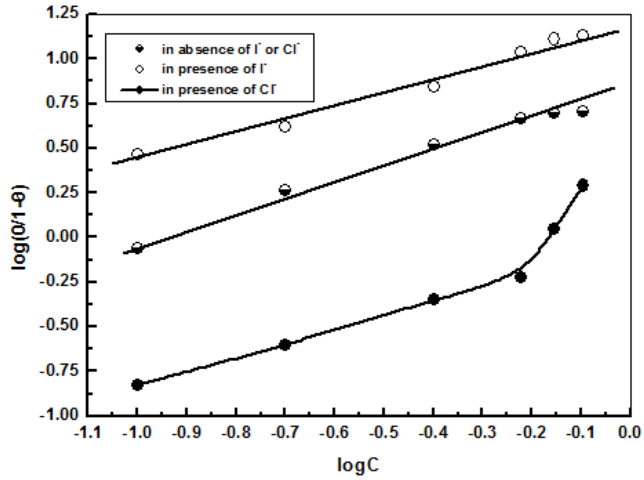

Figure 11. Application of the Kinetic - Thermodynamic model to the results of adsorption of extract on steel surface in absence and presence of iodide or chloride ion

Table 5. Linear fitting parameters of Silene marmarica to the Langmuir and the Kinetic-Thermodynamic models

Plant extracted	Model parameters		
	Langmuir	Kinetic-Thermodynamic	
	K	1/y	K
Silene Marmarica	9.90	1.16	9.28
Silene Marmarica + I^-	25.60	1.29	35.40
Silene Marmarica + Cl^-	0.05	0.95	0.06

The values of 1/y which is the number of active sites occupied by one inhibitor molecule, was nearly equal to 1 in the absence and presence of iodide or chloride ions, indicating that each inhibitor molecule occupied one active site. The values of K which is the binding constant was 9.28 in absence of iodide, 35.4 in presence of iodide and 0.06 in presence of chloride ion. The higher magnitude of the binding constant K was found in the presence of iodide rather than in its absence indicating the effect of the iodide ion on the strength of interaction of the extracted molecules with the metal surface. This confirmed the idea of the co-operative mechanism of adsorption [22, 25].

3.4. Effect of Halide on the Inhibition Efficiency of Silene Marmarica for Steel in 0.5 M H_2SO_4

Effect of Silene marmarica extract on the corrosion of steel in 0.5 M H_2SO_4 solution in absence and presence of different concentrations of iodide or chloride were examined by using potentiodynamic and electrochemical impedance spectroscopy. Figs. 12 and 13 show the potentiodynamic polarization curves for steel in 0.5 M H_2SO_4 containing 700 ppm Silane marmarica in absence and presence of different concentrations of iodide or chloride ions. The figures showed that the presence of iodide ion has an effect on both the anodic and cathodic tafel lines indicating that the iodide ion acted as mixed type inhibitor. On the other hand, the chloride ion had an acceleration effect on the potentiodynamic polarization curves.

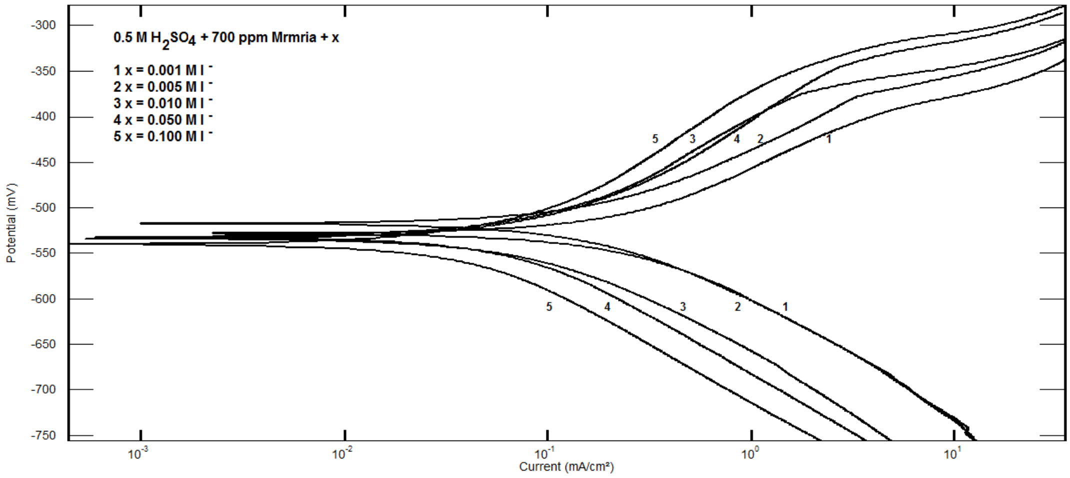

Figure 12. Potentiodynamic polarization curves for steel in 0.5 M H_2SO_4 containing 700 ppm Silene marmarica in absence and presence of different concentrations of iodide ions at 30°C

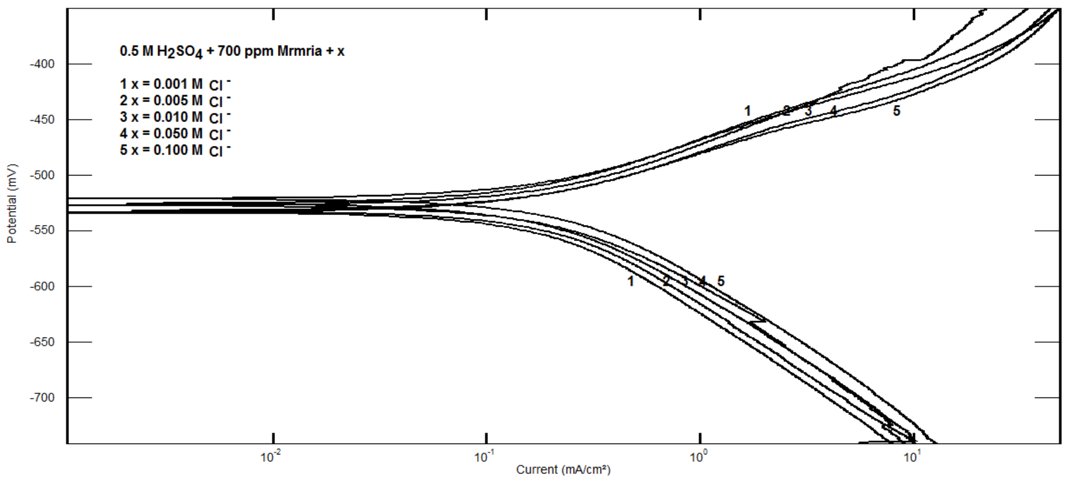

Figure 13. Potentiodynamic polarization curves for steel in 0.5 M H_2SO_4 containing 700 ppm Silene marmarica in absence and presence of different concentrations of chloride ions at 30°C

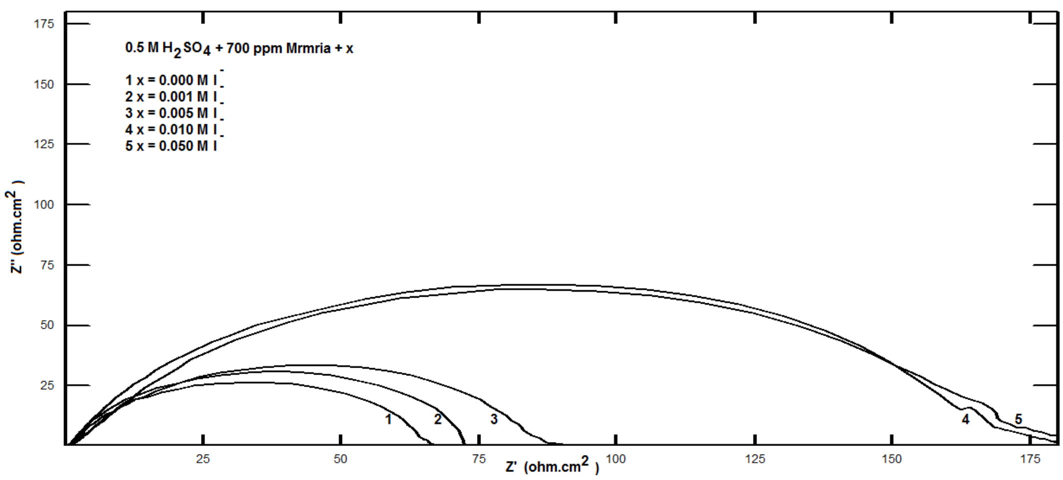

Figure 14. Nyquist plots for steel in 0.5 M H_2SO_4 containing 700 ppm Silene marmarica in absence and presence of different concentrations of iodide ions at 30°C

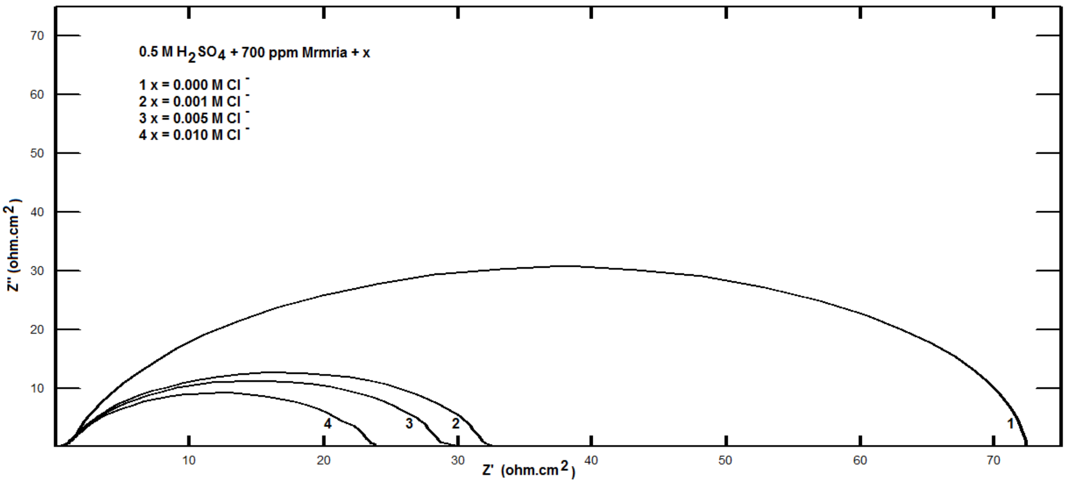

Figure 15. Nyquist plots for steel in 0.5 M H_2SO_4 containing 700 ppm Silene marmarica in absence and presence of different concentrations of chloride ions at 30°C

Figs. 14 and 15 show the Nyquist plots for steel in 0.5 M H_2SO_4 containing 700 ppm silane marmarica in absence and presence of different concentrations of iodide or chloride ions. The figures showed only one capacitive depressed semicircle. The diameter of the semicircle increased with the increasing concentration of iodide ion indicating the synergestic effect of iodide ion on the inhibition efficiency of the extract.

Table 6. The variation of R_{ct} of solution containing 700 ppm silene marmarica with different concentrations of chloride or iodide ions

Concentration (mol/L)	R_{ct} (ohm cm^2)	
	Iodide	Chloride
0.000	72.2	72.2
0.001	62.0	25.3
0.005	87.5	28.0
0.010	170.0	31.0
0.050	176.0	32.0

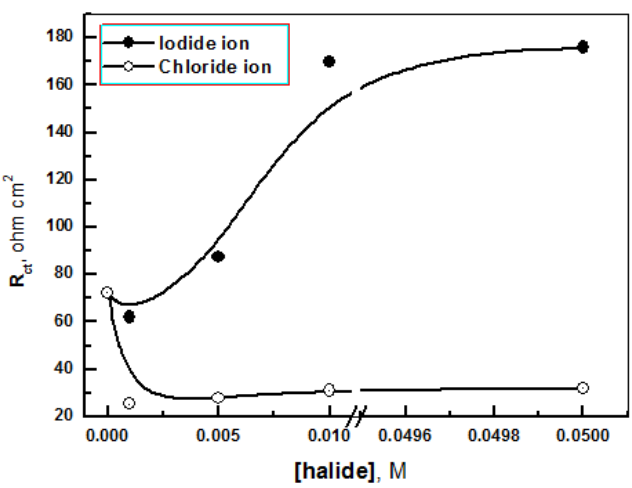

Figure 16. The variation of R_{ct} of solution containing 700 ppm silene marmarica with different concentrations of chloride or iodide ions

However, the presence of chloride ion had a negative effect on the inhibition efficiency of silene marmarica. The impedance data were analyzed by fitting the experimental data to the equivalent circuit model given in Fig. 7. The charge transfer resistance R_{ct} in absence and presence of 700 ppm silene marmarica in absence and presence of different concentrations of iodide or chloride are presented in table 6.

Fig. 16 represents the relation of R_{ct} vs the halide ion concentration. The figure showed that the presence of iodide increases the R_{ct} and consequently the inhibition efficiency of Silene marmarica while the R_{ct} decreased in presence of chloride ion. These results confirmed the results discussed above and suggested that the iodide ion enhanced the adsorption of the inhibitor through the co-adsorption mechanism.

4. Conclusions

The extract of Silene marmarica acted as good inhibitor for the corrosion of steel in 0.5 M H_2SO_4. Silene marmarica extract is considered as mixed type inhibitor. The inhibition efficiency was found to increase with the increasing of extract concentration up to a maximum value. Iodide ion enhanced the inhibition efficiency of Silene marmarica while chloride ion decreased the inhibition efficiency. Langmuir adsorption isotherm is applicable to fit the data of Silene marmarica indicating the ideal behavior in the adsorption processes of these extracts on the steel surface. The Kinetic - Thermodynamic model fit the data of Silene marmarica, where higher values of the binding constant K in the presence of iodide ion was revealed, rather than in its absence were obtained indicating strong adsorption of the inhibitor in the presence of iodide compared to its decrease in absence.

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