investigated compounds. The presence of tetrahydrocarbazole derivatives decreased the activation energies of Zn indicating strong adsorption of the inhibitor molecules on the metal surface and the presence of these additives induces chemical bonds with Zn surface. These chemical bonds increased with increase of the additive concentrations. Values of the entropy of activation ΔS* in the absence and in presence of the studied compounds are negative .This implies that the activated complex in the rate determining step represents an association rather than a dissociation step (AbdEl-Rehim et al., 1999). This means that the activated molecules were in higher order state than that at the initial stage (Abdallah, 2003; Fouda et al., 2006).

3.4 Electrochemical measurement

Fig. (4) showed the potentiodynamic polarization curves for zinc in 0.4 M HCl solution in the absence and presence of different concentrations of compound (1). The effect of increased concentration were studied for all compounds, revealed that the presence of increase of the concentration of inhibitor caused a decrease in the corrosion rate .The corrosion current density (j_{corr}) was calculated by the extrapolation of anodic and cathodic Tafel lines. Table (4) showed that increase of the concentration of compound decreased the corrosion current density and shifts the corrosion potential to more negative values .Both anodic and cathodic Tafel slopes decreased by the addition of compound.

The % inhibition increased with increasing the concentration of the compounds, the inhibition efficiency of the four tested compounds measured by polarization method decreased in the following order: (1) > (2) > (3) > (4). This sequence is in accordance with that obtained from weight-loss measurements.

3.5 Electrochemical impedance spectroscopy

Figures (5& 6) showed the Nyquist and Bode plots for Zn metal in 0.4 M HCl solution in the absence and presence of different concentrations of compound (1). The impedance response consisted of characteristic semicircles for all solutions examined indicating that the dissolution process occurs under charge transfer control and the presence of the additive compound did not alter the mechanism of the acid dissolution. The impedance spectra for different Nyquist and Bode plots were analyzed by fitting the experimental spectra data to a simple equivalent circuit model, Fig. (7), which includes the solution resistance (R_s) and the double layer capacitance (C_{dl}) which is placed in parallel to charge transfer resistance element, (R_{ct}). Values of R_{ct} and C_{dl} for Zn in 0.4 M HCl containing different concentration of compound (1) and the inhibition efficiencies are given in Table (5). In an activated controlled system, the corrosion current density was calculated using the Stern-Geary equation (Stern and Geary, 1957):

$$j_{corr} = [(\beta_a \beta_b) / 2.303 (\beta_a + \beta_b) R_{ct}] \quad (12)$$

The cathodic and anodic Tafel slopes β_a and β_c were calculated from the corresponding polarization curves. From the impedance data given in Table (5), we conclude that:

1) As the impedance diagram obtained has a semicircle appearance, it shows that the corrosion of Zn is mainly controlled by a charge transfer process.

2) The value of R_{ct} increased with increase of the concentration of the inhibitors and this indicated the increase in the corrosion inhibition efficiency in acidic solution.

3) The value of double layer capacitance decreased by increasing the inhibitor concentration. This is due to the adsorption of these compounds on the electrode surface leading to a film formation on the Zn surface. The order of inhibition efficiency obtained from EIS measurements is as follows: (1) > (2) > (3) > (4)

This sequence is in accordance with that obtained from weight-loss and polarization measurements.

3.6 Electrochemical Frequency Modulation Technique (EFM)

Results of EFM experiments is a spectrum of current response as function of frequency .The spectrum is called the "inter modulation spectrum" and an example was shown in Figures.8-12. However, Figures.8-12 showed the corresponding current response in the inter modulation spectrum .The harmonic and inter modulation peaks are clearly visible and are much larger than background noise. The two large peaks, with amplitudes of about200μA, are the response to the 2 and 5 Hz excitation frequencies. Those peaks between1 and 20μA are the harmonic, sums, and differences of the two excitation frequencies. Analysis of these peaks at inter modulation frequencies can reveal the corrosion rate and Tafel parameters. It is important to note that between the peaks the current response is very small .The corrosion parameters such as inhibition efficiency (%IE), corrosion current density ($\mu A/cm^2$), Tafel constants and causality factors, at different concentrations of additive compounds in 0.4 M HCl solution at 30 ºC are presented in Table (6). Table (6) The corrosion current densities decreased by increasing the concentration of compound (1). The causality factors in Table (6) indicated that the measured data are of good quality .The standard values for CF-2 and CF-3 are 2 and 3, respectively. The causality factor is calculated from

the frequency spectrum of the current response. If the causality factors are approximately equal to the predicted values of 2 and 3, there is a causal relationship between the perturbation signal and the response signal .Then the data are assumed to be reliable (Bosch et al., 2001). When CF-2 and CF-3 are in the range 0-2 and 0-3, respectively, then the EFM data is valid. The deviation of causality factors from their ideal values might due to that the perturbation amplitude was too small or that the resolution of the frequency spectrum is not high enough also another possible explanation that the inhibitor is not performing very well (Abdel-Rehim et al., 2006).

4. Conclusions

1) The used new biologically active tetrahydrocarbazole derivatives as corrosion inhibitors for zinc in 0.4 M HCl act as an efficient inhibitor.

2) The inhibition efficiency increases with the increase of inhibitor concentration and with rising of temperature.

3) The data obtained from all different techniques namely weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy and electrochemical frequency modulation is in good agreement.

4) Adsorption of tetrahydrocarbazole derivatives on the Zn surface from acidic solution followed Langmuir isotherm, indicating that the main inhibition process occurred via adsorption.

5) The activation parameters E_a^*, $\Delta H^*$and ΔS^* for the corrosion of Zn in HCl solution containing inhibitors are presented.

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Table 1. Effect of inhibitors concentrations on the percentage inhibition efficiency (I %) of zinc in 0.4 M HCl solution from weight – loss method at 30 °C

Conc., (M)	I %			
	(1)	(2)	(3)	(4)
$1x10^{-6}$	53.4	38.1	30.0	28.2
$5x10^{-6}$	61.4	51.2	46.2	44.4
$9x10^{-6}$	68.0	58.8	56.1	55.7
$13x10^{-6}$	76.0	68.3	66.8	64.1
$17x10^{-6}$	80.8	79.4	78.6	74.1
$21x10^{-6}$	88.4	84.3	82.8	77.5

Table 2. Number of active sites (1/y), slopes of Langmuir isotherm lines, equilibrium constant of the adsorption process (K) and free energy of adsorption (ΔG°_{ads}) of inhibitors for Zn in 0.4 M HCl at 30 ºC

Inhibitors	Langmuir isotherm			Kinetic model		
	Slope=y	K x10^{-5} M^{-1}	$-\Delta G^{\circ}_{ads}$ (kJ/ mol)	1/y	K x10^{-5} M^{-1}	$-\Delta G^{\circ}_{ads}$ (kJ/ mol)
(1)	1.039	4.07	42.7	1.751	6.7	43.9
(2)	1.093	3.01	41.9	1.782	4.0	42.6
(3)	1.099	2.08	41.0	1.889	2.5	41.2
(4)	1.122	1.64	40.4	2.111	2.1	41.0

Table 3. Effect of inhibitors concentrations on the activation energy, activation enthalpy and activation entropy of Zn dissolution in 0.4 M HCl

	Conc., M	Compounds			
		(1)	(2)	(3)	(4)
ΔE^{*}, kJ/ mol	Blank		35.46		
	9×10^{-6}	24.1	24.6	32.6	33.3
	1.3×10^{-5}	23.1	22.9	29.5	33.1
	1.7×10^{-5}	20.5	23.4	28.7	32.9
	2.1×10^{-5}	18.0	22.2	27.0	30.2
ΔH^{*}, kJ/ mol	Blank		33.68		
	9×10^{-6}	22.4	22.7	29.6	31.5
	1.3×10^{-5}	19.9	21.7	27.9	31.5
	1.7×10^{-5}	16.9	21.5	27.0	30.6
	2.1×10^{-5}	16.0	20.4	24.9	28.5
ΔS^{*}, J/ mol/ K	Blank		165.41		
	9×10^{-6}	209.3	204.7	186.3	174.9
	1.3×10^{-5}	226.1	209.6	190.8	184.6
	1.7×10^{-5}	231.0	209.8	197.8	198.1
	2.1×10^{-5}	238.3	222.1	207.6	220.4

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Table 4. Corrosion parameters of zinc electrode in 0.4 M HCl solution containing different concentrations of compounds (1-4).

Comp.	Conc., (M)	$-E_{corr.}$ (V)	$j_{corr.}$, (mA/ cm^2)	β_c (mV/dec)	β_a (mV/dec)	R_p (Ω cm^2)	θ	% IE
	Blank	1.015	33.09	1018	700	5.44	-	-
	$1x10^{-6}$	1.047	5.36	339	309	12.28	0.838	83.8
	$5x10^{-6}$	1.033	4.86	332	299	14.25	0.853	85.3
1	$9x10^{-6}$	1.061	4.41	358	290	15.75	0.867	86.7
	$1.3x10^{-5}$	1.057	4.15	347	286	15.95	0.875	87.5
	$1.7x10^{-5}$	1.051	3.86	342	277	17.23	0.883	88.3
	$2.1x10^{-5}$	1.053	2.30	299	255	25.45	0.930	93.0
	1x10-6	1.021	7.67	537	463	12.28	0.768	76.8
	5x10-6	1.022	6.71	515	374	12.93	0.797	79.7
2	9x10-6	1.015	6.27	489	340	14.02	0.810	81.0
	1.3x10-5	1.014	5.04	438	324	16.05	0.848	84. 8
	1.7x10-5	1.010	4.15	450	308	19.16	0.875	87.5
	2.1x10-5	1.030	3.61	407	304	20.9	0.891	89.1
	1x10-6	1.066	8.91	543	396	9.91	0.73	73.1
	5x10-6	1.064	8.50	490	388	11.07	0.743	74.3
3	9x10-6	1.056	8.31	473	377	13.50	0.749	74.9
	1.3x10-5	1.015	7.74	452	349	11.05	0.766	76.6
	1.7x10-5	1.017	7.13	428	341	11.31	0.785	78.5
	2.1x10-5	1.052	4.05	418	329	21.43	0.878	87.8
	1x10-6	1.071	16.53	696	525	7.89	0.501	50.1
	5x10-6	1.058	11.00	556	406	9.27	0.668	66.8
4	9x10-6	1.055	9.79	535	384	9.92	0.704	70.4
	1.3x10-5	1.052	9.00	510	394	10.72	0.728	72.8
	1.7x10-5	1.053	7.62	451	356	11.3	0.770	77.0
	2.1x10-5	1.036	6.53	460	345	13.11	0.803	80.3

Table 5. The values of the electrochemical impedance parameters and % inhibition for zinc in 0.4 M HCl solution in the absence and presence of different concentrations of compounds (1-4) at 30 ºC

Compound	Conc., M	C_{dl} $\mu F/cm^2$	R_{ct} Ω cm^2	θ	% IE
	Blank	115.9	0.86	-	-
	$9x10^{-6}$	114.2	1.05	0.18	18.38
1	$1.3x10^{-5}$	78.61	1.86	0.54	53.974
	$1.7x10^{-5}$	73.6	1.92	0.55	55.25
	$2.1x10^{-5}$	79.36	2.21	0.613	61.29
	$9x10^{-6}$	101.1	1.462	0.41	41.38
2	$1.3x10^{-5}$	93.66	1.64	0.48	47.74
	$1.7x10^{-5}$	95.56	1.75	0.51	51.53
	$2.1x10^{-5}$	73.5	2.153	0.60	60.20
	$9x10^{-6}$	104.1	1.23	0.30	30.38
3	$1.3x10^{-5}$	92.23	1.52	0.44	43.47
	$1.7x10^{-5}$	70.63	1.9	0.55	54.90
	$2.1x10^{-5}$	66.26	2.0	0.57	57.17
	$9x10^{-6}$	104.7	1.19	0.28	27.98
4	$1.3x10^{-5}$	79.42	1.54	0.44	44.49
	$1.7x10^{-5}$	83.33	1.68	0.49	49.11
	$2.1x10^{-5}$	64.78	1.95	0.56	56.03

Table 6. Electrochemical kinetic parameters obtained by EFM for zinc in 0.4 M HCl solution, in the absence and presence of different concentrations of compounds (1-4) at 30 ºC

Comp.	Conc., M	j_{corr} (mA/cm^2)	β_1 (mV/dec)	β_2 (mV/dec)	Causality Factor (2)	Causality Factor (3)	θ	IE%
	Blank	2.14	0.43	0.49	1.8	2.86	-	-
1	$9X10^{-6}$	1.2	0.35	0.37	2.12	3.09	0.44	43.8
	$1.3X10^{-5}$	1.16	0.34	0.35	2.21	2.74	0.46	45.9
	$1.7X10^{-5}$	1.08	0.31	0.39	2.15	3.17	0.50	49.5
	$2.1X10^{-5}$	1.01	0.26	0.30	2.13	3.14	0.53	52.9
2	$9X10^{-6}$	1.21	0.36	0.37	2.01	3.04	0.43	43.3
	$1.3X10^{-5}$	1.16	0.34	0.35	2.23	2.90	0.46	45.8
	$1.7X10^{-5}$	1.11	0.31	0.35	1.82	2.67	0.48	48.2
	$2.1X10^{-5}$	1.07	0.30	0.31	1.62	2.77	0.50	50.1
3	$9X10^{-6}$	1.2	0.36	0.39	2.12	3.02	0.43	42.6
	$1.3X10^{-5}$	1.2	0.34	0.36	2.31	3.13	0.45	45.5
	$1.7X10^{-5}$	1.2	0.31	0.41	1.79	3.29	0.46	46.0
	$2.1X10^{-5}$	1.1	0.30	0.34	1.84	2.87	0.49	49.1
4	$9X10^{-6}$	1.3	0.39	0.41	1.86	2.65	0.40	39.6
	$1.3X10^{-5}$	1.2	0.30	0.38	2.12	2.73	0.45	44.6
	$1.7X10^{-5}$	1.2	0.34	0.36	2.23	3.19	0.45	45.4
	$2.1X10^{-5}$	1.1	0.31	0.33	1.86	2.86	0.49	48.8

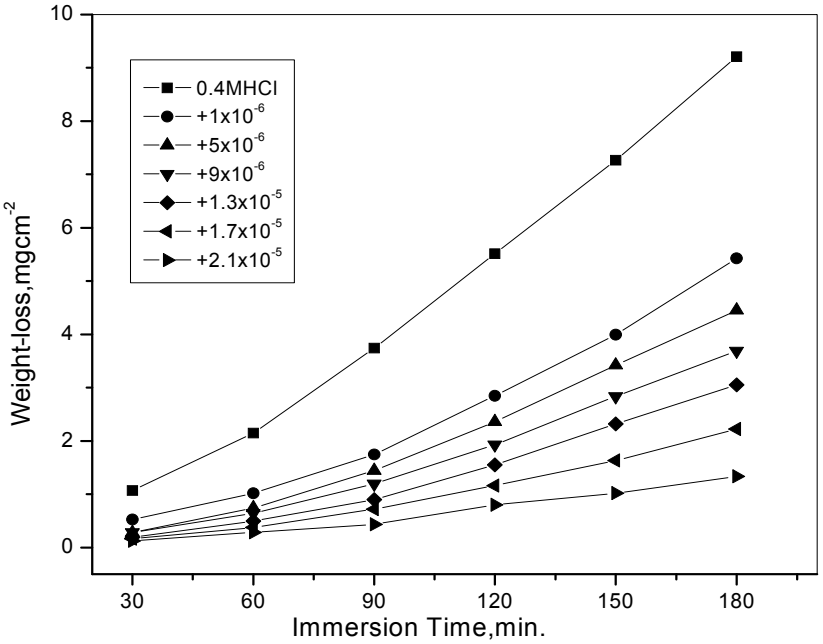

Fig. (1): Weight-loss versus immersion time for zinc immersed in 0.4 M HCl in the absence and presence different concentrations of compound(1) at 30^{0}C.

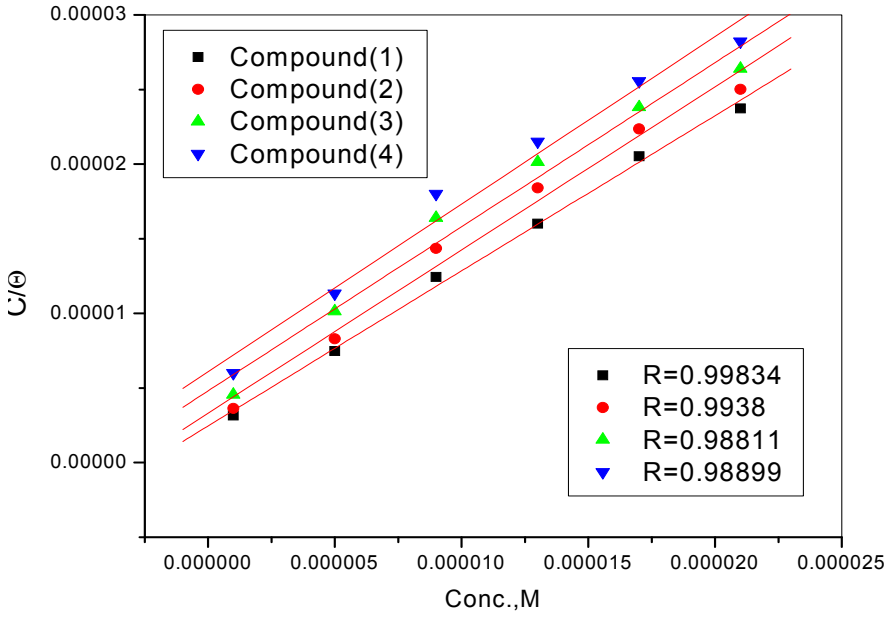

Figure 2. Langmuir adsorption isotherm plotted as (C/θ) vs. Conc. of inhibitors for the corrosion of Zn in 0.4 M HCl solution at 30º C.

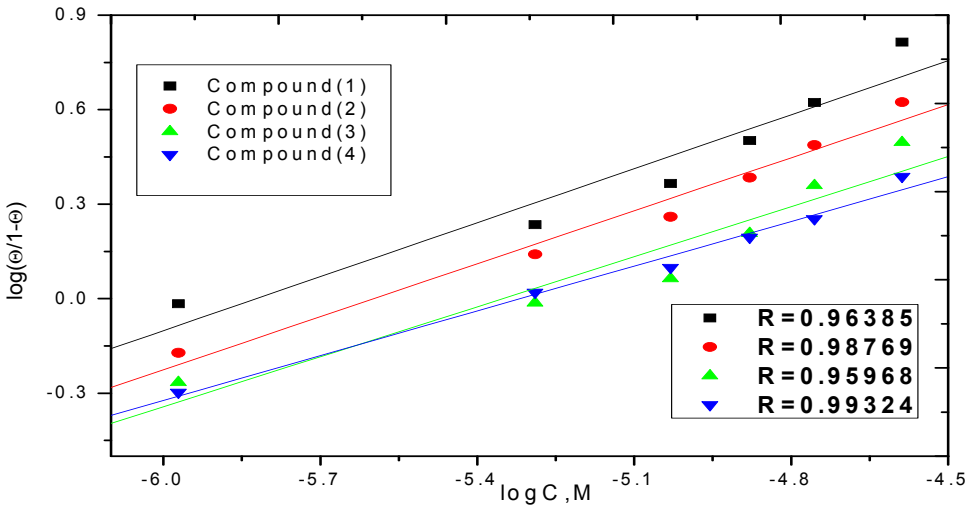

Fig.(3) : El-Awady model plotted as log(Θ/1-Θ) vs.logC of inhibitors for corrosion of Zn in 0.4 M HCl at 30^{0}C.

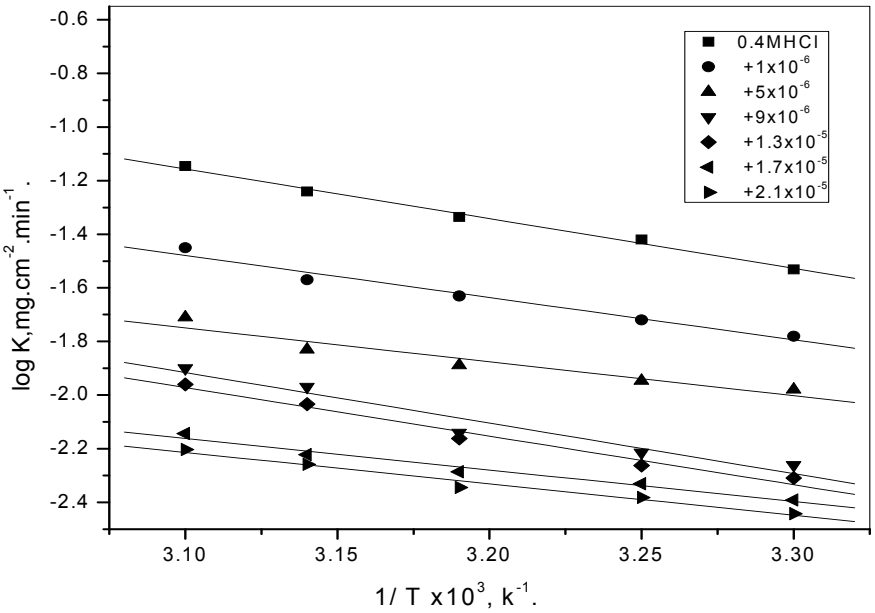

Fig.(4) Arrhenius plots (logk vs.1/T) for Zn in 0.4M HCl in the absence and in presence of different concentrations of compound(1).

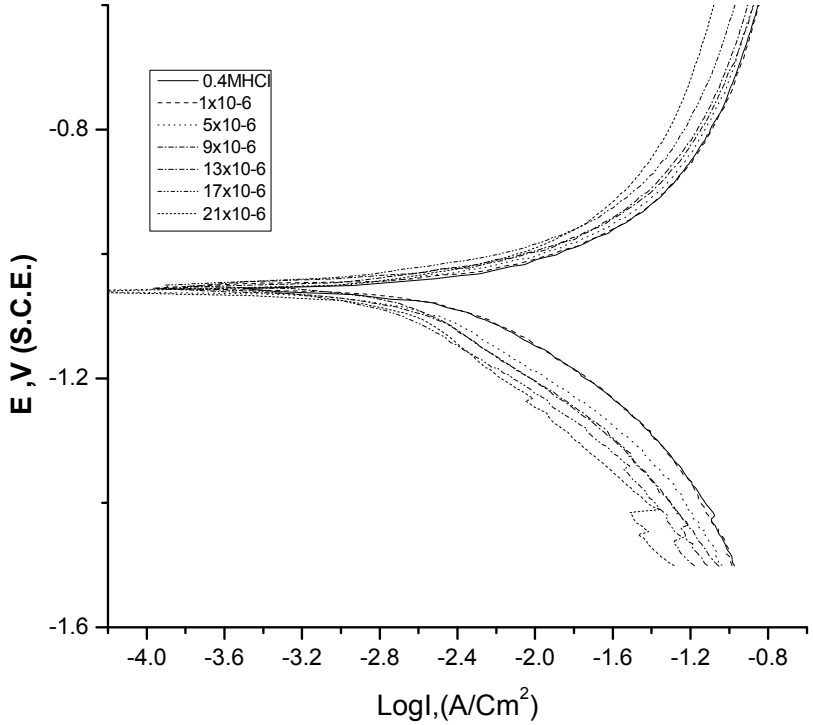

Fig.(5):The potentiodynamic Polarization curves for zinc in 0.4 M HCl solution in the absence and presence of different concentrations of compound (1) at 30^0C.

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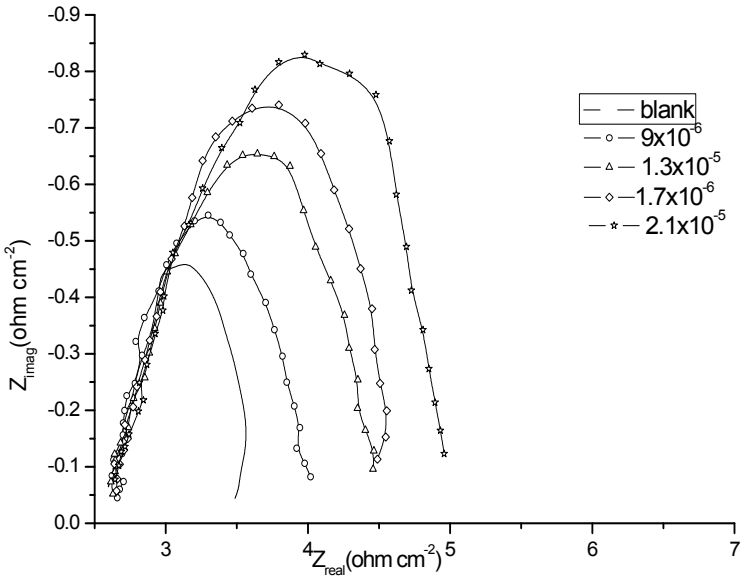

Fig.(6): Nyquist plots for Zn in 0.4 M HCl solution in the absence and presence of different concentrations of compound(1) at 30^{0}C.

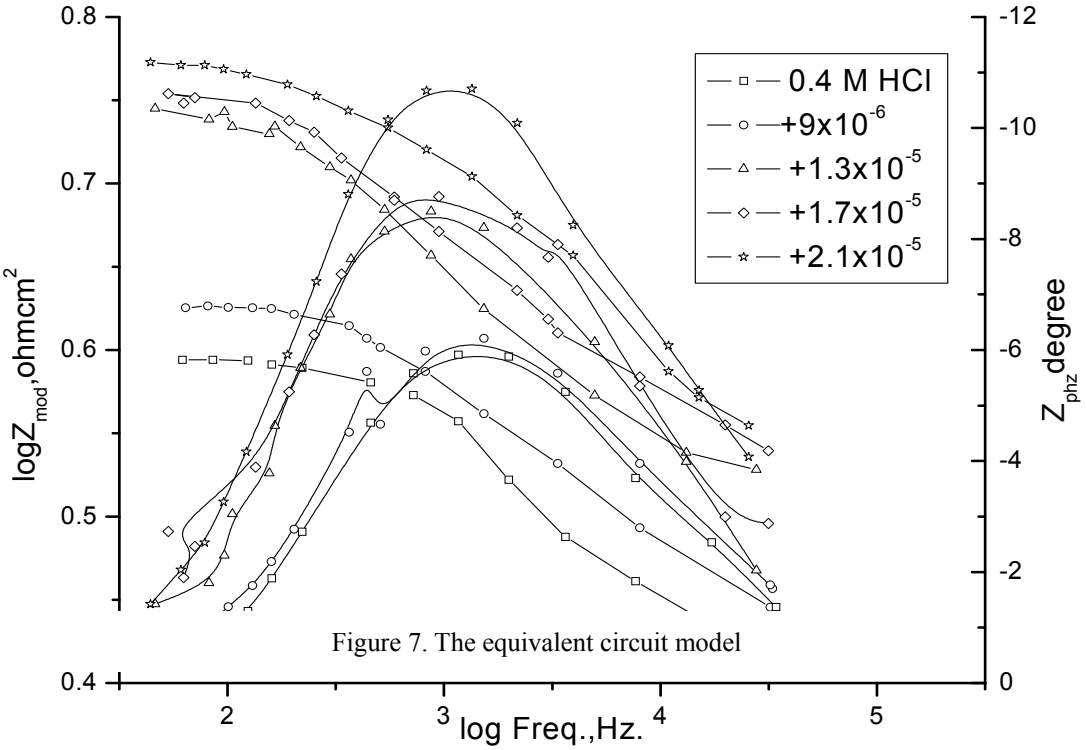

Figure 7. The equivalent circuit model

Fig.(7)The Bode plots for the corrosion of Zn in 0.4M HCl in the absence and presence of different concentrations of inhibitor(1)at 30^{0}C.

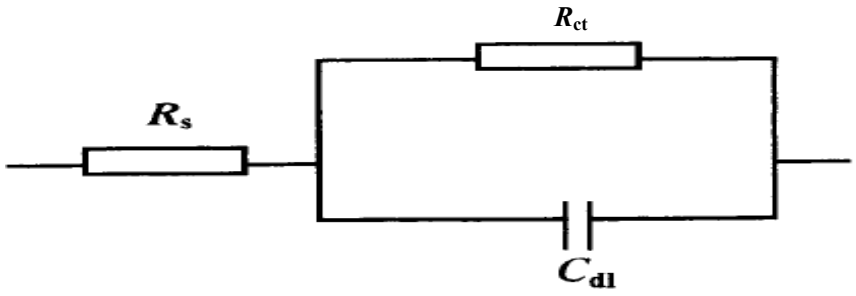

Figure 8. The equivalent circuit model

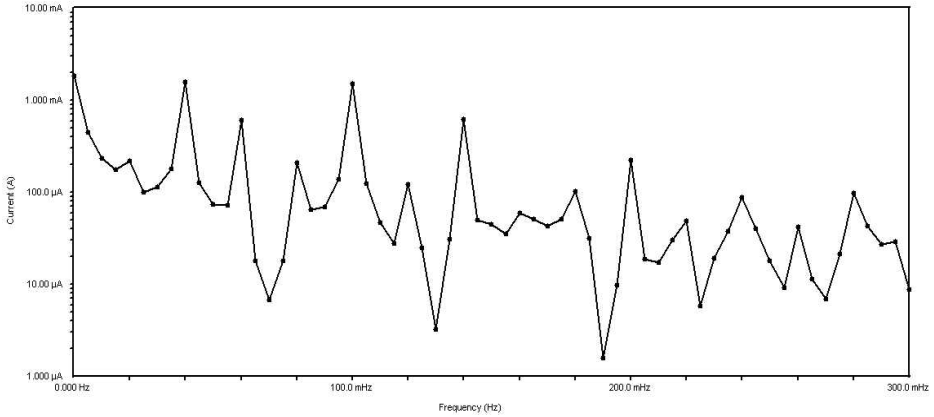

Figure 9. Inter modulation spectrum for zinc metal in 0.4 M HCl (Blank) at 30ºC

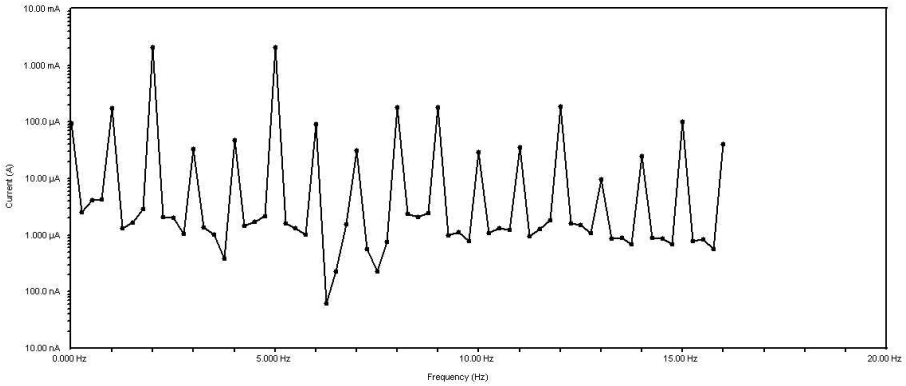

Figure 10. Inter modulation spectrum for zinc metal in 0.4 M HCl in presence of 9 x10^{-6} M Inhibitor (1) at 30ºC

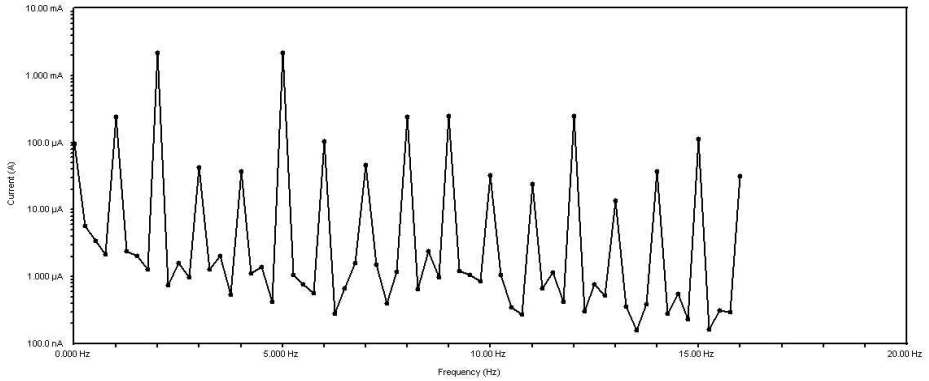

Figure 11. Inter modulation spectrum for zinc metal in 0.4 M HCl in presence of 13x10^{-6} M inhibitor (1) at 30ºC

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3. Results and Discussion

3.1 Weight – loss measurements

Fig 1 shows the effect of increasing concentrations of compound 1 on the weight loss of Zn vs. time curves at 30 °C. Similar curves (not shown) were obtained for the other three compounds. It is obvious that the weight loss of Zn in presence of inhibitors varies linearly with time, and is much lower than that obtained in blank solution. The linearity obtained indicated the absence of insoluble surface film during corrosion and that the inhibitors were first adsorbed onto the metal surface and, therefore, impede the corrosion process (Abdallah, 2004). The calculated values of the percentage inhibition efficiency (I %) are listed in Table 1. Inspection of Table 1 reveals that, the inhibition efficiency increases with an increase in inhibitor concentration. This behavior could be attributed to the increase of the number of adsorbed molecules at the metal surface. At one and the same inhibitors concentration I % decreases in the following order: (1) > (2) > (3) > (4)

3.2 Adsorption isotherm

Basic information on the interaction between the inhibitors and the Zn can be provided by the adsorption isotherm. Two main types of interaction can describe the adsorption of the organic compound: physical adsorption and chemical adsorption. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte, the charge and nature of the metal. The surface coverage,θ, of the metal surface by the adsorbed inhibitor was evaluated from weight loss measurements using equation 3. The θ values of different inhibitor concentrations at 30 °C were tested by fitting to various isotherms including, Frumkin, Langmuir, Temkin and Flory-Huggins. By far the best fit was obtained with the Langmuir isotherm. A plot (C/θ) against C, for all concentrations of inhibitors (Fig 2) a straight line relationship was obtained in all cases with a correlation coefficients (R^2) in the range $0.998 > R^2 > 0.994$. Also, the kinetic-thermodynamic model of (El- Awady et al., 1985) with the formula:

$$\log (\theta / 1 - \theta) = \log K' + y \log C \quad (9)$$

is valid and verify the present adsorption data (Fig 3). The equilibrium constant of adsorption K = K' (1/y), where 1/y is the number of the surface active sites occupied by one inhibitor molecule and C is the bulk concentration of the inhibitor. The negative $\Delta G°_{ads}$ values (Table 2) are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the Zn surface (Popova et al., 2003).

It generally accepted that the values of $\Delta G°_{ads}$ up to -20 kJ mol^{-1} the types of adsorption were regarded as physisorption , the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal, while the values around -40 kJ mol^{-1} or smaller, were seen as chemisorptions, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form covalent bond (Szlarska-Smialowska et al, 1978, Yurt et al, 2006). The $\Delta G°_{ads}$ values obtained in this study range from - 40.4 to - 42.7 kJ mol^{-1}. It suggested that the adsorption mechanism of investigated inhibitors on Zn in 0.4 M HCl solution was typical of chemisorptions.

3.3 Kinetic-thermodynamic corrosion parameters

As noticed previously, the adsorption process was well elucidating by using a thermodynamic model, in addition a kinetic-thermodynamic model was another tool to explain the mechanism of corrosion inhibition for an inhibitor. The apparent effective activation energies (E^*_a) for the corrosion reaction of Zn in HCl in the absence and presence of different concentrations of investigated compounds were calculated from Arrhenius-type equation (Bochris and Reddy 1970):

$$k = A \exp (-E_a^* / RT) \quad (10)$$

where A is the Arrhenius pre-exponential factor. A plot of log k (corrosion rate) vs. 1 / T gave straight lines as shown in Fig.2. The entropy of activation (ΔS^*) and the enthalpy of activation (ΔH^*) for the intermediate complex in the transition state for the corrosion of Zn in HCl in the absence and presence of different concentrations of investigated compounds were obtained by applying the transition-state equation (Martinez and Stern 2002; Tebbji et al., 2007; Mihit et al.,2006)

$$k = RT / Nh \exp (\Delta S^*/R) \exp (-\Delta H^* / RT) \quad (11)$$

where h is the Planck's constant and N is the Avogadro's number

A plot of log k (corrosion rate) / T vs. 1 / T should give a straight lines (Fig.3), with a slope of ($-\Delta H^* / 2.303R$), and an intercept of [(log(RT / Nh) + ($\Delta S^*/2.303R$)] (Bouklah et al., 2006; Bouklah et al., 2006), from which the values of ΔH^* and ΔS^* were calculated, respectively. Table (3) exhibited values of apparent activation energy, apparent enthalpies ΔH^* and entropies ΔS^* for Zn dissolution in 0.4 M HCl solution in the absence and presence of different

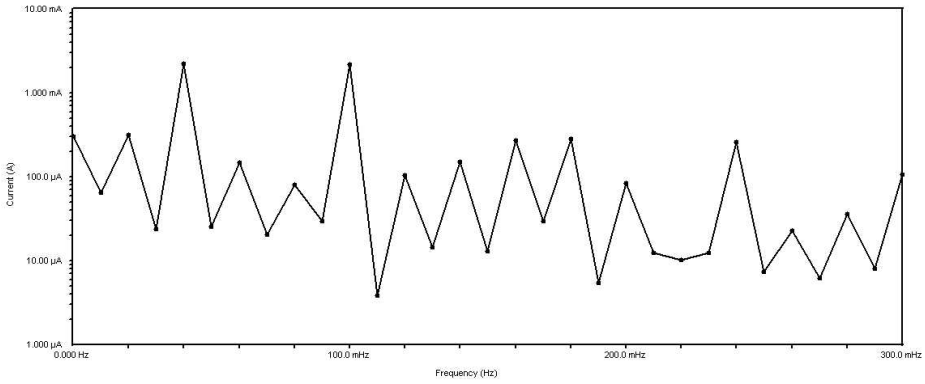

Figure 12. Inter modulation spectrum for zinc metal in 0.4 M HCl solution in presence of $17x10^{-5}$ M inhibitor (1) at 30ºC.

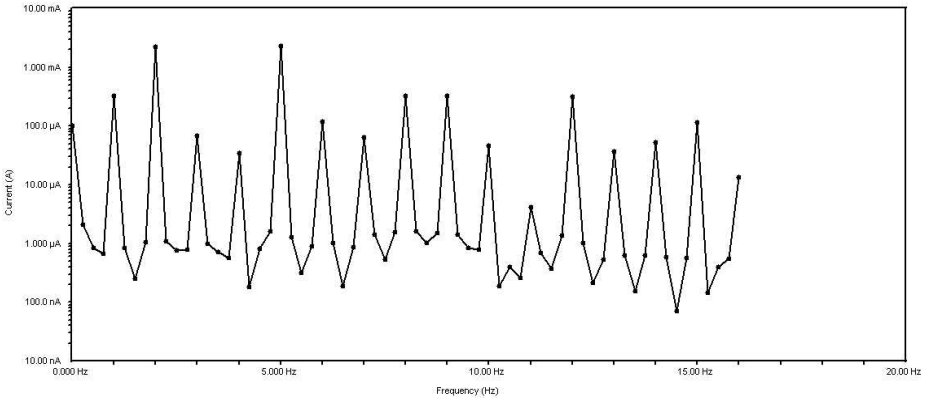

Figure 13. Inter modulation Spectrum for Zinc metal in 0.4M HCl in presence of $21x10^{-5}$ M inhibitor (1) at 30ºC