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GREEN INHIBITORS FOR CORROSION PROTECTION OF N80 CARBON STEEL IN 1M HCl AQUEOUS SOLUTIONS

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ABSTRACT

The inhibitive action of Saponinic extract of both Zygophyllum album and Zygophyllum aegyptium leafs which could serve as eco-friendly materials was investigated on the corrosion of N80 carbon steel in 1M HCl solution .The techniques employed for study were weight loss measurements, potentiodynamic polarization, electrochemical frequency modulation (EFM) and electrochemical impedance spectroscopy (EIS). The results obtained show that these extracts could serve as effective inhibitor for N80 carbon steel. The percentage inhibition increases with increasing concentration of the inhibitor at 25 °C. The percentage inhibitor efficiency above 90% was obtained at concentration of 700 ppm for both extracts. The corrosion rates of steel and inhibitive efficiencies obtained from impedance and polarization measurements were in good agreement with those obtained from weight loss measurements. Potentiodynamic polarization studies clearly reveal that both extracts act as mixed type inhibitor. The study shows that the inhibition efficiency decreased with temperature rise of the medium. Heat of adsorption (ΔH_{ads}) and thermodynamic parameters (ΔG) and (ΔS) indicated that the adsorption process is mainly controlled by physical adsorption process.

KEYWORDS

Green Inhibitors, N80 Carbon steel, Corrosion Protection

RESUMO

A inibição da corrosão do aço carbono N80 foi estudada na presença de extratos saponínicos de folhas de Zygophyllum álbum e Zygophyllum aegyptium em solução aquosa de HCl. Foram usadas técnicas de perda de peso, polarização potenciodinâmica, modulação da freqüência eletroquímica e espectroscopia de impedância eletroquímica, Os resultados experimentais mostraram que os extratos são eficientes na inibição da corrosão. O processo de inibição depende da concentração de extrato e da temperatura.

PALAVRAS CHAVE

Inibidores Verdes, Aço Carbono N80, Proteção da Corrosão

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1-INTRODUCTION

Chemical inhibitors play an important role in the protection and mitigation strategies for retarding corrosion (1). Most acid inhibitors are organic compounds containing nitrogen, oxygen and/or sulpher. These compounds are adsorbed on the metallic surface, blocking the active corrosion sites (2-5). Due to the negative effects of these compounds caused in the environment (6), the development of novel corrosion inhibitors of natural sources and non-toxic type has been considered to be more important and desirable (7). Some investigations have been made recently on the corrosion inhibition properties of naturally occurring plant extracts, which have been reported to have generally good inhibition efficiencies for carbon steel (8-16) and for other metals like tin (17), copper (18), aluminum (19-20) and zinc (21). The aqueous extract of one of the plants under investigation (Zygophylium album) has been formerly investigated for X52 Mild Steel in sulfuric acid (22). However, the constituents that provide inhibitive action, the mechanisms and the best condition for inhibition are still unclear.

As a contribution to the current interest on eco- friendly, green, corrosion inhibitors, the present study investigates the inhibiting effect of saponin extracts of the leafs of Zygophyllum aegyptium, which grows in the deltaic Mediterranean coast of Egypt (23) and Zygophyllum album on N80 carbon steel corrosion in 1 M HCl .

2. EXPERIMENTAL

2-1. Preparation of plant extracts

Zygophyllum album and Zygophyllum aegyptium leaves which grow in the deltaic Mediterranean coast of Egypt were collected. These were crushed and extracted using methanol. The methanol crude extracts were partitioned against several solvents like petroleum ether , ethyl acetate and dichloromethane using a separatory funnel to get a high polar compound crude extract and passed through a diion column using methanol to get a moderate polar compound crude extract followed by the addition of acetone in order to get the crude saponien fraction . Plant extracts test solutions were prepared at concentrations of 50, 100, 300, 500 and 700 mg/L.

2.2. Specimen preparation

Al metal was provided from the pipeline Casing of ''Mansoura Petroleum Company, Mansoura Fields'' . Its chemical composition is (0.42%) C, (0.20%) Si, (1.03%) Mn, (0.012%) P, (0.007%) S, (0.019%) Cr, (0.002%) Ni, (0.005%) Ti, (0.04%) Cu and Fe balance. Coupons were cut into 2 × 2 × 1 cm dimensions used for weight loss measurements, whereas specimens with 1 × 1 × 1 cm dimensions, sealed by polyester resin, leaving a surface area of 1 cm^2, were used as working electrode for polarization , EFM and EIS measurements. The surfaces of the sample were mechanically polished by grit silicon carbide paper progressively up to 1200 mesh, rinsed with acetone washed with bidistilled water and then dried before each experiment.

2.3. Solutions preparation

All chemicals and reagents were of analytical grade. A 1 M HCl stock solution was prepared by dilution of 37% HCl using distilled water. The concentration range of the employed extracts was varied from 50 to 700 mg/l.

2.4. Weight loss measurements

Weight loss study was carried out at 25, 35 & 45 °C for 3 hours time duration in HCl solution. The inhibition efficiency (IE) is determined by following equation:

$$IE = (1 - [Wi / W0]) \times 100 \qquad (1)$$

Where W_0 and W_i are the weight loss values in absence and in presence of inhibitor.

2.5. Polarization measurements

Potentiostatic polarization studies were carried out using a typical three-compartment glass cell consisted of the iron specimen as working electrode with an exposed working area of 1.0 cm2 , saturated calomel electrode (SCE) as a reference electrode and a platinum foil (1.0 cm^2) as a counter electrode. The reference electrode was connected to a Luggin capillary to minimize IR drop. The cells were under athmospheric conditions without stirring and at the room temperature. All potential values were reported versus SCE. Prior to every experiment, Tafel polarization curves were obtained by changing the electrode potential automatically from -500 to 500 mVSCE at open circuit potential with a scan rate of 5 mVs-1. Stern-Geary method used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines of charge transfer controlled corrosion reactions to a point which gives log(I_{corr}) and the corresponding corrosion potential (E_{corr}) for inhibitor free acid and for each concentration of the used inhibitors. Then (I_{corr}) was used for calculation of inhibition efficiency and surface coverage (Θ) as below:

$$\%IE = (1 - [i_{corr\,(inh)} / i_{corr\,(free)}]) \times 100 \qquad (2)$$

$$\theta = 1 - [i_{corr\,(inh)} / i_{corr\,(free)}] \qquad (3)$$

Where $i_{corr\,(free)}$ and $i_{corr\,(inh)}$ are the corrosion current densities in the absence and presence of inhibitor

2.6. Electrochemical impedance spectroscopy (EIS)

Impedance measurements were carried out in frequency range from 100000 Hz to 0.5 Hz with amplitude of 10 mV peak-to-peak using Ac signals at open circuit potential. The experimental impedance were analyzed and interpreted on the basis of the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagram are the resistance of charge transfer R_{ct} (diameter of high frequency loop) and the capacity of double layer C_{dl} which is defined as:

$$Cdl = 1/ (2 \pi fmax\ Rct) \qquad (4)$$

Where *fmax*, is the frequency at which the imaginary component of the impedance is maximal

The inhibition efficiencies and the surface coverage (θ) obtained from the impedance measurements are defined by the following relations:

$$\%IE= (1- [R^{o}_{ct}/R_{ct}]) \times 100 \qquad (5)$$

□$\theta = 1-[R^{o}_{ct}/R_{ct}]$ (6)

where R^{o}_{ct} and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor,

2.7. Electrochemical frequency modulation (EFM)

Electrochemical frequency modulation, EFM, was carried out using two frequencies 2 and 5 Hz. The base frequency was 0.1 Hz, so the waveform repeats after 1 s. The higher frequency must be at least two times the lower one. The higher frequency must also be sufficiently slow that the charging of the double layer does not contribute to the current response. Often, 10 Hz is a reasonable limit. The Intermodulation spectra contain current responses assigned for harmonical and intermodulation current peaks. The larger peaks were used to calculate the corrosion current density (I_{corr}), the Tafel slopes (β_c and β_a) and the causality factors CF2& CF3

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements:

The corrosion rate and inhibition efficiency for N80 carbon steel in 1M HCl Solution at 25 °C, 35 °C and 45 °C in the absence and presence of the Zygophyllum album and Zygophyllum Aegyptium extracts are given in Table (1) and Table (2). It is indicated that inhibitions efficiency for N80 carbon steel increases with the increase of the inhibitor concentration up to 89.32% for both Zygophyllum album and Zygophyllum Aegyptium at 25°C. As the temperature increases the inhibition efficiency decreases. At 35 and 45 °C maximum inhibition efficiencies of 73.90% and 66.53% is observed for Zygophyllum album , but for Zygophyllum Aegyptium extract the maximum inhibition efficiencies were 85.29% and 73.93% obtained in 1M HCl solution containing 700 ppm for both plants extracts. This indicates that Zygophyllum Aegyptium extract as a corrosion inhibitor has more resistance for temperature changes than Zygophyllum album extract. Figures (1) and (2) represent the relation between weight loss and time in absence and presence of different concentrations of Zygophyllum album and Zygophyllum Aegyptium extracts.

Conc. (ppm)	Temperature								
	25°C			35°C			45°C		
	Corrosion rate (mg/cm2 h)	☐	IE (%)	Corrosion rate (mg/cm2 h)	☐	IE (%)	Corrosion rate (mg/cm2 h)	☐	IE (%)
blank	0.0206	0	0	0.02525	0	0	0.04592	0	0
50	0.0089	0.56796	56.796	0.01336	0.47089	47.089	0.02672	0.41811	41.811
100	0.0077	0.62621	62.621	0.01285	0.49108	49.108	0.02313	0.49629	49.629
300	0.00451	0.78106	78.106	0.01028	0.59287	59.287	0.02028	0.55836	55.836
500	0.00211	0.89757	89.757	0.00846	0.66495	66.495	0.01691	0.63175	63.175
700	0.0022	0.89320	89.320	0.00659	0.73900	73.900	0.01537	0.66528	66.528

Table 1. Calculated values of corrosion rate, inhibition efficiency, Surface Coverage for N80 Carbon steel coupons in 1M HCl solutions containing Various Conc. n of Zygophyllum album.

Conc. (ppm)	Temperature								
	25°C			35°C			45°C		
	Corrosion rate (mg/cm2 h)	☐	IE (%)	Corrosion rate (mg/cm2 h)	☐	IE (%)	Corrosion rate (mg/cm2 h)	☐	IE (%)
blank	0.02066	0	0	0.02985	0	0	0.05051	0	0
50	0.01113	0.46135	46.135	0.01336	0.55242	55.242	0.02227	0.55909	55.909
100	0.01028	0.50249	50.249	0.01285	0.56951	56.951	0.02056	0.59295	59.295
300	0.00676	0.67284	67.284	0.00901	0.69815	69.815	0.01803	0.64304	64.304
500	0.00423	0.79528	79.528	0.00634	0.78760	78.760	0.0148	0.70698	70.698
700	0.00220	0.89352	89.352	0.00439	0.85293	85.293	0.01317	0.73925	73.925

Table 2. Calculated values of corrosion rate, inhibition efficiency, Surface Coverage for N80 Carbon steel coupons in 1M HCl solutions containing Various Conc. of Zygophyllum Aegyptium.

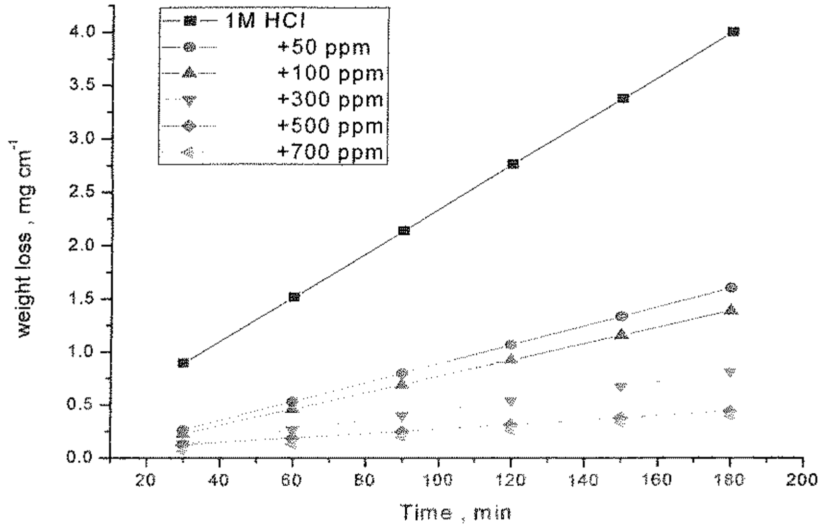

Fig. 1. Weight loss-time curves for the dissolution of N80 Carbon steel in the absence and presence of different concentrations of Zygophllum album at 25 °C

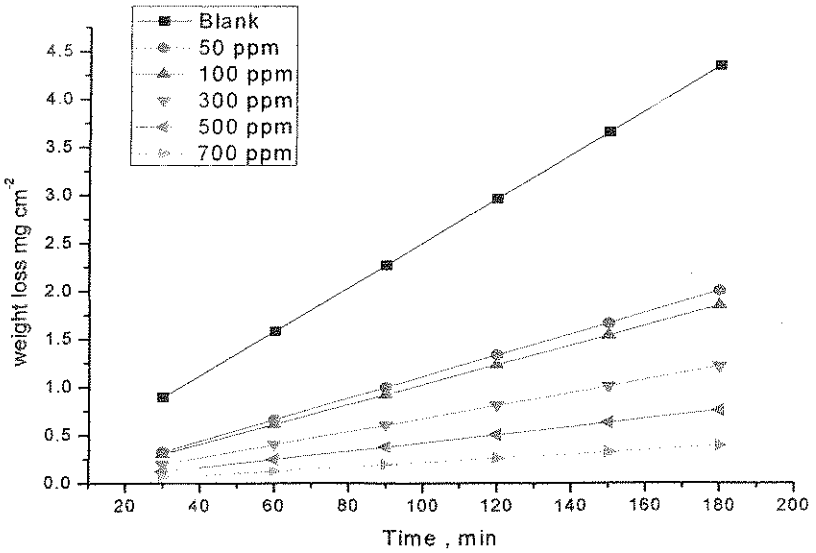

Fig. 2. Weight loss-time curves for the dissolution of N80 Carbon steel in the absence and presence of different concentrations of Zygophllum aegyptium at 25 °C

3.2 Potentiodynamic polarization

The potentiodynamic polarization curves for Carbon steel (N80) in 1 M HCl solutions containing different concentrations plant extracts at 20 °C are shown in Figure 3 and 4. The intersection of Tafel regions of cathodic and anodic branches gives the corrosion current density (icorr) and the corrosion potential (Ecorr). Tables 3 and 4 show the electrochemical parameters (Ecorr, anodic and cathodic Tafel slopes, βa, βc, and icorr,) obtained from Tafel plots for the Carbon Steel (N80) alloy electrode in 1 M HCl solution in the absence and presence of different concentrations of investigated plant extracts.

Inspection of Figures 3 and 4 show that the addition of plant extracts has an inhibitive effect in both anodic and cathodic parts of the polarization curves and the addition of plant extracts generally has no effect on the Ecorr value and also decreases icorr value compared to the uninhibited Carbon Steel alloy. Thus, addition of these inhibitors reduces the Carbon Steel alloy dissolution as well as retards the hydrogen evolution reaction. In addition, parallel cathodic Tafel curves in Figures 3 and 4 show that the hydrogen evolution is activation-controlled and the reduction mechanism is not affected by the presence of the inhibitor [24]. The anodic curves of N80 Carbon Steel in

1 M HCl in the presence of plant extract show that the tested compounds have no effect at potential higher than Ecorr, This behavior may be the result of significant Carbon Steel alloy dissolution leading to a desorption of the inhibiting layer. In this case, the desorption rate of the inhibitor is higher than its adsorption rate [25]. So, it could be concluded that these compounds are of the mixed-type but dominantly act as a cathodic inhibitor (βc>βa) for Carbon Steel alloy in 1 M HCl medium, which may be adsorbed on the cathodic sites of the Carbon Steel alloy and reduce the evolution of hydrogen. This limitation of inhibitory action on cathodic domain is found by different researchers [26, 27]. The data of Tables 3 and 4 revealed that icorr decreases considerably with increasing inhibitor concentration, while no definite trend was observed in the shift of Ecorr values. The Tafel slopes show slight changes with addition of inhibitors, which suggests that the inhibiting action occurred by simple blocking of the available cathodic and anodic sites on Carbon Steel alloy surfaces. The dependence of % IE versus inhibitor concentration is also presented in Tables 3 and 4. The obtained efficiencies indicate these investigated plant extracts act as effective inhibitor.
The order of decreasing inhibition efficiency of the investigated compounds was found to be: for Zygophllum extract: Aegyptium >Album.

Figure 3. Potentiodynamic polarization curves for Carbon Steel in 1M HCl solution without and with various concentrations (50-700 PPM) of Zygophllum album at 20°C.

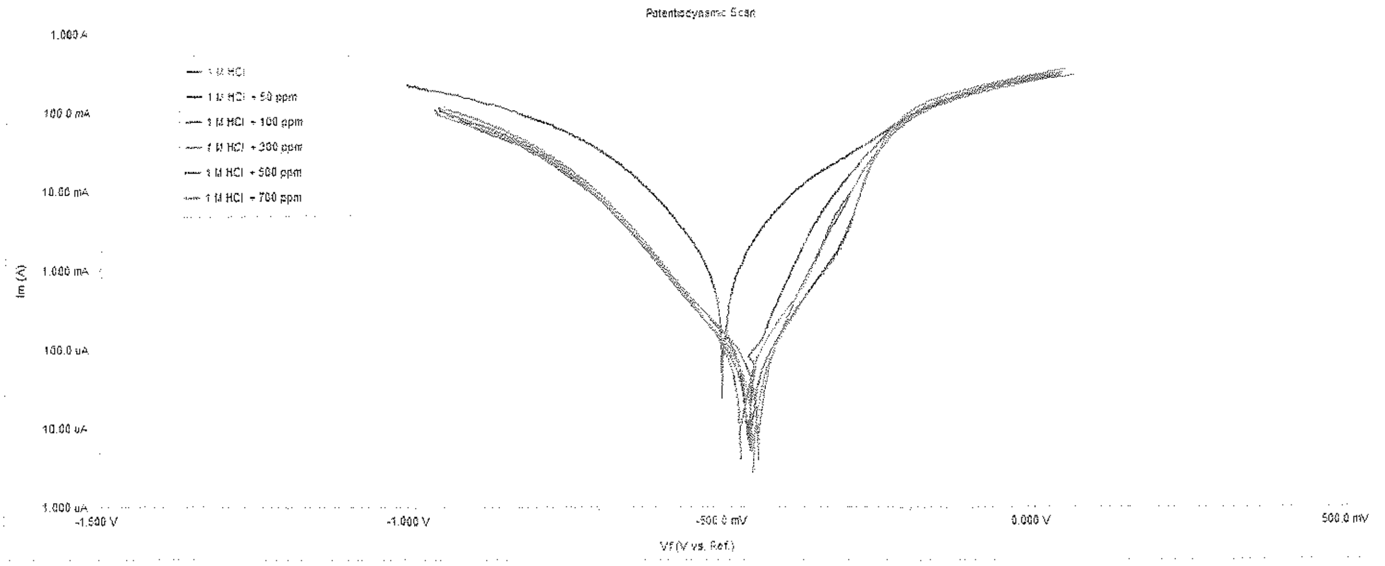

Figure 4. Potentiodynamic polarization curves for Carbon Steel in 1M HCl solution without and with various concentrations (50-700 PPM) of Zygophllum Aegyptium at 20°C.

Concentration, PPM	icorr, A cm-2	Ecorr, V vs.SCE	βa, VSCE dec-1	βc, VSCE dec-1	θ	% IE
1M HCl	1.74E-03	-5.02E-01	0.1691	0.1686	--	--
50	6.72E-04	-4.85E-01	0.1196	0.1813	0.613793	61.37931
100	2.69E-04	-4.86E-01	0.1031	0.15	0.845402	84.54023
300	2.55E-04	-4.68E-01	0.0918	0.144	0.853448	85.344828
500	2.36E-04	-4.80E-01	0.094	0.1509	0.864368	86.436782
700	1.49E-04	-4.86E-01	0.0933	0.1306	0.914368	91.436782

Table 3. The effect of concentration of the investigated Zygophllum Album on the free corrosion current density (icorr), corrosion potential (Ecorr) , Tafel slopes (βa& βc), corrosion rate ,degree of surface coverage (θ) and inhibition efficiency (% IE)for the corrosion of Carbon Steel in 1 M HCl at 20°

Concentration, PPM	icorr, A cm-2	Ecorr, V vs.SCE	βa, VSCE dec-1	βc, VSCE dec-1	θ	% IE
1M HCl	1.62E-03	-5.02E-01	0.1768	0.2012	--	--
50	11.50E-05	-4.62E-01	0.0781	0.1399	0.613793	61.37931
100	7.41E-05	-4.43E-01	0.0732	0.133	0.845402	84.54023
300	5.89E-05	-4.50E-01	0.0844	0.126	0.853448	85.344828
500	5.92E-05	-4.59E-01	0.0896	0.1216	0.864368	86.436782
700	5.88E-05	-4.71E-01	0.0827	0.1112	0.914368	91.436782

Table 4. The effect of concentration of the investigated Zygophllum Aegyptium on the free corrosion current density (icorr), corrosion potential (Ecorr) , Tafel slopes (βa& βc), corrosion rate ,degree of surface coverage (θ) and inhibition efficiency (% IE)for the corrosion of Carbon Steel in 1 M HCl at 20°

3.3. Electrochemical impedance spectroscopy measurements:

Electrochemical impedance spectroscopy provides a new method to characterize the film coverage on the electrode, which is related to charge transfer resistance (Rct). The interface capacitance can also be used to determine the film quality [28-32]. It is known that the coverage of an organic substance on the metal surface depends not only on the structure of the organic substance and the nature of the metal, but also on the experimental conditions such as immersion time and concentration of adsorbent.

Figures 5 and 6 show the Nyquist plots for Carbon steel (N80) in 1M HCl solution in the absence and presence of different concentrations of plant extracts at 25 ° C. All the impedance spectra were measured at the corresponding open-circuit potentials. The fact that impedance diagrams have an approximately semi-circular appearance shows that the corrosion of Carbon steel (N80) in 1M HCl is controlled by a charge-transfer resistance process. Small distortion was observed in some diagrams. This distortion has been attributed to frequency dispersion as a result of surface roughness, impurities, dislocations, grain boundaries, and adsorption of inhibitors, formation of porous layers and in homogenates of the electrode surface. Inspections of the data reveal that each impedance diagram consists of a large capacitive loop with one capacitive time constant in the Bode phase plots -Figures (5-1&6-1)-which was assigned to presence of oxide film on the surface of Carbon Steel (N80) and its dielectric properties. The diameter of the capacitive loop increases with increasing concentration and were indicative of the degree of inhibition of the corrosion process. In addition to the high frequency capacitive loop, the semi-circles rolled over and extended to the fourth quadrant, and a pseudo-inductive loop at low frequency end was observed, indicating that Faradic process is taking place on the free electrode sites. This inductive loop is generally attributed to the adsorption of species resulting from the Carbon steel dissolution and the adsorption of hydrogen [33].

The electrical equivalent circuit model (Randles circuit) shown in Figure 7 was used to analyze the obtained impedance data. The circuit consists of the solution resistance (Rs), the charge-transfer resistance of the interfacial corrosion reaction (Rct) and the double layer capacitance (Cdl). Excellent fit with this model was obtained with our experimental data.

EIS data (Tables 5 and 6) show that the Rct values increases and the Cdl values decreases with increasing the inhibitor concentrations. This is due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface, decreasing the extent of dissolution reaction. The high (Rct) values, are generally associated with slower corroding system. The decrease in the Cdl can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer [34], suggested that the inhibitor molecules function by adsorption at the metal/solution interface.

The % IE obtained from EIS measurements are close to those deduced from polarization. It can be seen that the inhibition efficiency decreases in the order: Aegyptium> Album.

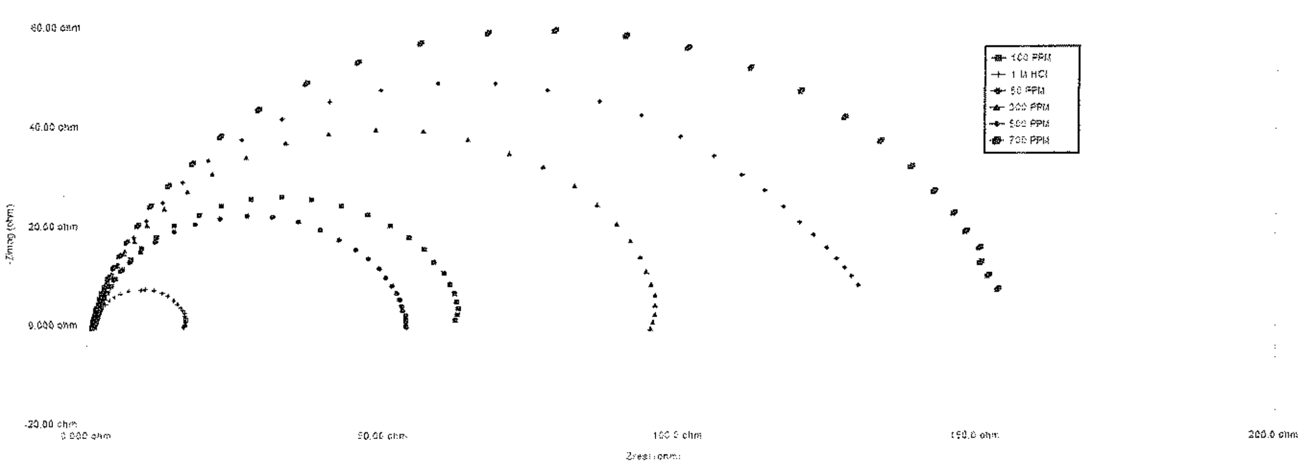

Figure 5. Nyquist plots recorded for Carbon Steel in 1M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum Album at the respective corrosion potentials and 20°C.

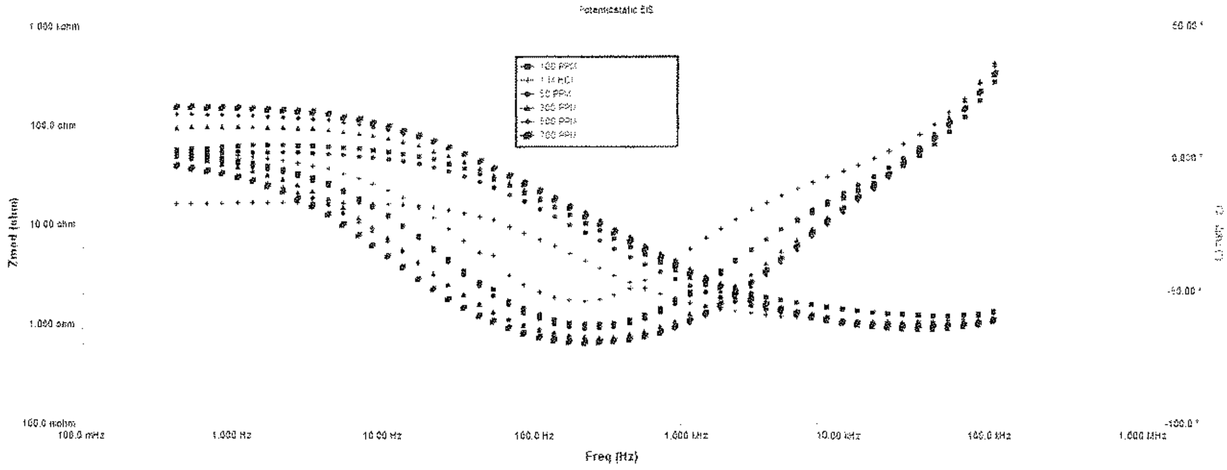

Figure (5-1). Bode plots recorded for Carbon Steel in 1M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum Album at the respective corrosion potentials and 20°C.

Concentration, PPM	Rct, Ω cm2	Ru, Ω cm2	Cdl, F cm-2	θ	% IE
1M HCl	15.59	1.077	2.23E-04	--	--
50	52.84	1.004	1.25E-04	0.704958	70.49584
100	61.18	1.259	1.00E-04	0.745178	74.51782
300	96.06	8.82E-01	1.03E-04	0.837706	83.77056
500	124.5	9.26E-01	8.66E-05	0.874779	87.47791
700	149.7	9.17E-01	9.70E-05	0.895858	89.58584

Table 5.Electrochemical kinetic parameters obtained by EIS technique for Carbon steel in 1MHCl solution containing various concentrations of the investigated Zygophllum Album Extract at 20°C.

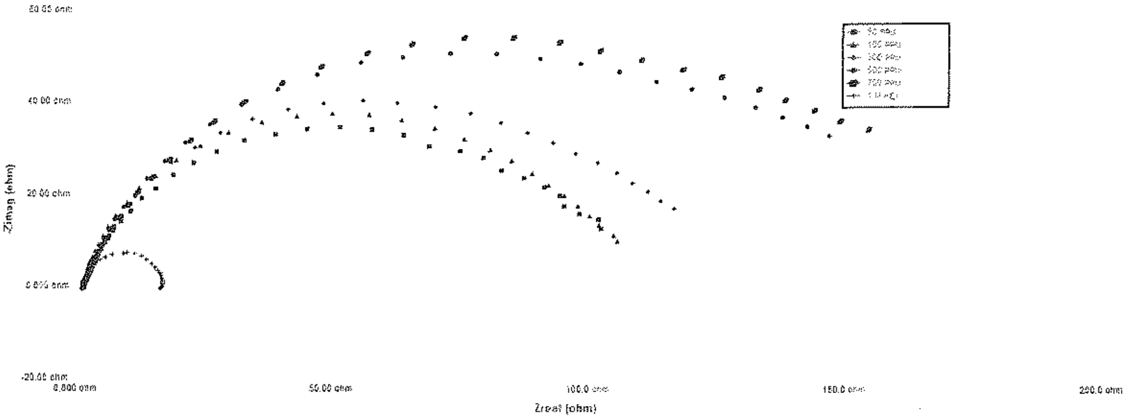

Figure 6. Nyquist plots recorded for Carbon Steel in 1M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum Aegyptium at the respective corrosion potentials and 25°C.

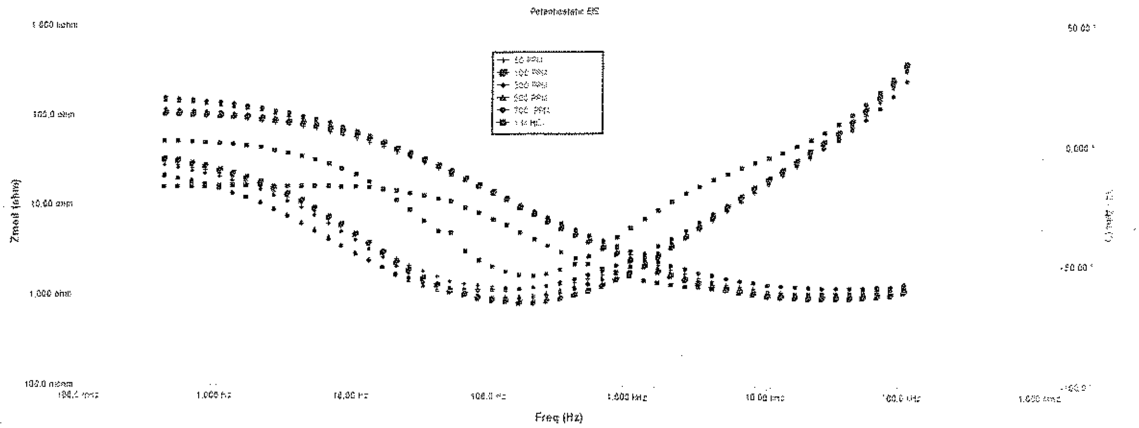

Figure (6-1): Bode plots recorded for Carbon Steel in 1M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum Aegyptium at the respective corrosion potentials and 25°C.

Concentration, PPM	Rct, Ω cm2	Ru, Ω cm2	Cdl, F cm-2	θ	% IE
1M HCl	15.59	1.077	2.23E-04	--	--
50	100.6	9.73E-01	1.97E-04	0.84503	84.50298
100	100.7	9.19E-01	1.63E-04	0.845184	84.51837
300	113	9.70E+02	1.86E-04	0.862035	86.20354
500	147.4	9.49E-01	2.21E-04	0.894233	89.42334
700	159.6	1.17E+00	2.29E-04	0.902318	90.23183

Table 5. Electrochemical kinetic parameters obtained by EIS technique for Carbon steel in 1MHCl solution containing various concentrations of the investigated Zygophllum Aegyptium Extract at 25°C.

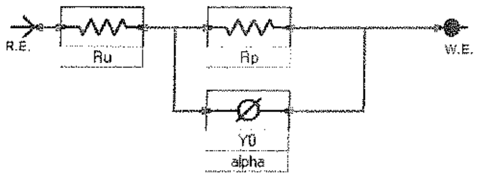

Figure 7. Electrical equivalent circuit used to fit the impedance data.

3.4. Electrochemical frequency modulation measurements (EFM)

The EFM is a nondestructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants. Like EIS, it is a small signal ac technique. Unlike EIS, However, two sine waves (at different frequencies) are applied to the cell simultaneously.

Studying effect of addition of Zygophllum album and Zygophllum Aegyptium plant extracts on the Corrosion of (N80) Carbon steel. ,Intermodulation spectra obtained from EFM measurements are presented in Figure 8 and 9 are examples of alloy in aerated 1 M HCl solutions devoid of and containing different concentrations of plant extracts at 25°C. Each spectrum is a current response as a function of frequency. The two large peaks are the response to the 2 Hz and 5Hz excitation frequencies. These peaks are used by the EFM 140 software package to calculate the corrosion current and Tafel constants.

The calculated corrosion kinetic parameters at different concentrations of the investigated extracts in 1 M HCl at 25 °C (icorr, βa, βc, CF-2, CF-3 and % IE) are given in Tables 7 and 8.

From Tables (7,8), the corrosion current densities decrease by increasing the concentration of investigated plant extracts and the inhibition efficiencies increase by increasing investigated plant extracts concentrations. The causality factors in Tables (7,8)are very close to theoretical values which according to EFM theory should guarantee the validity of Tafel slopes and corrosion current densities. Values of causality factors in Tables (7,8) indicate that the measured data are of good quality. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively. The deviation of causality factors from their ideal values might due to the perturbation amplitude was too small or the resolution of the frequency spectrum is not high enough also another possible explanation that the inhibitor is not performing very well. It can be seen that the inhibition efficiency slightly decreases in the order: Aegyptium > Album. The obtained results showed good agreement of inhibition efficiency obtained with the Potentiodynamic polarization, EIS and EFM methods.

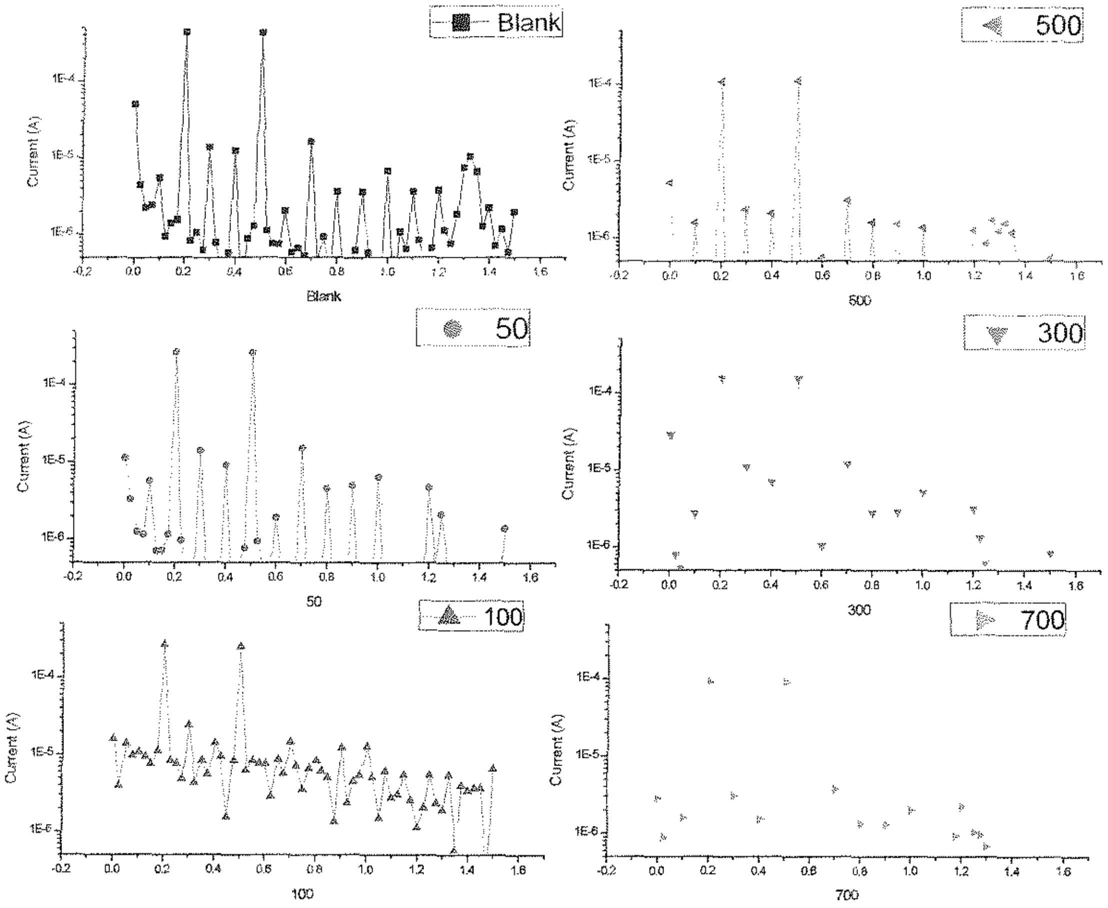

Figure 8. Intermodulation spectrum for Carbon steel in 1 M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum Album at 25°C.

Concentration, PPM	i_{corr}, µA cm^{-2}	β_a, mV_{SCE} dec^{-1}	β_c, mV_{SCE} dec^{-1}	Causality Factor (2)	Causality Factor (3)	C.R. mpy	θ	% IE
1 M HCl	799.4	0.1072	0.1388	1.559	2.074	365.3	--	--
50	361.8	0.0761	0.1022	1.874	2.978	165.3	0.547	54.7
100	274.3	0.0585	0.0798	1.439	1.155	125.3	0.657	65.7
300	215.1	0.0746	0.1127	1.891	3.067	98.31	0.731	73.1
500	172	0.0935	0.1087	1.592	2.685	78.6	0.785	78.5
700	126.5	0.0806	0.0984	1.926	4.218	57.8	0.842	84.2

Table 7. Electrochemical kinetic parameters obtained by EFM technique for Carbon Steel in 1M HCl solutions containing various concentrations of the investigated Zygophyllum album plant extract at 25°C.

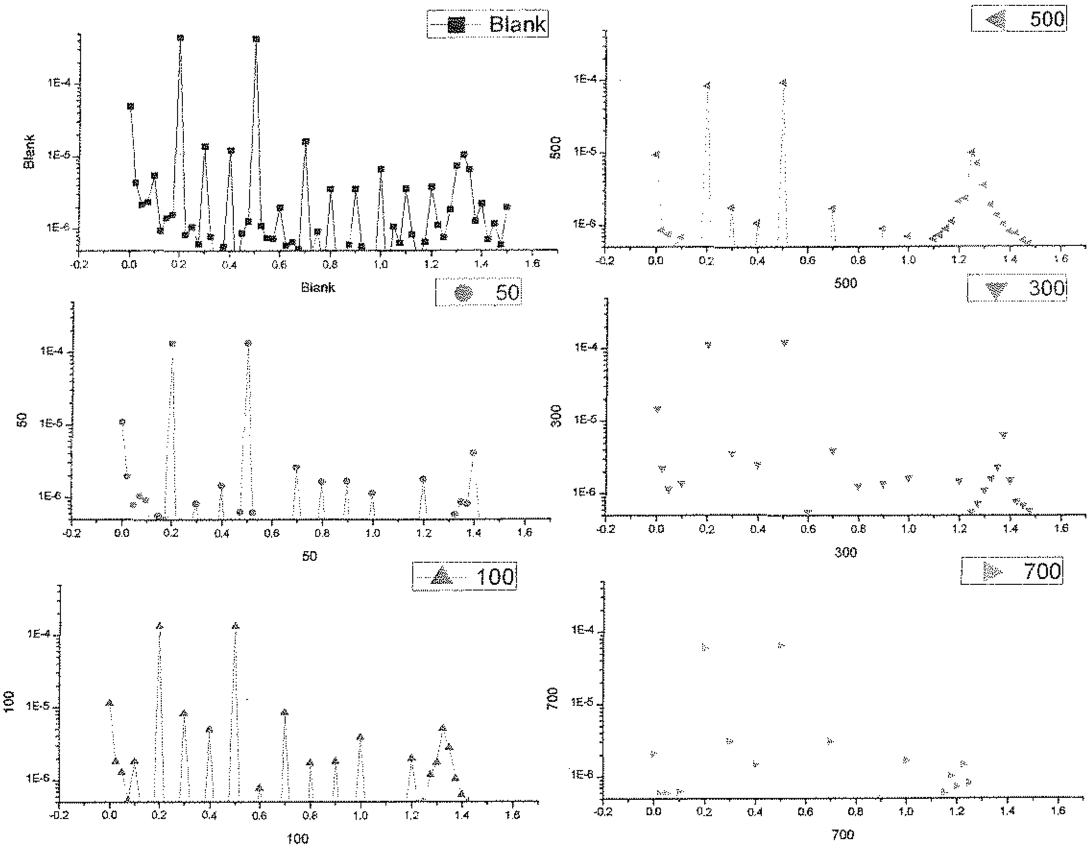

Figure 9. Intermodulation spectrum for Carbon steel in 1 M HCl solutions without and with various concentrations (50-700 PPM) of Zygophyllum aegyptium at 25°C.

Concentration, PPM	i_{corr}, μA cm^{-2}	β_a, mV_{SCE} dec^{-1}	β_c, mV_{SCE} dec^{-1}	Causality Factor (2)	Causality Factor (3)	C.R. mpy	θ	% IE
1 M HCl	799.4	0.1072	0.1388	1.559	2.074	365.3	--	--
50	222.9	0.1039	0.1132	1.292	6.254	101.8	0.7212	72.12
100	218.9	0.0871	0.1312	1.914	3.142	100	0.7262	72.62
300	200.8	0.0987	0.1220	1.807	3.071	91.75	0.7488	74.88
500	151.3	0.1021	0.1161	1.957	3.235	69.14	0.8107	81.07
700	123.6	0.1077	0.1599	1.932	3.97	56.47	0.8454	84.54

Table 8.Electrochemical kinetic parameters obtained by EFM technique for Carbon Steel in 1M HCl solutions containing various concentrations of the investigated Zygophyllum aegyptium plant extract at 25°C.

3.5. Adsorption isotherms:

(It is generally assumed that the adsorption of the inhibitors on the metal surface is the essential step in the inhibition mechanism [49]. To determine the adsorption mode, various isotherms were tested and the Langmuir mode was the best Fitted, given by Eq. (7) [35]:

$$\theta / 1 - \theta = Ka\ C \qquad (7)$$

where θ is the surface coverage, C is the inhibitor concentration (g/L) and Ka is the equilibrium constant of adsorption process and is related to the standard free energy of adsorption ΔG°_{ads} by the equation:

$$Ka = 1/55.5 \exp(-\Delta G^{\circ}_{ads}/RT) \qquad (8)$$

The value of 55.5 is the concentration of water in solution expressed in mole per liter, R is the universal gas constant and T is the absolute temperature. The Weight loss results were used to calculate the adsorption isotherm parameters. The surface coverage θ data are very useful while discussing the adsorption characteristics. The plot of C/ θ vs. C for all investigated Compounds gave a straight line (Figure 10) characteristic of the Langmuir adsorption isotherm. The calculated ΔG°ads values, using 8), were also given in Table (9). ΔG expressed in kJ mol-1 adsorbed. The negative values of ΔG°_{ads} ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the N80 carbon steel surface. It is well known that values of ΔG°ads of the order of 40 kJ mol-1 or higher involve charge sharing or transfer from the inhibitor molecules to metal surface to form coordinate type of bond (chemisorptions); those of order of 20 kJ mol-1 or lower indicate a physisorption. [36-39].

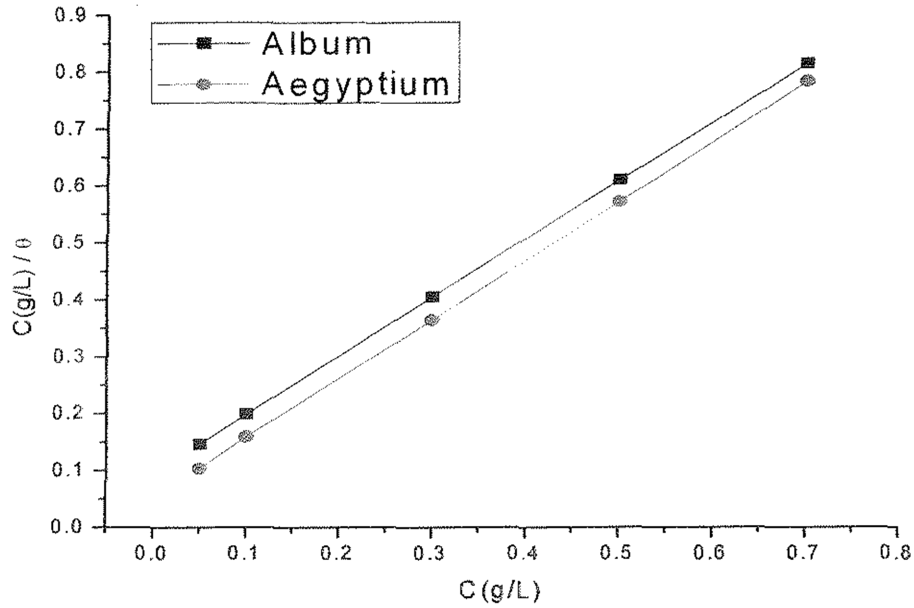

Figure 10 . Curve fitting of corrosion data for N80 carbon steel in 1M HCl in the presence of different concentrations of Zygophyllum album and Zygophyllum aegyptium extracts to Langmuir adsorption isotherm at 25° C.

Inhibitor	Langmuir Isotherm		
	i	K	$-\Delta G^{o}_{ads}$
Zygophyllum album	0.0493	20.2968	17.0272
Zygophyllum aegyptium	0.0928	10.7721	15.4922

Table 9. Equilibrium constant and adsorption free energy of the investigated compounds adsorbed on N80 carbon steel surface.

The calculated ΔG^{o}_{ads} values (Table 9) are less negative than -20 kJmol-1 indicate, therefore, that the adsorption mechanism of the investigated extract on N80 carbon steel in 1 M HCl solution is typical of physisorption.

3.6. Effect of temperature and activation parameters of inhibition process:

The influence of temperature on the corrosion rate of N80 carbon steel in 1 M HCl in the absence and presence of a various range of the tested plant extracts was investigated by the Weight loss technique in temperature range 25, 35 and 45 °C
The dependence of corrosion current density on the temperature can be expressed by Arrhenius equation:

$i_{corr} = A \exp(-E_a^* / RT)$ (9)

Where A is the pre-exponential factor and E_a^* is the apparent activation energy of the corrosion process. Tables (10&11) showed that the value of E_a^* for inhibited solution is higher than that for uninhibited solution, suggesting that dissolution of Al is slow in the presence of inhibitor. It is known from Eq. (9) that the higher E_a^* values lead to the lower corrosion rate.

Enthalpy and entropy of activation (ΔH^*, ΔS^*) of the corrosion process were calculated from the transition state theory -Tables (10&11):

Rate (i_{corr}) = $(RT/ Nh) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$ (10)

where h is Planck's constant and N is Avogadro's number. A plot of log (icorr/ T) vs. 1/ T for Al in 1 M HCl for the investigated extracts , gives straight lines as shown in Figure (12&14). Values of ΔH^* are positive. This indicates that the corrosion process is endothermic one .The entropy of activation is large and negative. This implies that the activated complex represents association rather than dissociation step , indicating that a decrease in disorder takes place, going from reactants to the activated complex [57].

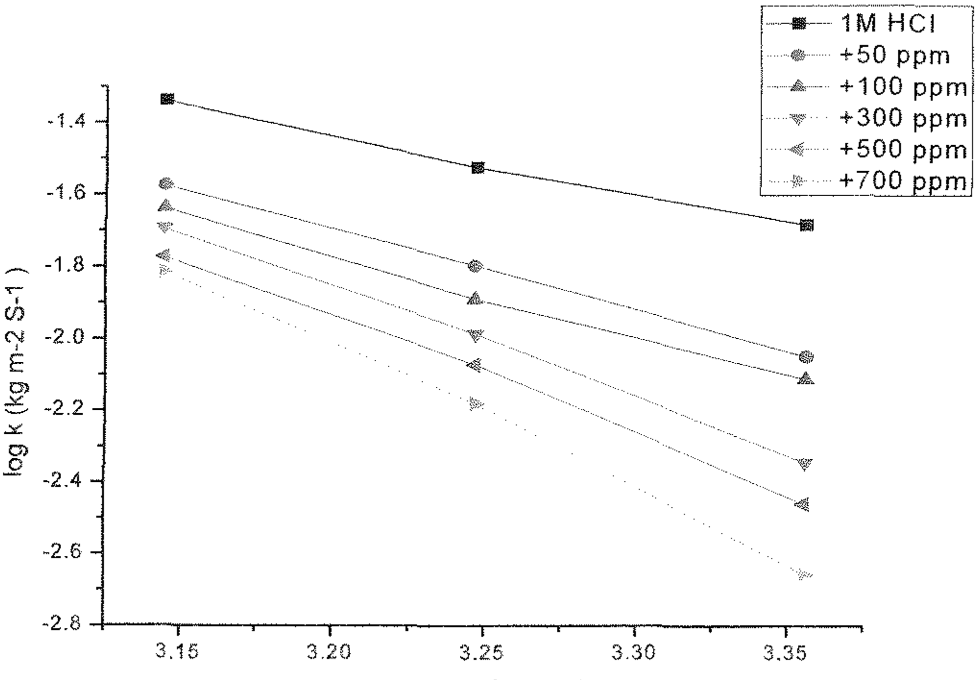

Figure 11 . log k (corrosion rate) – 1/T curves for N80 carbon steel dissolution in 1 M HCl in the absence and presence of Various conc. Range of Zygophyllum album extract.

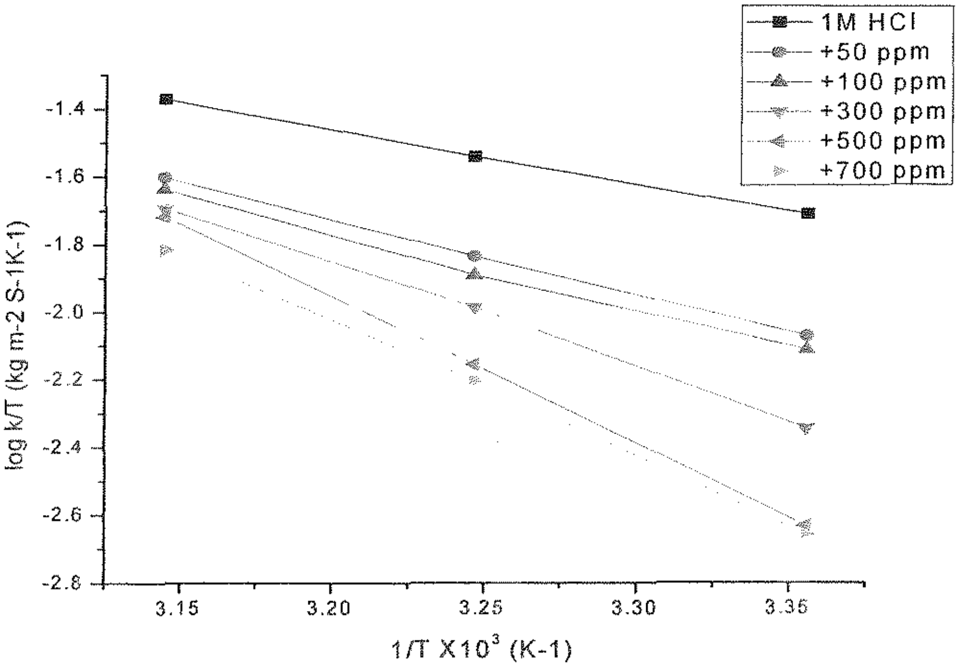

Figure 12 . log k (corrosion rate)/T – 1/T curves for N80 carbon steel dissolution in 1 M HCl in the absence and presence of Various conc. Range of Zygophyllum album extract.

conc.	Species : Zygophyllum album		
	E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J mol^{-1}K^{-1}
1M HCl	5.92	3.56	40.16
50 ppm	5.42	4.94	36.69
100 ppm	5.33	4.84	37.17
300 ppm	7.17	6.68	31.62
500 ppm	9.69	9.21	23.96
700 ppm	9.24	8.75	25.61

Table 10 . Activation parameters of the corrosion of N80 carbon steel in 1M HCl at various concentration ranges of Zygophyllum album extract.

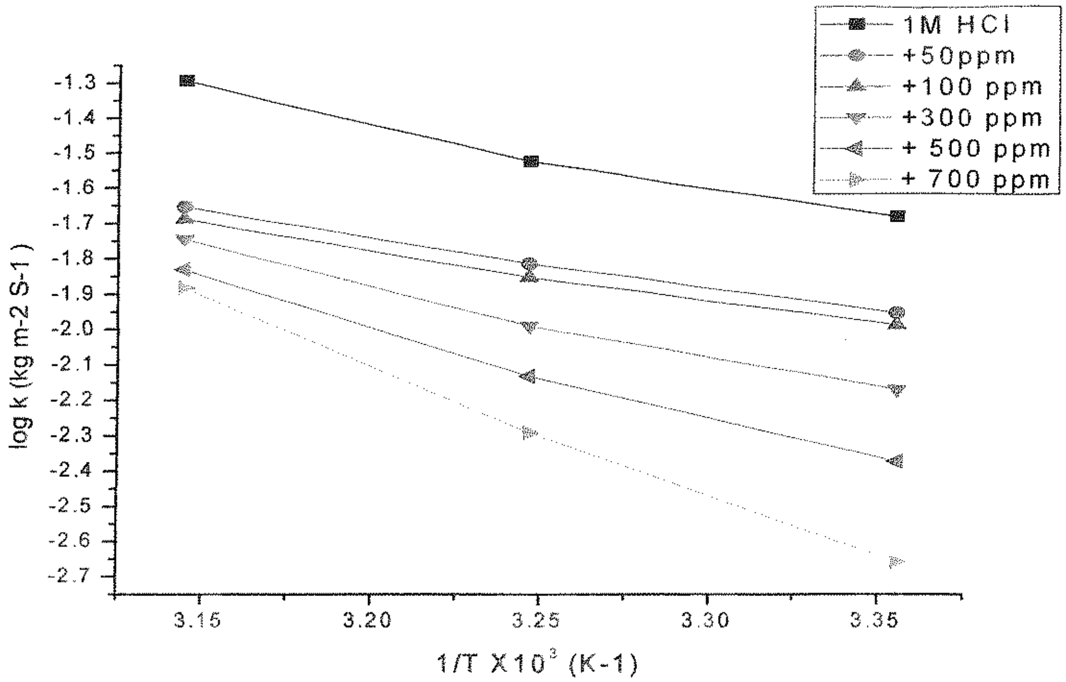

Figure 13 . log k (corrosion rate) – 1/T curves for N80 carbon steel dissolution in 1 M HCl in the absence and presence of Various conc. Range of Zygophyllum Aegyptium extract.

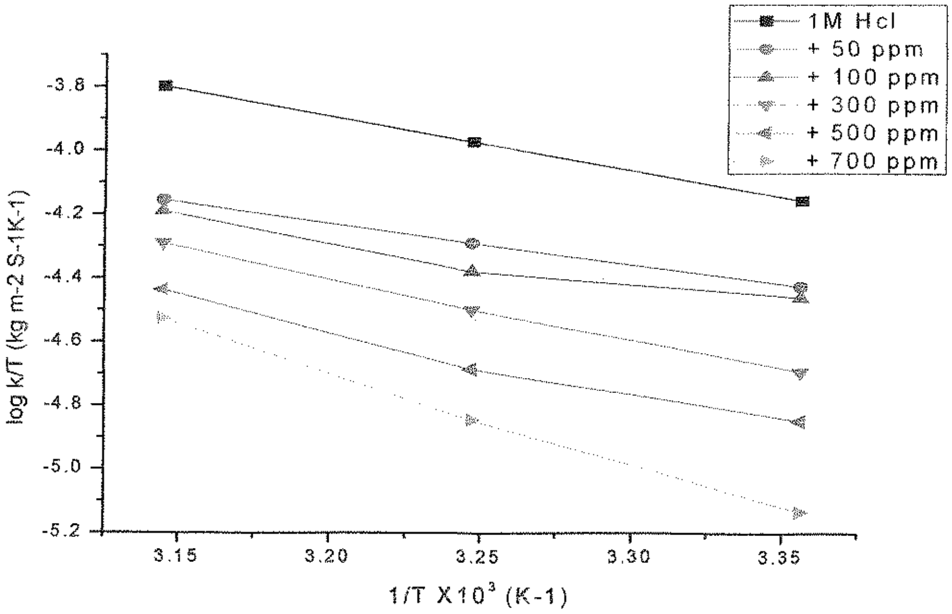

Figure 14 . log k (corrosion rate)/T – 1/T curves for N80 carbon steel dissolution in 1 M HCl in the absence and presence of Various conc. Range of Zygophyllum Aegyptium extract.

conc.	Species : Zygophyllum Aegyptium		
	E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J $mol^{-1}K^{-1}$
1M HCl	5.92	3.56	40.16
50 ppm	3.49	3.01	42.99
100 ppm	3.45	2.97	43.22
300 ppm	4.91	4.43	38.93
500 ppm	6.23	5.75	35.13
700 ppm	8.80	8.32	27.33

Table 11 . Activation parameters of the corrosion of N80 carbon steel in 1M HCl at various concentration ranges of Zygophyllum Aegyptium extract.

4. GENERAL CONCLUSIONS

Zygophyllum album and Zygophyllum aegyptium extracts acts as inhibitors for N80 carbon steel corrosion in 1M HCl solution. The corrosion process is inhibited by adsorption of the extract species on the N80 carbon steel surface following the Langmuir isotherm. The results suggested the use of Zygophyllum Aegyptium as a corrosion inhibitor because it has more resistance for temperature changes than Zygophyllum album extract.

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