International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Corrosion Inhibition of Zinc in Acid Medium using some Novel Organic Compounds

A. S. Fouda^{1*}, S. Rashwan², A. Emam², F. E. El-Morsy¹

¹ Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura-35516, Egypt, ² Department of Chemistry, Faculty of Science, Suez Canal University, Ismailia, Egypt

*E-mail: asfouda@hotmail.com, asfouda@mans.edu.eg

Received: 24 November 2017 / Accepted: 18 January 2018 / Published: 6 March 2018

The corrosion performance of zinc in 0.5M HCl in the attendance of organic compounds has been examined using AC impedance (EIS), electrochemical frequency modulation (EFM), potentiodynamic polarization (POTENTIODYNAMIC POLARIZATION) and weight reduction (WR) techniques. The protection efficiency (IE) improved by improving the organic compound concentrations and decreased by raising the temperature. Polarization results revealed that these examined compounds act as mixed-kind inhibitor and they adsorbed on Zn surface obeying isotherm of Langmuir. The surface examination of protected Zn was evaluated by SEM (scanning electron microscope), AFM (atomic force microscopy), EDX (the energy dispersive X-ray spectra), and FTIR (Fourier transform infrared spectra). The results of electrochemical and non-electrochemical tests were in excellent agreement.

Keywords: Adsorption, Corrosion inhibition, Zn, HCl, SEM, EDX, AFM, FTIR

1. INTRODUCTION

Corrosion is an important process playing significant role in safety and economics, mostly for metals. A corrosion inhibitor is a chemical compound adsorbed on Zn surface to give film in order to isolate the surface of the metal from reaction with the environment or by lowering the ions which attack the metal surface [1, 2]. Zn is one of the good significant non-ferrous metals, which founds wide applications in metallic covering. Zn dissolves in solution with pH upper than 12.5 and lesser than 6, while between pH 6 to 12.5 the dissolution is very lower [3]. Under destructive conditions, Zn metal suffers from corrosion which gives the rust with white color [4, 5]. Lowering the creation of white corrode; the investigation for new inhibitors is important [6]. A noteworthy test to hindrance the metals from decomposition are by adding substances in order to protect the corrosion interaction and lower the rate of corrosion. The majority of the productive corrosive inhibitors are organic compounds that

3720

include different heteroatoms like oxygen, sulfur or nitrogen atoms in their construction. The IE ratio of organic compounds is depended on the construction and chemical assets of the film designed on the metals. Organic compounds are used for their efficiencies as corrosion inhibitors and those containing nitrogen have been frequently referred to in the literature [7-9]. Several organic compounds were utilize as corrosion protection for zinc in different media such as: Meta-substituted aniline-N-salicylidenes [10], Schiff bases of ethylenediamine [11], Ethoxylated fatty acids [12], Ortho-, meta-, and. para-aminophenol-N-salicylidenes [13], Ortho-substituted aniline-N-salicylidenes [14], Pyridine and its derivatives [15], benzotriazole [16] and so on...,

The choice of these tested compounds is due to: a) are extremely have large molecular weights, and b) include functional polar (such as -C=O, N=N and CN) and multiple bonds (triple and double bonds) and wide connection in the form of aromatic ring among which they can adsorb on surface of metal. The objective of this research is to examine the inhibitive behavior of these investigated organic compounds in the direction of the corrosion of Zn in 0.5 M HCl utilized non-electrochemical and electrochemical test. The surface morphology of the Zn samples was also analyzed.

2. MATERIALS AND TECHNIQUES

2.1. Materials and solutions

The conformation of metal sample in weight % is: Cd 0.52, Fe 0.035, Mn 0.005, Pd 0.18, Sn 0.07 and Zn the rest

2.2. Inhibitors

The inhibitors were synthesized in the laboratory according to experimental method before [17, 18], characterized and purified by IR, NMR spectra and elemental examination before used. All the data of these compounds are recorded in Table 1.

Table 1. Chemical constructions of the studied compounds

Compound	Structures, Names	Mol. Formulas, Mol. Weights
А	(E)-N,N'-(1,4-phenylene)bis(2-cyano-2-((E)-(4-methoxyphenyl)diazenyl)acetamide)	C ₂₆ H ₂₂ N ₈ O ₄ 510.50



2.3. Chemicals and solutions

The working anode for (WR) and electrochemical studies were set up from zinc specimens. The aggressive solution utilized set up by dissolution of analytical reagent HCl 37% with twicedistilled water and its concentration was titrating by Na₂CO₃. Solutions of 0.5 M HCl set up by dilution with twice-distilled water. 100 ml stock solutions (10^{-3} M) of each examined compounds were set up by dissolution of a precisely measured amount of the material in suitable volume with dimethylformamide (DMF), then with absolute ethanol at the point of required concentrations ($1 \times 10^{-6} - 21 \times 10^{-6}$ M) were prepare by dilution with twice distilled water.

2.4. Techniques utilized for corrosion estimations

2.4.1. Mass loss (ML) technique

The ML tests were completed utilizing square specimens of size $(2 \times 2 \times 0.2 \text{ cm}) \text{ x2}$. The coins were first made as a mirror by the process of utilizing (400, 800 and 1500 grit size from emery papers),

washed by $(CH_3)_2CO$ lastly wash away with twice distilled water and dried previously start weighed and soaked into the investigation solution. The ML estimations was completed in a 100 ml glass beaker set in water thermostat which include 100 ml of 0.5 M HCl and existence of various concentrations of examined compounds. The entire corrosive medium was air open. After this period (3 hrs) of immersion the samples were removed, rinsed, dried, and weighed again. The ML of the Zn sheets then obtained. The % IE and the θ of organic derivatives for the corrosion of Zn were computed from Eq. (1)

% IE =
$$\theta \ge 100 = [(W^{\circ} - W)/W^{\circ}] \times 100$$
 (1)

Where W^{o} and W are the data of the ML existence and nonexistence various concentrations of inhibitors, respectively. The θ values were obtained at various concentrations of the organic inhibitors in 0.5M HCl solution

2.4.2. Potentiodynamic polarization technique

Potentiodynamic polarization tests were done in a traditional three-electrode (platinum gauze as the auxiliary electrode (1.0 cm^2) , saturated calomel (SCE) as reference electrode and working electrode (WE). WE were specimens from Zn sheet of equivalent piece fixed in epoxy resin with an area of 1.0 cm². Before any estimation the electrode surface was pretreated as in the ML tests. Previously estimations, the working electrode was abraded by emery papers of various sizes up to 1200 grit size, washed a few times with twice distilled water and degreased with (CH₃)₂CO, lastly washed several times with twice distilled water and dried. The electrode potential was automatically changed from (--1.5 to -0.7 V vs. SCE) at open circuit potential with a scan rate 1 mVs⁻¹ to obtain Tafel polarization diagrams.

2.4.3. EIS technique

EIS estimations were completed utilizing AC signs of 5 mV peak to peak amplitude and at frequency range of 10^7 Hz to 0.1 Hz. All EIS results fitted to proper proportional circuit utilizing the Gamry Echem Analyst programmer. The (% IE) and (θ) of the examined compounds were computed from the EIS tests using eq. (2) [19]:

% IE = 100 x θ = 100 x $[1 - (R_{ct}^{\circ} / R_{ct})]$ (2) where R_{ct}° and R_{ct} are the resistances of charge transfer with and without inhibitor, correspondingly.

2.4.4- EFM test

EFM tests achieved by using two frequencies of range 2 and 5 Hz depended on three conditions [20]. The greater peaks were utilized to measure (i_{corr}), the (β_c and β_a) and CF-2 and CF-3 (Causality factors) [21]. Every analysis was completed at 25±1°C, utilizing Gamry PCI300/4 Galvanostat/Potentiostat/Zra analyzer. This computer was used to collect the results by Gamry

applications which include DC105 for polarization, EIS300 for EIS, EFM140 for EFM measurements and Echem Analyst 5.5 for results plotting, graphing, data fitting and calculating.

2.4.5. Surface examination

Surface analysis of Zn pieces are done in several test solutions for 24 hours, after abrading mechanically by utilized various emery papers up to 1200 size. Then, after this period of time, the coins were cleaned lightly with twice distilled water, dried and keep in a desiccator until the analysis by (SEM), (EDX), (FTIR) and (AFM). AFM is turning into recognized tests of roughness analysis [22, 23].

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization tests



Figure 1. Potentiodynamic polarization diagrams for the Zn corrosion with and without different concentrations of compound (A) at 25°C

Figure 1 shows the potentiodynamic polarization behavior of Zn electrode in 0.5M HCl with and without various concentrations of compound (A). Similar diagrams have given for other derivatives (not shown). The obtained data of electrochemical parameters such as (i_{corr}), (E_{corr}), (β_c), (β_a), (θ) and (% IE) were calculated from the curves of (Figure 1) and are verified in (Table 2) for all investigated compounds. The data obtained in Table 2 showed that both the cathodic and anodic reactions are influenced by the adding of examined organic derivatives and the IE rises as the inhibitor concentration improved, implying that the adding of investigated derivatives decreases the anodic dissolution of Zn and furthermore impedes the cathodic reactions. In the presence of these derivatives,

% IE =
$$\theta x \ 100 = [(i_{corr} - i_{corr(inh)}) / i_{corr}] x \ 100$$
 (3)

where i_{corr} is the corrosion current without inhibitor and $i_{corr(inh)}$ with inhibitor. The IE% of the examined compounds is in the order: A > B > C > D > E.

Table 2. Data from potentiodynamic polarization of Zn corrosion with and without different concentrations of studied compounds at 25° C

Comp	Conc., x10 ⁶ M	$i_{corr,}$ $\mu A \text{ cm}^{-2}$	- E _{corr,} mV vs SCE	$\beta_a mV_1 dec^-$	β_c mV	C.R mpy	θ	% IE
Blank	0.0	22.8	982	150	235	25.4		
	1	6.9	985	154	253	7.7	0.697	69.7
	5	2.7	990	89	234	3.1	0.880	88.0
	9	2.2	989	95	256	2.5	0.903	90.3
А	13	2.02	997	94	231	2.3	0.911	91.1
	17	1.6	996	88	204	1.8	0.929	92.9
	21	0.79	981	105	226	0.8	0.965	96.5
	1	7.8	997	146	232	8.6	0.658	65.8
	5	3.9	994	124	249	4.3	0.829	82.9
	9	2.7	990	91	221	3.1	0.881	88.1
В	13	2.04	994	89	216	2.3	0.911	91.1
	17	1.7	998	91	198	1.8	0.927	92.7
	21	1.33	990	82	215	1.5	0.942	94.2
	1	13.4	991	196	226	14.9	0.412	41.2
	5	7.4	984	137	211	8.5	0.675	67.5
С	9	3.32	995	109	262	3.6	0.854	85.4
Ũ	13	2.7	990	95.5	238	2.9	0.884	88.4
	17	2.2	994	90.0	203	2.4	0.903	90.3
	21	1.85	995	84.2	191	2.1	0.919	91.9
	1	13.8	995	193.1	244	15.4	0.395	39.5
	5	12.5	994	197	295	13.9	0.452	45.2
	9	12.1	996	202	212	13.5	0.469	46.9
D	13	11.1	995	184	280	12.4	0.513	51.3
	17	9.5	997	159	295	10.6	0.583	58.3
	21	4.89	998	127	233	5.4	0.786	78.6
	1	16.3	980	207	226	18.1	0.285	28.5
	5	13.1	997	189	243	14.6	0.425	42.5
	9	12.7	992	192	232	14.1	0.443	44.3
Е	13	11.4	993	182	291	12.6	0.500	50.0
	17	10.1	984	155	217	11.2	0.557	55.7
	21	7.13	999	145	287	7.9	0.687	68.7

3.2. (EIS) tests

Figure 2 display the Nyquist and Bode plots of the Zn electrode with and without different concentrations of compound (A) at 25° C. The same diagrams were given for other compounds (not shown). As the inhibitor concentration improve, the semi-circle diameter rise. EIS spectra of the investigated derivatives were studied utilizing the circuit (Fig. 3), CPE is produced in the circuit as a temporary of a pure double layer capacitor to obtain a further perfect fit [24]. The C_{dl}, for a circuit containing a CPE data (Y⁰ and n) were measure from eq. (4) [25]:

 $C_{dl} = Y^0 \omega^{n-1} / \sin[n(\pi/2)]$ (4)

where $\omega = 2\pi f_{max}$, f_{max} is the greater frequency and the factor ,n, is a customizable parameter that as a rule lies in the vicinity of 0.5 and 1.0. An increase in R_{ct} refers to rise in the thickness of the double layer that formed by the adsorption of inhibitor [26]. In adding, the data of the (C_{dl}) lower by the existence of inhibitor in the aggressive medium .Moreover; C_{dl} can be measure from eq.(5):

 $C_{dl} = \varepsilon \varepsilon_o (A/\delta)$ (5)

where δ the thickness of double-layer. For the most part, the lower in C_{dl} data is attributing to the change of the water molecules adsorbed at the Zn surface by the inhibitor molecules having lesser C_{dl} [27]. The parameters obtained from electrochemical were recorded in Table 3. The sequence of IE given from EIS tests is: A> B > C > D > E.



Figure 2. EIS Bode and Nyquist diagrams for Zn with and without various concentrations of compound (A) 25°C



Figure 3. Circuit utilized to fit the data obtained from EIS in 0.5M HCl.

Comp	Conc.,	R _{ct} ,	C _{dl} ,	0	0/ 10
	x10 ⁻⁰ M	$\Omega \text{ cm}^2$	µFcm ⁻²	θ	%IE
Blank	0	0.5	102		
	1	2.8	13	0.826	82.6
	5	5.4	5.4	0.909	90.9
٨	9	8.0	2.7	0.939	93.9
A	13	8.3	2.5	0.940	94.0
	17	12.1	1.2	0.959	95.9
	21	26.4	0.8	0.981	98.1
	1	1.9	23.3	0.742	74.2
	5	3.4	9.3	0.857	85.7
р	9	5.6	4.7	0.912	91.2
D	13	8.1	2.7	0.940	94.0
	17	9.0	2.3	0.945	94.5
	21	11.2	1.5	0.956	95.6
	1	1.8	24.8	0.737	73.7
	5	2.5	15.6	0.807	80.7
C	9	5.5	5.1	0.911	91.1
C	13	6.7	3.7	0.927	92.7
	17	7.0	3.5	0.930	93.0
	21	8.1	2.9	0.940	94.0
	1	1.8	26	0.726	72.6
	5	2.0	22	0.757	75.7
D	9	2.0	21	0.764	76.4
D	13	2.2	20	0.777	77.7
	17	2.6	15.7	0.816	81.6
	21	3.5	10	0.862	86.2
	1	0.8	30	0.385	38.5
	5	0.9	29.7	0.479	47.9
F	9	2.3	23	0.794	79.4
Ľ	13	2.4	22	0.797	79.7
	17	2.6	19	0.810	81.0
	21	2.5	14	0.812	81.2

Table 3. Parameters obtained from EIS tests for Zn with and without different concentrations of studied inhibitors at 25°C

3.3. Electrochemical frequency modulation (EFM) tests

EFM is a non-degradation corrosion test that can be quickly and directly calculate the current data lacking earlier information of Tafel slopes, and with just a little polarizing signal [28]. The pronounced power of the EFM is (CF) that attends as an internal check on the validity of obtained data from EFM. Figure 4 displays the EFM (current versus frequency) of Zn in HCl solution enclosing various concentrations of compound (A). Similar intermodulation spectra were given for different compounds (not shown). The higher peaks were utilized to measure (CF-2 and CF-3), (β_c and β_a) and (i_{corr}). The CF attained under various test conditions are roughly equivalent to the theoretical data (2

and 3) proving that the calculated data are confirmed and of best quality. The IE_{EFM}% increases by raising the inhibitor concentrations and was measured as in eq. (3). The order of IE is as next: A > B > C > D > E.



Figure 4. EFM diagrams for Zn without and with different concentrations of compound (A) at 25°C

Table	4.	Parameters	obtained	from	EFM	tests	for	diagrams	for	Zn	without	and	with	different
	co	ncentrations	of inhibite	ors in ().5M H	HCl at	25°	2						

Comp	$\frac{\text{Conc., x}}{10^6 \text{ M}}$	i _{corr} µAcm ⁻²	$\begin{array}{c} \beta_{c},\\ mVdec^{-}\\ 1 \end{array}$	$\begin{array}{c} \beta_a,\\ mVdec^-\\ 1 \end{array}$	C.R , mpy	CF-2	CF-3	θ	%IE
Blank	0.0	19.8	656	235	14.8	2.0	2.9		
	1	10.1	354	160	4.1	1.9	3.7	0.488	48.8
	5	8.1	322	151	3.9	1.9	3.4	0.593	59.3
•	9	4.2	339	108	3.5	1.9	3.7	0.786	78.6
A	13	4.1	326	107	3.1	2.0	3.2	0.793	79.3
	17	3.1	334	102	2.9	2.1	3.4	0.842	84.2
	21	0.98	313	99	2.7	1.9	3.8	0.951	95.1
	1	12.8	442	199	5.8	1.9	3.7	0.352	35.2
	5	9.4	354	153	5.1	2.0	2.8	0.521	52.1
р	9	5.8	344	137	4.6	1.9	2.9	0.704	70.4
Б	13	4.6	340	109	3.9	2.0	2.8	0.763	76.3
	17	3.5	349	105	3.4	1.9	3.4	0.819	81.9
	21	2.7	427	101	3.1	2.0	3.0	0.863	86.3
	1	14.8	374	218	6.7	1.9	2.8	0.248	24.8
C	5	12.2	216	207	5.8	2.0	3.4	0.340	34.0
	9	9.1	357	112	5.1	2.0	2.7	0.537	53.7
	13	7.1	370	259	4.5	2.1	3.4	0.640	64.0

	17	4.8	345	109	3.9	2.0	3.4	0.753	75.3
	21	3.1	336	113	3.8	1.9	3.8	0.847	84.7
	1	16.4	375	115	7.1	1.9	2.6	0.170	17.0
	5	15.7	371	126	6.5	1.9	2.9	0.203	20.3
D	9	14.8	320	193	6.1	1.9	2.5	0.248	24.8
D	13	12.9	339	187	5.2	2.1	2.9	0.345	34.5
	17	11.3	301	170	4.8	1.9	3.8	0.426	42.6
	21	8.4	223	205	4.3	1.8	3.1	0.575	57.5
	1	17.3	322	203	7.9	2.0	3.4	0.124	12.4
	5	16.7	345	118	7.1	1.8	2.7	0.152	15.2
Б	9	15.1	263	130	6.7	1.7	3.4	0.236	23.6
E	13	13.1	392	188	6.1	2.0	2.9	0.335	33.5
	17	12.9	382	106	5.8	1.9	3.5	0.344	34.4
	21	9.9	348	155	4.9	1.9	3.5	0.499	49.9

3.4. Mass loss (ML) tests

The ML of Zn coins in 0.5M HCl solution without and with different concentrations from the studied derivatives was measured after 3 hours of inundation at 30 ±1°C. Figure 5 shows this for composite (A) as an example. Alike diagrams were give form other compounds (not presented). Obtained values of %IE are given in Table 5 at various concentrations from the investigated compounds at 30°C. The results displayed that the presence of investigated compounds decreased the ML (mg cm⁻²) and the corrosion rate (mg cm⁻² min⁻¹). The (%IE) and the θ , of the studied compounds for the corrosion of Zn were measured from eq. (1) [29]. % IE obtained by these inhibitors was in the order: A > B > C > D > E.



Figure 5. ML-time curves for the corrosion of Zn without and with various concentrations of compound (A) at 30°C

Comp	A	A	В		С		D		Е	
Conc., x 10^6 M	θ	% IE								
1	0.906	90.6	0.900	90.0	0.839	83.9	0.633	63.3	0.439	43.9
5	0.910	91.0	0.906	90.6	0.880	88.0	0.705	70.5	0.462	46.2
9	0.921	92.1	0.914	91.4	0.918	91.8	0.822	82.2	0.639	63.9
13	0.928	92.8	0.928	92.8	0.934	93.4	0.849	84.9	0.679	67.9
17	0.934	93.4	0.930	93.0	0.939	93.9	0.850	85.0	0.862	86.2
21	0.947	94.7	0.975	97.5	0.958	95.8	0.884	88.4	0.871	87.1

Table 5. % IE of all compounds at 120 min for Zn without and with different concentrations of studied compounds as determined from ML technique at 30°C

3.5. Influence of temperature

It was establish that the IE lower with raising temperature but at lower rate than in unprotect solutions with increasing the concentration of the inhibitor, as displayed in Table 6, also the value from (Table 6) for compound (A) indicate that %IE decreases with increasing the temperature. Similar Tables were given form other compounds (not shown). Figure 6 shows the variation of IE of compound (A) with various temperatures using different concentrations of compound (A) for Zn corrosion. The decrease of % IE with improving the temperature designates that these compounds are adsorbed physically on the Zn surface.



Figure 6. Influence of temperature on % IE at different concentrations of compound (A) for Zn corrosion at various temperatures

Table 6. D	ata of %IE, (0) and	nd (C.R.) fo	or Zn corrosion after	120 min	n without	and with	different	
conc	concentrations of compound (A) at various temperatures							
	Conc., x 10^6 M	Temp, K	C.R., mg cm ⁻² min ⁻¹	θ	%]	E		

,	1			
blank		0.127		
1		0.012	0.906	90.6
5		0.011	0.910	91.0
9		0.010	0.921	92.1
13	303	0.009	0.928	92.8
17		0.008	0.934	93.4
21		0.006	0.947	94.7
blank		0.131		
1	200	0.015	0.882	88.2
5	308	0.013	0.897	89.7.5
9		0.012	0.904	90.4
13		0.011	0.910	91.0
17		0.009	0.929	92.9
21		0.008	0.938	93.8
blank		0.143		
1		0.027	0.810	81.0
5		0.024	0.828	82.8
9	313	0.020	0.859	85.9
13		0.016	0.886	88.6
17		0.011	0.918	91.8
21		0.008	0.943	94.3
blank		0.149		
1		0.064	0.665	66.5
5		0.036	0.758	75.8
9	318	0.029	0.804	80.4
13		0.025	0.833	83.3
17		0.024	0.836	83.6
21		0.012	0.916	91.6
blank		0.171		
1		0.076	0.653	65.3
5		0.050	0.706	70.6
9	323	0.045	0.736	73.6
13]	0.035	0.793	79.3
17		0.031	0.816	81.6
21		0.016	0.905	90.5

The energy of activation (E_a^*) of the corrosion process was measured utilized Arrhenius eq. (6) [30]:

C.R. = A exp (- E_{a}^{*}/RT) (6)

where E_a^* values of energy for activation and T is the kelvin temperature. The E_a^* data can be gotten from the slope of lines (Figure 7) without and with investigated compounds are given in Table 7. The values of E_a^* increases in the existence of inhibitors than in their absence. The measured E_a^*

demonstrate that the studies compounds inhibit corrosion more effectively at greater concentrations. Likewise, improve in E_a^* with the adding of various concentrations of investigated compounds showing raising energy barrier for the corrosion reaction. These values showed that the presence of these inhibitors increases the E_a^* of the metal dissolution reaction and that the process is diffusion controlled $(E_a^* > 40 \text{ kJ mol}^{-1})$ [31]. (ΔH^* , ΔS^*) are measured from transition state theory using eq. (7) [32]:

C.R. = RT/Nh exp ($\Delta S^*/R$) exp ($-\Delta H^*/RT$) (7)

Figure 8 shows a plan of log (C.R. /T) vs. (1/T). Straight lines are achieved with an intercept of (log R/Nh + $\Delta S^*/2.303$ R) and a slope of ($\Delta H^*/2.303$ R) with linear regression (R²) is close to 1 from which the value of ΔH^* and ΔS^* are measured and also verified in Table 7. Typically, the enthalpy of a chemisorption process reached (100 kJ mol⁻¹) [33]. The increase in the (ΔH^*) in existence of the inhibitors means rise in the height of the energy barrier of the corrosion procedure to magnitude depends on the concentration of the compound. The values of ΔS^* are negative; this show that the activated complex in the rate-determining step signifies an association rather than dissociation [34].



Figure 7. Arrhenius diagrams of log C.R. vs 1/T for the dissolution of diagrams for Zn without and with different concentrations of compound (A)



Figure 8. Plots of 1/ T vs. (log C.R. / T) for the dissolution of diagrams for Zn without and with different concentrations of compound (A)

Comp	Conc.,	E _a *,	ΔH^* ,	$-\Delta S^*$,
	$x 10^{6} M$	kJ mol ⁻¹	kJ mol ⁻¹	$J \text{ mol}^{-1} K^{-1}$
Blank	0.0	11.5	4.1	231.5
	1	41.5	14.5	223.7
	5	46.7	19.8	220.3
A	9	46.5	22.7	201.1
	13	47.1	26.4	198.5
	17	49.4	27.8	185.1
	21	52.7	28.4	169.1
	1	31.7	13.3	218.7
	5	36.5	17.5	215.0
В	9	36.3	21.1	198.5
	13	37.4	24.3	194.4
	17	39.2	25.3	183.3
	21	42.1	26.8	160.9
	1	21.5	7.5	217.5
	5	23.9	7.8	211.0
C	9	27.6	8.4	197.7
	13	32.3	12.2	190.6
	17	37.1	13.8	180.3
	21	47.2	18.7	156.2
	1	24.1	9.2	201.0
	5	25.3	9.8	198.8
D	9	28.0	12.5	179.5
	13	32.2	13.4	175.1
	17	36.4	14.2	170.5
	21	37.9	14.5	149.5
	1	24.3	10.5	187.0
	5	24.4	10.7	186.9
E	9	24.6	12.3	177.0
	13	26.7	11.6	183.1
	17	34.4	13.9	167.2
	21	36.5	14.3	141.7

Table 7. Activation parameters for diagrams for Zn without and with different concentrations of different compounds

3.7. Adsorption isotherms

Attempts were ready to fit (θ) qualities to dissimilar adsorption isotherms; it is obvious that the data of (Θ) rise with raising the concentration of organic compounds. By utilizing these data of surface coverage, for applied various isotherms to obey with experimental value. Langmuir isotherm found to fit the experimental value. The mathematical expression of Langmuir had given as follows [35-36].

$$C/\Theta = 1/k_{ads} + C$$

where, K_{ads} is the adsorption equilibrium constant. Diagrams (C) against (C/ Θ) of organic derivatives at different temperatures is shown in Figure 9. This relationship was linear, the intercept equal to (1/ K_{ads}) and slope nearly to unity, alike plots were gotten form other compounds (not displayed). Table

(8)

(9)

8 shows the influence of temperature on adsorption for examined compounds; the data of K_{ads} and ΔG^{o}_{ads} are calculated. The data obtained of K_{ads} and ΔG^{o}_{ads} are obtained in Table 8. The (ΔG^{o}_{ads}) determine by adsorption as next:

$$\Delta G^{o}_{ads} = - RT \ln (55.5 K_{ads})$$

where 55.5 is the molar concentration of water in mol L⁻¹. The ΔG°_{ads} and K_{ads} data for investigated compounds computed and are listed in Table 8. The data of ΔG°_{ads} are negative sign and increase as the % *IE* rise which indicate that these examined compounds are adsorbed on the zinc surface spontaneously. Usually, data of ΔG°_{ads} up to -20 kJ mol⁻¹ are physical adsorption while those more negative sign than -40 kJ mol⁻¹ are chemisorptions [37].

Thermodynamic data such as ΔH°_{ads} and ΔS°_{ads} can be measured from Vant't Hoff equation [38] expressed by:

$$Ln K_{ads} = \frac{-\Delta H^{\circ}_{ads}}{RT} + const$$
(10)

Figure 10 displays the plots of log K_{ads} vs 1/T. This plot is straight line with slope (- ΔH°_{ads} / 2.303R). values of ΔH°_{ads} and ΔS°_{ads} were calculated using eqs. (10, 11):

 $\Delta G^{o}_{ads} = \Delta H^{o}_{ads} - T \Delta S^{o}_{ads} \qquad (11)$

The outcome data of thermodynamic for the inhibitors adsorption were computed at temperature (30°C- 55°C) and are listed in Table 8, which can elucidate the mechanism of corrosion protection [39], an exothermic adsorption procedure ($\Delta H^{o}_{ads} < 0$) may be either chemisorption or physisorption or mixture of both procedures. The data of $\Box G^{o}_{ads}$ obtained were around equal to $\Box 49 \pm 1 \text{ kJ mol}^{-1}$, lead to the adsorption mechanism of the examined inhibitors on zinc in 0.5M HCl solution includes both chemisorptions and physisorption [40]. The parameters point near both physisorption (main contributor) and chemisorptions (slight contributor). Negative sign of ΔS^{o}_{ads} showed that decreasing in disorder of corrosion process on Zn surface in 0.5M HCl using organic compounds as corrosion inhibitors (Table 8) [41].



Figure 9. Langmuir adsorption isotherm for the adsorption of compound (A) on Zn in 0.5M HCl at various temperatures



Figure 10. Plots Log K_{ads} vs 1/T for the adsorption of inhibitor (A) in 0.5M HCl

Table 8. Thermodynamic parameters for diagrams for Zn without and with different concentrations for examined compounds at various temperatures

Comp	Temp., K	${f K}_{ads} {f M}^{-1}$	$-\Delta G^{\circ}_{ads}$ kJ mol ⁻¹	$-\Delta H^{\circ}_{ads}$ kJ mol ⁻¹	$-\Delta S^{\circ}_{ads}$ J mol ⁻ K ⁻¹
	298	854	46.6		161
	303	618	46.7		159
	308	534	47.4	25	151
Α	313	398	49.2	55	146
	318	210	49.7		143
	298	381	45.8		156
	303	280	46.1		154
	308	251	46.6	25	149
В	313	223	47.4	23	141
	318	208	48.2		140
	298	273	44.8		151
	303	266	45.1		149
	308	264	45.9	23	145
С	313	218	46.4	23	140
	318	205	47.5		139
	298	263	43.8		149
	303	256	44.4		144
	308	234	45.1	17	141
D	313	210	45.9	1/	139
	318	201	46.5		138
	298	243	42.9		141
	303	234	42.5		140
	308	222	43.7	10	139
Е	313	205	44.7	10	137
	318	198	44.2		136

3.8. (AFM) analysis

AFM is a very significant test for determining the roughness of a sample surface at a great resolution in the order of fraction of nanometer [42]. The three-dimensional (3D) of AFM images appear as shown in Figure 11. The average roughness Ra can be distinct as the average variation of all points' roughness profile that is calculated from a mean line. Rq is the average deviations that are measured from the mean line.



Compound (B)

Compound (A)



Figure 11. (3D) AFM images of Zn before immersion in acid (free), Zn immersion in 0.5M HCl alone (blank), and Zn metal immersed in 0.5 M HCl at 21×10^{-6} M of examined compounds (A-E) for 24 hours at 25° C

Table 9. AFM roughness data of compounds (A-E) at 21x10⁻⁶M for 24 hours at 25°C

Specimen	Average roughness(Sa) nm
Free	23
Blank	617
compounds (A)	291
compounds (B)	183
compounds (C)	181
compounds (D)	98
compounds (E)	91

Int. J. Electrochem. Sci., Vol. 13, 2018

The average roughness can be measured from AFM image. Sa sensitive to large and slight high deviations from the mean. Table 9 contributes the conforming average roughness Sa data. A comparative view of the above roughness Table clearly creates that the surface of the zinc is smoothened due to the adsorption covering formed due to active site in the inhibitors [43].

3.9- SEM test

Figure 12, signifies the micrograph given for Zn coins in without and with 21×10^{-6} M of inhibitors (A-E) after exposure for 24 hours immersion



Compound (C)

Compound (\overline{D})



Compound (E)



It is clear that Zn surfaces help and strong corrosion attack in the blank coins. It is significant to stress out that when the composite is existence in the HCl solution, the image of Zn is quite unlike from the preceding one, and the coins surface was smoother. Because the adsorption of the examined compounds on the surface of Zn and create the passive layer in order to block the active center existence on the Zn surface [44].

3.10- EDX tests

The EDX were employ to measure the elements existence on the zinc surface and afterward 24 hours of produce in 0.5M HCl acid with best concentration of inhibitors (A-E). Figure 13, provides the EDX measure of Zn in 0.5M HCl existence of 21×10^{-6} M of examined compounds. The spectra appearance added lines signifying the presence of carbon (remaining to the carbon atoms of some organic compounds). These values indicate that the carbon, oxygen and nitrogen atoms coated the coins surface for inhibitor (A). Similar data were given for different compounds (not shown). The EDX tests indicate that only, carbon, nitrogen and oxygen were noticed, the percent % weight of adsorbed elements N, C and O existed in the spectra and verified in Table 10.



Free Zn



Inhibitor (A)

Figure 13. EDX test on Zn without and with 21×10^{-6} M of inhibitor (A) after immersion for 24 hours at 25°C

Table 10. Weight % of Zn after 24 hours of dipping in 0.5M HCl without and with 21×10^{-6} M of investigated compounds (A-E).

(Mass %)	Zn	С	0	Ν
Free	94.8	0.3	4.9	
0.5M HCl	81.5	6.3	12.2	
А	72.1	9.0	16.6	2.3
В	75.0	7.7	14.2	3.1
С	76.9	7.5	13.1	2.5
D	78.1	7.1	12.7	2.1
Е	78.9	6.9	12.4	1.8

3.11. Theoretical study of investigated compounds

The reactive capacity of the inhibitor is associated to E_{HOMO} , E_{LUMO} [45]. Greater E_{HOMO} of the adsorbent indicated to greater electron donating capability [46]. Small E_{LUMO} led to the acceptor receives electrons simply. The measured quantum chemical (E_{HOMO} , E_{LUMO} , μ) of examine compounds are recorded in Table 11. The change in $\Delta E = E_{LUMO}-E_{HOMO}$ is the energy need to transfer an electron

from HOMO to LUMO. The (ΔE) rise from (A) to (E). This fact elucidates the lowering protection efficiency in this order: A > B > C > D > E.

Tables 11 and Figure 13 display the adjusted structures of the three studied compounds. So, the measured (ΔE) display reasonably excellent correlation with the efficiency of corrosion protection. Table 11 also indicates that inhibitor (A) takes the lowest total energy that gave compound (A) adsorbed simply and is favored by the maximum softness. It was exposed from Table 11 that inhibitor (A) molecule has the minimum ΔE with respect to the other molecules. Therefore, it could be predictable that compound (A) molecule has more characters to adsorb on the zinc surface than the other compounds. It was noteworthy that the presence of an electron donating substituent such as - OCH₃ and -CH₃, are more favored than -Cl and $-NO_2$ group to increase the IE of the inhibitor.





Figure 13. The frontier molecular orbital for the investigated inhibitors (HOMO and LUMO)

Inhibitor	_E _{HOMO} (ev)	_E _{LUMO} (ev)	$\begin{array}{c} \Delta E, \\ (ev) \\ (E_L-E_H) \end{array}$	μ (Debye)
А	8.92	1.13	7.79	4.990
В	8.94	1.09	7.85	4.541
С	8.97	1.11	7.86	4.480
D	9.00	1.13	7.87	3.720
Е	9.33	1.44	7.89	1.640

Table 11. Parameters obtained from quantum chemical calculations for examined derivatives

3.12. Chemical structures and corrosion protection

The corrosion protection of Zn in 0.5M HCl solution by some organic derivatives, utilized chemical and electrochemical measurements was examined. These compounds can be adsorbed in a flat orientation among the S, O and N atoms and the type of groups in para position [47]. In addition, the decrease in IE with higher in temperature, the order of %IE of the examined compounds in 0.5 M HCl solution was: A > B > C > D > E. Linear free energy relationships (LFERs) have been utilized to correlate corrosion rate with and without the examined compounds with their Hammett constituent constants (σ) giving indication for IE order. The LFER or Hammett relation [48] is given by:

$$Log (k_{rate of corr}/k^{o}_{rate of corr}) = -\rho\sigma$$
(12)

where k^o and are k the corrosion rates with and without the inhibitor, correspondingly. ρ is the reaction constant σ is the constituent in para-position, thus (ρ) is a relative measure of the electron density at the reaction center. The sign of constituent's " σ is positive for groups which attract electrons from the reaction center (electron withdrawing groups) and negative for groups which donate electrons. Plot of Log (rate) vs σ and the slope is ρ and its sign designates whether the process is protect by rise or lower of the electron density at the reaction site, the magnitude of ρ led to the relative sensitivity of the protection process to electronic belongings. Fig.14 shows that the examined compounds give a best correlation with correlation coefficient (R²) (0.932). The positive slope of the correlation line (σ = 0.276) shows the reliance of the adsorption character of the reaction center on the electron density of the ring, with electron releasing substituent improving the protection. This is because, in this kind of derivatives, the center of adsorption is link to the ring. Inhibitor (A) has the maximum percentage protection efficiency, this being due to the existence of p-OCH₃ group which is an electron donating group with negative Hammett constant ($\sigma_{pCH3} = -0.27$); this group will increase the electron charge density on the atom and may add an additional center of adsorption to the molecule. Inhibitor (B) comes after (A); this is due to the existence of *p*-CH₃ group which is an electron-donating group ($\sigma_{CH3} = -0.17$), Also this group will improve the electron charge density on the molecule but with lesser amount than p-OCH₃group in composite (A). Inhibitor (C) with Hammett constant ($\sigma_H = 0.0$) comes after (B) in %IE", because H-atom in para position has no effect on the charge density on the molecule. Finally inhibitor (D) and (E) are the lowest in %IE. This is due to the presence of p-Cl and p-NO₂ groups which being electron withdrawing group with positive Hammett constants ($\sigma_{Cl} = +0.23$ and $\sigma_{NO2} = +0.78$), depends on magnitude of their withdrawing character.



Figure 14. Relation between Log k_{corr} vs σ (Hammett constants) of the substituent of investigated compounds

4. CONCLUSIONS

The tested organic compounds (A-E) establish a very excellent protection for Zn corrosion in HCl solution, where IE% increased by increasing in organic compound (A-E) concentration. The reduction in corrosion hindrance with rise temperature led to desorption of the adsorbed organic compound molecules from the Zn surface. An organic compound inhibits Zn corrosion by adsorption on its surface and follow Langmuir adsorption isotherm. Potentiodynamic polarization curves showed that investigated organic compounds are mixed-kind inhibitors. (C_{dl}) lowered with increase the inhibitors concentration added. While (R_{ct}) rise. The existence of the protecting film on the surface of Zn was proved by AFM, SEM, EDX and FTIR analysis. The obtained data of IE from the various tests used are compatible with each.

References

- 1. S. Thomas, N. Birbilis, M.S. Venkatraman and I.S. Cole, Corrosion, 68 (1) (2012) 9.
- 2. E. Yousif, Y. Win, A.H. Al-Hamadani, A.A. Al-Amiery, A.H. Kadhum and A. Mohamad, *Int. J. Electrochem. Sci.*, 10 (2015)1708.
- 3. R.T. Vashi and K. Desai, Der Pharma Chemica, 4(5) (2012) 2117.
- 4. A.S. Fouda, A. Abdel Nazeer and A. Saber, J. Korean Chem. Soc., 58(2) (2014) 160.
- 5. A. Shanbhag, T. Venkatesha, R. Prabhu and B. Praveen, Bull. Mater. Sci., 34(3) (2011) 571.
- 6. M. Abdallah, I.A. Zaafarany and B.A. Zn Jahdaly, J. Mate. Environ. Sci., 7 (4) (2016) 1107.
- S. Junaedi, A. Al-Amiery, A. Kadihum, A. Kadhum and A. Mohamad, *Int. J. Mol. Sci.*, 14(6) (2013) 1915.
- A. Kadhum, A. Mohamad, L. Hammed, A. Al-Amiery, N. Hooi San and A. Musa, *Materials*, 7 (6) (2014) 4335.
- 9. A.S. Fouda, M. Abdallah, S.T. Atwa and M.M. Salem, *Modern Appl. Sci., Canda*, 4 (12) (2010) 41.
- 10. J.D.Talati, M.N.Desai and N.K. Shah, Mater. Chem. Phys., 93 (2005) 54
- 11. Y.K. Agrawal, J.D. Talati, M.D. Shah, M.N. Desai and N.K. Shah, *Corros.Sci.*, 46 (2004) 633
- 12. E.E.Foad El-Sherbini, S.M.Abdel Wahaab and M.Deyab, Mater. Chem. Phys., 89(2-3) (2005) 183
- 13. J.D. Talati, M.N.Desai, N.K.Shah, Anti-Corrosion Methods and Materials, 52(2) (2005) 108
- 14. M.N.Desai, J.D.Talat, N.K.Shah, Indian Journal of Chemistry, Section A : Inorganic, Bioinorganic, Physical, . Theoretical and Analytical Chemistry, 42A(121 (2003) 3027
- 15. N.Mani, S.Iyer Venkatakrishna and Lai Bahadur, *Journal of the Electrochemistry Society of India*, 52(1) (2003) 23.
- 16. K.Wang, H.W.Pickering and K.G.Weil, *Journal of the Electrochemical Society*, 150(41 (2003) B176.
- 17. A. A. Fadda, R.Rabie and H. A. Etman, J. heterocyclic chem., 54(2) (2017)1015
- 18. A. A. Fadda, R. Rabie, H. A. Etman and A. S. Fouda, *Research on Chemical Intermediates*, 41(10) (2015) 7883
- 19. H. Ma, S. Chen, L. Niu, S. Zhao, S. Li, and D. Li, J. Appl. Electrochem., 32(2002) 65.
- 20. R. W. Bosch, J. Hubrecht, W. F. Bogaerts, and B. C. Syrett, Corrosion, 57(2001)60.
- 21. S. S. Abdel–Rehim, K. F. Khaled and N. S. Abd–Elshafi, *Electrochim. Acta* 51 (2006) 3269.
- 22. Z. Khiati, A.A. Othman, M. Sanchez-Moreno, M. C. Bernard, S. Joiret, E.M.M Sutter and V. Vivier, *Corros. Sci.*, 35 (2011) 3092.
- 23. W.H. Smyrl, J.O.M. Bockris, B.E.Conway, E. Yeager and R.E. White (Eds.), Comprehensive Treatise of Electrochemistry, *Plenum Press, New York*, 4(1981) 116.
- 24. M. El Achouri, S. Kertit, H.M. Gouttaya, B. Nciri, Y. Bensouda, L. Pere, M. RInfante and K. Elkacemi, *Prog. Org. Coat.*, 43(2001) 267.
- 25. S. F. Mertens, C. Xhoffer, B. C. Decooman and E. Temmerman, Corrosion, 53 (1997) 381.
- 26. M. Lagrenée, B. Mernari, M. Bouanis, M. Traisnel and F. Bentiss, Corros. Sci., 44 (2002) 573.
- 27. F. Bentiss, M. Lagrenée, and M. Traisnel, Corrosion, 56 (2000)733.
- 28. E. Kus and F. Mansfeld, Corros. Sci., 48 (2006) 965.
- 29. D. Q. Zhang, Q. R. Cai, X. M. He, L. X. Gao, and G. S. Kim, Mater. Chem. Phys., 114(2009) 612.
- 30. 30. G. Trabanelli, in "Corrosion Mechanisms" (Ed. F. Mansfeld) Marcel Dekker, New York, (1987)119.
- 31. A.S. Fouda, A. Abd El-Aal and A.B. Kandil, Desalination, 201 (2006) 216.
- 32. A. Fiala, A. Chibani, A. Darchen, A. Boulkamh and K. Djebbar, Appl. Surf. Sci., 253(2007)9347.
- 33. W. Durnie, R.D. Marco, A. Jefferson and B. Kinsella, J. Electrochem. Soc., 146(1999) 1751.
- 34. M. K. Gomma and M. H. Wahdan; Mater. Chem. Phys. 39 (1995) 209.
- 35. A. S Fouda, A.M. El-desoky and A.Nabih, Advances in Materials and Corrosion, 2 (2013)9.

- 36. A. N. Frumkin, Zeitschrift für Physikalische Chemie, 116 (1925) 466.
- 37. F. Bensajjay, S. Alehyen, M. El Achouri, S. Kertit, Anti-Corros. Meth. Mater. 50 (2003) 402.
- 38. L.Tang, X.Li, Y.Si, G.Mu and G.Liu, Mater. Chem. Phys., 95 (2006) 29.
- 39. S.S. Abd El-Rehim, S.A.M. Refaey, F. Taha, M.B. Saleh and R.A. Ahmed, J. Appl.Electrochem.31 (2001) 429.
- 40. A. S. Fouda, D. Mekkia and A. H. Badr, J.Korean Chem. Soc., 57(2013) 264.
- 41. G.Mu, X. Li and G.Liu, Corros. Sci., 47 (2005) 1932.
- 42. B. Wang, M. Du, J. Zang and C.J, Gao, Corros.Sci., 53 (2011) 353.
- 43. S. Rajendran, C. Thangavelu and G. Annamalai, J. Chem. Pharm. 1 Res., 4 (2012) 4836.
- 44. A.S. Fouda, Y.M. Abdallah and D. Nabil, IJIRSET 3(2014)12965
- 45. J.M.Costa and J.M.Lluch, Corros.Sci., 24 (1984) 929.
- 46. C. Lee, W. Yang and R. G. Parr., Phys. Rev. B, 37 (1988) 785.
- 47. L. R. Chauhan and G. Gunasekaran, Corros. Sci., 49 (2007) 1143.
- 48. H. Ashassi-Sorkhabi, B. Shaabani, and D. Seifzadeh, Appl. Surf. Sci., 239(2005)154.

© 2018 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).