

ISSN 0975-413X CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(2):318-331 (http://derpharmachemica.com/archive.html)

Studies on the inhibition of corrosion of carbon steel in acidic solutions using some thiosemicarbazide derivatives

A. S. Fouda, O. A. El Gammal, A. A. Hassan and S. M. Taha

Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura, Egypt

ABSTRACT

Thiosemicarbazide derivatives have been used as inhibitors for corrosion of steel in acidic medium by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. Poteniodynamic polarization measurements means that they acts as a type of chemical inhibitors. The inhibition efficiency increases with increasing the inhibitor concentration, and also increase with increasing the temperature. The adsorption of thiosemicarbazide derivatives on the surface of carbon steel obeys Langmuir's adsorption isotherm. From EFM the causality factors are very close to theoretical values which indicate that the measured data are of good quality. Nyquist plots show a single capacitive loop in uninhibited and inhibited solutions.

Keywords: Inhibition of corrosion; Carbon steel; HCl; thiosemicarbazide derivatives; EIS.

INTRODUCTION

Carbon steel is the most useful substance for mechanical engineering techniques, as its low cost; its great strength. Deterioration of metals by the reaction with the environment is the mean of corrosion. For the protection of corrosion inhibitors are used .Most widely inhibitors are organic compounds contains nitrogen, oxygen and sulfur. These centers are adsorption centers. Thiosemicarbazide derivatives inhibitors are used as organic inhibitor that contains nitrogen, oxygen and sulfur .Most of these organic inhibitors are adsorbed on the carbon steel surface. The strength of the inhibitor depends on its structure ;the properties of the environment;....etc .The important aim of this paper was done by some thiosemicarbazide derivatives effects of as inhibitors for the corrosion of carbon steel in 1M hydrochloric acid. The most important techniques were employed, chemical weight loss, electrochemical (potentiodynamic, electrochemical frequency modulation, EFM and electrochemical impedance frequency).these techniques were employed in 1M HCl without and with different compound concentrations ranges.

MATERIALS AND METHODS

2.1 Materials

The compositions of commercial C steel are listed in Table: 1

С	Mn	Р	Si	Fe
0.200	0.91	0.007	0.002	Rest

2.2 Solutions

Hydrochloric acid and organic additives were of analytical grade .The organic inhibitors used in this study were phenyl, ally and ethyl thiosemicarbazide derivatives

2.3 inhibitors

Table 2: includes structures of the thiosemicarbazide derivatives



2.4 Methods

2.4.1Weight lose measurements

Specimens of C-Steel were abraded up and degreased by acetone rinsed with bidistilled water then finally dried between filter paper. After this we must weight with great accuracy the specimens were dipped in 100 ml of 1M HCl without and with different concentrations of thiosemicarbazide derivatives. After various time (30 : 180 min). After 3 h, the coins were obtain, washed, dried, and weighed accurately. The efficiency of inhibition (%IE) and the degree of coverage surface of investigated compound for metal corrosion in HCl were measured from Eq. (1) (2):

% I E = 100 x
$$\theta = [1 - (W / W^{\circ})] \times 100$$

(1)

Where W° = the data of the mean mass reduction without inhibitor.

W = data of the mean mass reduction in presence of inhibitor.

The results leads to a comparative way between the inhibitors according to the surface coverage and % IE show that phenyl > ally > ethyl.

2.4.2 Electrochemical Techniques

Three different electrochemical techniques were conducted using three electrode system arranged in a glass cell as follows; carbon steel specimen as working electrode (1cm^2) , saturated calomel electrode (SCE) acts a reference electrode, and platinum wire serves as an auxiliary electrode. In the present work, the working electrode was made of square specimen of carbon steel welded with copper rod from one side and totally encapsulated into a glass rod, of larger diameter (5 mm) so that only one face of the carbon steel specimen, of dimension $(1\text{cm} \times 1\text{cm})$, was left to be exposed to the test solution. The electrode reference was related to a Luggin capillary and the tip of the capillary is set to be very near to the surface of the electrode working in order to partially eliminate error originated from IR drop. All the measurements were performed under stagnant conditions. Before starting electrochemical experiments, the working electrode was prepared in the same manner of sample preparation for mass loss method and the electrode potential was stabilized for 20 min. All results from electrochemical were utilized by Gamry Instrument (PCI4/750) with a Gamry system depend on the ESA400 and computerized frameworks contain DC105 software for

potentiodynamic polarization measurements, EIS300 software for electrochemical impedance (ac) spectroscopy, and EFM140 software for electrochemical frequency modulation techniques. In addition, Echem Analyst 6.03 software was used for data fitting, graphing and plotting.

2.4.2.1 Potentiodynamic Polarization

Tafel curves obtained from potential polarization scan by automatically sweeping the working electrode potential from (-0.7 to 0.7 V vs. SCE) (3),utilized for calculated The current corrosion by extrapolation of cathodic and anodic Tafel solp (β a and β c) to gives log i_{corr} and potential of corrosion (Ecorr) for acid free with each concentration of the investigated plant extract. The inhibition efficiency (%IE) and surface coverage (θ) were calculated using the obtained values of i_{corr}. Then (i_{corr}) was utilized for measured of (IE %) and (θ) as in equation 2:

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

(2)

(3)

Where $i_{corr(free)}$ = corrosion current densities without inhibitor, $i_{corr(inh)}$ = corrosion current densities with of inhibitor.

2.4.2.2 Electrochemical impedance spectroscopy (EIS)

At open circuit potential, alternative current signals, in range of frequency from 100 kHz to 0.5 Hz, were applied to measure the impedance of the corrosion process. An equivalent electrical circuit was tested to analyze and explain the impedance. The coverage surface (θ) and inhibition efficiencies given from the impedance results are measured from equation 3:

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

Where R_{ct}^{o} =the charge transfer resistance without inhibitors. R_{ct} = charge transfer resistance with inhibitor.

2.4.2.3 Electrochemical frequency modulation (EFM)

Two different frequencies 2 : 5 Hz with frequency base equals to 0.1 Hz were applied to obtain the intermodulation spectra of the electrochemical frequency modulation. It is necessary for the value of lower frequency to be not greater than a half of the higher frequency. The current responses, obtained from EFM spectra, assigned for intermodulation and harmonically current peaks. The biggest peaks were utilizes to measure the Tafel slopes (β a and β c), the current density for corrosion (i_{corr}), and the causality factors CF-2&CF-3 (4,5).

2.5 Surface results

The surface morphology was obtained with carbon steel coins by put in solution of inhibitor for a one day. After the immersion period, the coins were dried and the nature of the film obtained on the surface of the metal was measured by SEM methods. Analyses of C-Steel morphology after one day exposed to 1 Molar HCl.

RESULTS AND DISCUSSION

3.1 Chemical Method (Weight-loss measurements)

Figure 1 shows the weight loss-time curves for C-Steel in 1M hydrochloric acid in the presence and absence of different concentrations of thiosemicarbazide derivatives at 25°C. These curves are characterized by a sharp rise in weight loss from the beginning. Curves for additives containing system fall below that of the free acid. These curves indicated that, the weight loss of C-Steel depends on both the type and concentration of the inhibitor. Increase in bulk concentration and consequently increase of surface coverage by the additive increases their inhibition efficiencies towards C-Steel dissolution. The results of Table 3 show that the inhibition efficiency of all additives increases with the increase of their concentrations in the corrosive medium. It is thus obvious that increase of bulk concentration and consequently, increase of surface area coverage by the additive retards the dissolution of C-steel.

Table 3: Values of inhibition efficiencies (% IE) and (θ) of thiosemicarbazide derivatives for the C-steel corrosion in acidic medium from mass reduction method at various Concentrations and at room temperature

Compound	Conc., x 10 ⁻⁶ M	C.R., mg cm ⁻² min ⁻¹	Θ	% IE
Blank	0.0	0.0103	-	-
	1	0.008	0.221	22.1
Dhanyl	5	0.0055	0.466	466
Phenyi	9	0.00452	0.56	56
	13	0.00382	0.628	62.8
	17	0.00346	0.663	66.3
	21	0.00316	0.693	69.3
	1	0.00859	0.122	12.2
	5	0.0067	0.349	34.9
A 11-1	9	0.00542	0.473	47.3
Aliyi	13	0.00481	0.532	53.2
	17	0.0042	0.592	59.2
	21	0.0039	0.621	62.1
	1	0.00925	0.098	9.8
	5	0.00675	0.342	34.2
Etherl	9	0.00545	0.47	47
Ethyl	13	0.00491	0.521	52.1
	17	0.00432	0.58	58
	21	0.00401	0.61	61

Figure 1: Weight loss-time curves for the corrosion of C-Steel in 1 M HCl in the absence and presence of different concentrations of phenyl thiosemicarbazide at 25 $^{\circ}$ C



3.1.1. Adsorption isotherm

One of the most convenient ways of expressing adsorption quantitatively is by deriving the adsorption isotherm that characterizes the metal/inhibitor/ environment system (6). Various adsorption isotherms were applied to fit Θ values, but the best fit was found to obey Langmuir adsorption isotherm which are represented in Figures for inhibitors phenyl, allyl and ethyl respectively, Langmuir adsorption isotherm may be expressed by: (C/ Θ =1/K+T)

Where C is the concentration (mol L^{-1}) of the inhibitor in the bulk electrolyte, Θ is the coverage surface degree ($\Theta = \% IE/100$), the efficiency of inhibition % (I E) = 100 x Θ (7), K ads is the adsorption equilibrium constant. A plot of versus C/ Θ should give lines straight with 1/K ads intercept. The variation of the adsorption equilibrium constant (K ads) of the inhibitors with the molar concentrations was obtained The experiments give good curves of adsorption isotherm .figures(2,3,4) give the adsorption isotherm s of the three inhibitors as shown:



Figure 2: Langmuir isotherm adsorption of phenyl thiosemicarbazide on surface of C-Steel in 1M hydrochloric acid at various temperatures



Figure 3: Langmuir adsorption isotherm of ally thiosemicarbazide on C-steel surface in1M HCl at different temperatures



Figure 4: Langmuir adsorption isotherm of ethyl thiosemicarbazide on C-Steel in 1M HCl at different temperatures

Inhibitor	Temperature°C	K _{ads} x 10 ⁻⁴ M ⁻¹	Slope	R^2
	25	25.25	1.27	0.996
	30	35.8422	1.19	0.9992
Phenyl	35	48.5436	1.14	0.9991
-	40	64.1025	1.09	0.998
	45	96.1538	1.02	0.9973
	25	13.3155	1.26	0.9973
	30	19.2307	1.2	0.9972
Allyl	35	29.6735	1.16	0.9974
-	40	51.5463	1.14	0.9971
	45	66.666	1.09	0.99938
	25	11.5473	1.22	0.998
	30	13.8312	1.18	0.9977
Ethyl	35	17.1821	1.17	0.9979
-	40	23.8663	1.16	0.997
	45	33.8983	1.09	0.9603

Table (4): Adsorption parameters for inhibitors in 1M HCl obtained from Langmuir adsorption isotherm at different temperatures

These data obtained given that these thiosemicarbazide derivatives are adsorbed on the surface of C steel through the (S, N, O) protonated atoms or via the lone pair of electrons of this atoms. The degree of inhibition is directly due to the presence of adsorption layer which related to the molecular structure function. The equilibrium constant of adsorption Kads obtained from the intercepts of Langmuir adsorption isotherm(8) is due to the energy free of adsorption ΔG° ads as follows: Kads=1/55.5 e^{((- $\Delta G^{\circ} ads) / RT$)}

3.1.2 The temperature effect.

Temperature effect on the rate of corrosion of C-Steel in 1M hydrochloric acid and with of various concentrations of inhibitor was done in the range of temperature of $25-45^{\circ}C$. As rise temperature, the corrosion rate increase and the efficiency of inhibition of the thiosemicarbazide derivatives increase The adsorption behavior of thiosemicarbazide as inhibitors on the surface occurs through chemical, (9,10)

Table 5: Values of corrosion rate (C.R) of C-Steel corrosion by thiosemicarbazide derivatives in 1 M HCl from mass reduction methods at various concentrations at temperature rangesof25-45°C

$find ly 10^{-6}M$		$k_{corr} (mg \ cm^{-2} \ min^{-1}) x 10^3$						
[IIIII]X I	U M	25°C	30 °C	35 °C	40 °C	45°C		
	0	10.3	15	22.3	33.8	66.90		
	1	8	11	14.7	20.4	31.5		
	5	5.5	6.75	8.12	10	11.4		
phenyl	9	4.52	5.36	6.5	7.75	9.5		
	13	3.82	4.36	5.33	6.35	7.75		
	17	3.46	3.97	4.68	5.37	6.3		
	21	3.13	3.69	4.24	4.5	5		
	1	8.59	12.4	16.8	24.3	33.8		
	5	6.7	8.7	10.2	13.5	19.8		
o11v1	9	5.425	6.81	8.5	11	15.1		
anyi	13	4.81	5.6	6.8	9.25	12.5		
	17	4.2	5.03	6.15	7.5	10		
	21	8.59	12.4	16.8	24.3	33.8		
	1	9.25	11.7	19	29.2	41.66		
	5	6.75	9.16	12.8	19.5	28.8		
Etherl	9	5.45	7.33	10.4	14.8	22.6		
Etnyl	13	4.91	6.33	8.5	12.33	18.7		
	17	4.32	5.62	7.66	10.58	15.4		
	21	4.01	5	6.7	9.75	10.3		

3.4 Kinetic -thermodynamic corrosion parameter

The activation parameters for the corrosion process were calculated from Arrhenius-type plot according to eq. 6:

$$K_{corr=}A \exp(E_a^*/RT)$$

(6)

Where A = Arrhenius constant pre-exponential, T = temperature absolute, R = universal constant gas and E_{a}^{*} = activation corrosion energy apparent. Values of apparent activation energy of corrosion for C-Steel in1MHCl shown in Table 6, in presence and absence different thiosemicarbazide derivatives was measured from slope of 1/T versus log (k_{corr}) diagrams are shown in Figure 5. Inspection of the values obtained that the energy of activation is decreased in with inhibitor than without thiosemicarbazide derivatives inhibitors. This due to decrease rate of adsorption inhibitor with data approach to equilibrium due to the experiments at bigger temperatures according to Hoar and Holliday (11).But, Riggs and Hurd(12) "explained that the decrease in the activation energy of corrosion at higher levels of inhibition arises from a shift of the net corrosion reaction from the uncovered part of the metal surface to the covered one, Schmid and Huang found that organic molecules inhibit both the anodic and cathodic partial reactions on the electrode surface and a parallel reaction takes place on the covered area, but the reaction rate on the covered area is substantially less than on the uncovered area similar to the present study". (13) The alternative formulation of transition state equation is shown in Eq. 7: kcorr = (R T / Nh) e $(\Delta S^*/R) e^{(-\Delta H^*/R T)}$ (7)

Where ΔH^* activation enthalpy, k_{corr} = rate of metal dissolution, ΔS^* = activation entropy, N = Avogadro's number, and h = Planck's constant.



 $\label{eq:starsest} Figure 5: shows a curve of (log k_{corr}) against (1/T) of phenyl thiosemicarbazide in acidic medium. Straight lines are obtained with a slopes equal to (\Delta H^* / 2.303 R) and intercepts are [log (R/Nh + \Delta S^* / 2.303 R)]$



Figure 6: shows a curve of (log k_{corr}/T) vs. (1/T) for phenyl thiosemicarbazide in 1 M HCl. Straight lines are obtained with a slopes equal to (Δ H* /2.303R) and intercepts are [log (R/Nh + Δ S*/2.303R)]

Comp.	Conc.,M	$\mathbf{E_a}^*$	$\Delta \mathbf{H}^*$	ΔS^*
Blank		71.6	30.17	50.33-
	1X10 ⁻⁶	50.9	21.28	-120.79
	5X10 ⁻⁶	28.9	11.55	-198.8
Dhonyl	9X10 ⁻⁶	28.14	10.72	-206
Flienyi	13X10 ⁻⁶	27.76	9.97	-213
	17X10 ⁻⁶	23.55	9.22	-220
	21X10 ⁻⁶	17.99	6.73	-239
	1X10 ⁻⁶	55.71	21.61	-116
	5X10 ⁻⁶	40.01	16.21	-161.4
A 11x1	9X10 ⁻⁶	39.06	15.63	-167
Allyl	13X10 ⁻⁶	37.14	14.59	-173
	17X10 ⁻⁶	32.55	13.05	-189
	21X10 ⁻⁶	29.29	11.69	-200.6
	1X10 ⁻⁶	59.73	24.27	96.86
	5X10 ⁻⁶	55.14	23.36	-106.43
Ethyl	9X10 ⁻⁶	54.76	22.36	-115.62
Eury	13X10 ⁻⁶	51.5	21.2	-125.77
	17X10 ⁻⁶	46.9	20.7	-130.17
	21X10 ⁻⁶	46.3	19.62	-139.17

Table 6: parameters of activation for corrosion of metal with and without various concentrations of inhibitors in1M HCl

3.5Potentiodynamic Polarization Measurements

Figure 6: given the cathodic and anodic Tafel polarization diagrams for metal in 1 molar hydrochloric acid in the presence and absence of various phenyl derivative concentrations at room temperature, respectively. From Fig. 5, it is clear that both cathodic reduction H_2 reactions and anodic dissolution of metal were inhibited when added investigated phenyl derivative to 1 molar hydrochloric acid and this inhibition was more powerful with rise concentration of phenyl derivative. Tafel slope are shifted to more positive and more negative potentials with other the blank slope by raising the concentration of the investigated phenyl derivative additives play as mixed-type inhibitors (14, 15).

Figure 6: Tafel polarization diagrams for C-Steel corrosion in acidic medium without and with concentrations of phenyl derivative at 25 $^{\circ}C$



The data in Table 7 given that the rise in phenyl derivative concentration leads to lower the (i_{corr}) current corrosion density, but the (β_a, β_c) Tafel slopes are constant lead to that the resistance of the two reactions (anodic dissolution metal and cathodic reduction hydrogen) were obtained without exchange on mechanism of metal dissolution (16-18).

Inhibitors	Conc,M	$E_{corr}mV$	j _{corr} µA cm ⁻²	β_c mV dec ⁻¹	β_a mV dec ⁻¹	Θ	% IE
	blank	-499.00	427.0	150	100		
	1x10 ⁻⁶	-488.00	324.0	170	105	0.241	24.1
	5x10 ⁻⁶	-484.00	309.0	150	102	0.276	27.6
Phenyl	9x10 ⁻⁶	-479.00	296	120	110	0.307	30.7
	13x10 ⁻⁶	-482.00	247.0	120	96	0.422	42.2
	17x10 ⁻⁶	-490.00	116.0	120	76	0.728	72.8
	21x10 ⁻⁶	-496.00	97.10	110	78	0.77	77.26
	1x10 ⁻⁶	-500.00	208.0	150	100	0.494	49.4
	5x10 ⁻⁶	-455.00	186.0	170	200	0.547	54.7
A 11v1	9x10 ⁻⁶	-447.00	141	210	120	0.657	65.7
Allyl	13x10 ⁻⁶	-450.00	140.0	220	106	0.659	65.9
	17x10 ⁻⁶	-455.00	138.0	220	96	0.664	66.4
	21x10 ⁻⁶	-456.00	107.00	210	111	0.74	73.97
	1x10 ⁻⁶	-449.00	153.0	130	100	0.628	62.8
	5x10 ⁻⁶	-455.00	142.0	120	78	0.655	65.5
Ethyl	9x10 ⁻⁶	-464.00	137	120	79	0.667	66.7
Etnyi	13x10 ⁻⁶	-456.00	133.0	120	70	0.676	67.6
	17x10 ⁻⁶	-464.00	126.0	100	69	0.693	69.3
	21x10 ⁻⁶	-459.00	114.00	111	65	0.72	72.26

 $\label{eq:corr} Table \mbox{7: Corrosion potential} (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (\beta_c,\beta_a), degree of surface coverage (\theta), and inhibition efficiency (% IE) of C-Steel in 1 M HClat 25°C for phenyl derivative$

3.6 Electrochemical Impedance Spectroscopy (EIS)

"The effect of inhibitor concentration on the impedance behavior of C-Steel in 1M HCl solution at 25 °C is presented in Fig. 7 (a,b). The curves show a similar type of Nyquist plots (Fig.7a) for C-Steel in the presence of various concentrations of phenyl derivatives, the existence of single semi-circle showed the single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules, deviations from perfect circular shape are often referred to the frequency dispersion of interfacial impedance, which arises due to surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitor, and formation of porous layers and in homogenates of the electrode surface (19,20), 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 (Fig.7b), the electrical equivalent circuit model is shown in Figure 8, it used to analyze the obtained impedance data, the model consists of the solution resistance (R_s), the charge-transfer resistance of the interfacial corrosion reaction (R_{ct}) and the Constant phase element (CPE), excellent fit with this model was obtained with our experimental data".

The data of the C_{dl} interfacial capacitance can be measured from parameter CPE data Y_0 and n utilized the expression (21):

$$C_{dl} = Y_0 \left(\omega_{max}\right)^{n-1} \tag{8}$$

Where ω_{max} = angular frequency at which the imaginary component of the impedance reaches its maximum data n = deviation parameter of the CPE: $-1 \le n \le 1$ and Y_0 = magnitude of the CPE.

EIS value (Table 8) given that the R_{ct} values rise and the C_{dl} dates lower with raising the concentrations of inhibitor. Because the replacement gradual of water molecules by the inhibitor molecules adsorption on the surface of metal (22, 23).



Figure 7a: The Nyquist diagrams for the C-Steel corrosion in 1M hydrochloric acid with and without concentrations of phenyl derivative at room temperature



Figure 7b: The Bode diagrams for the C-Steel corrosion in 1M hydrochloric acid with and without concentrations of phenyl derivative at room temperature

Inhibitors	Conc. M	$C_{dl},$ $\mu F \text{ cm}^{-2}$	R _{ct} , ohm cm ²	Θ	% IE
	Blanc	1.27E-04	33.89		
	1x10 ⁻⁶	2.56E-04	75.37	0.550	55.0
	5x10-6	6.93E-05	138.70	0.756	75.6
phenyl	9x10 ⁻⁶	3.96E-04	241.20	0.859	85.9
_	13x10 ⁻⁶	4.52E-04	400.80	0.915	91.5
	17x10 ⁻⁶	5.30E-04	454.00	0.925	92.5
	21x10 ⁻⁶	3.78E-04	608.50	0.944	94.4
	1x10 ⁻⁶	4.51E-04	41.55	0.315	31.5
	5x10-6	2.41E-04	61.59	0.538	53.8
allyl	9x10 ⁻⁶	8.05E-05	70.33	0.595	59.5
	13x10 ⁻⁶	3.14E-04	71.00	0.599	59.9
	17x10 ⁻⁶	2.61E-04	78.43	0.637	63.7
	21x10 ⁻⁶	3.48E-04	129.80	0.781	78.1
	1x10 ⁻⁶	1.27E-04	28.45	0.376	37.6
	5x10- ⁶	1.91E-04	45.58	0.421	42.1
athyl	9x10 ⁻⁶	1.80E-04	49.14	0.621	62.1
ettiyi	13x10 ⁻⁶	1.92E-04	75.13	0.640	64.0
	17×10^{-6}	1.96E-04	78.92	0.676	67.6
	21x10 ⁻⁶	1.95E-04	87.92	0.706	70.6

Table 8: EIS value for the C-Steel corrosion in 1M hydrochloric acid with and without concentrations of phenyl derivative at room temperature

Figure 8: Equivalent electrical circuit model utilized to fit the results of impedance



3.7 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 ac signal, it is generally accepted that in most cases, the corrosion rates determined with the EFM technique, are much higher than the values determined with other techniques exhibiting low corrosion rates" (24).



Figure 9: EFM for the C-Steel corrosion in 1M hydrochloric acid with and without concentrations of phenyl derivative at room temperature

Inhibitor	[inh]x10 ⁻⁶	icorr	βa	βc	CE-2	CF-3	K _{corr.}	Θ	% IF
minutoi	Μ	µAcm ⁻²	mVdec ⁻¹	mVdec ⁻¹	CF-2		mpy		70 HL
Blank	0	628.1	98.66	126.3	2.77	1.94	287.0		
	1	413.5	131.1	183	2.30	2.23	188.9	34.2	0.342
	5	366.5	133.8	148.1	2.70	2.69	167.50	41.6	0.416
Dhamal	9	348.8	128.8	136.3	2.70	2.38	159.40	44.5	0.445
Phenyl	13	319.8	120.0	120	4.36	1.80	141.9	49.1	0.491
	17	202.2	116.8	125	4.11	1.18	92.41	67.8	0.678
	21	137.3	99.890	104.5	4.56	1.10	62.75	78.1	0.781
	1	446.5	72.620	193.6	2.19	1.94	204.00	28.9	0.289
	5	269.7	75.530	84.4	3.47	2.08	123.30	57.1	0.571
A 11-1	9	268.7	93.630	104.6	2.16	1.75	122.80	57.2	0.572
Allyi	13	257.5	86.780	92.63	2.65	1.59	117.70	60.0	0.600
	17	237.7	84.960	98.16	3.40	1.81	108.60	62.2	0.622
	21	231.4	84.260	90.06	2.87	1.69	105.70	63.2	0.632
	1	475	67.000	115	2.35	1.75	220.00	24.4	0.244
	5	379	71.300	105.1	3.10	1.99	195.00	39.7	0.397
Ethyl	9	357	80.000	98.5	2.80	1.87	172.00	43.2	0.432
	13	336	88.100	90.5	2.90	1.68	166.00	46.5	0.465
	17	250	85.500	88.1	3.10	1.71	128.00	60.2	0.602
	21	239	81.260	80.5	3.00	1.85	118.00	61.9	0.619

 Table 9: Electrochemical kinetic parameters obtained by EFM technique for C-Steel in the absence and presence of different concentrations of phenyl thiosemicarbazide in 1 M HCl at 25°C

The measured corrosion kinetic parameters at different concentrations of C-Steel in1 M HCl at 25 °C (i_{corr} , β_a , β_c , CF-2, CF-3 and % IE) are given in Table 9. "The corrosion current densities decrease by increasing the concentration of investigated compound and the efficiency of inhibition increases by increasing investigated compound concentrations, the causality factors in Table 9 are very close to theoretical values which according to EFM theory (5, 25) should guarantee the validity of Tafel slopes and corrosion current densities, data of causality factors in Table 9 indicate that the measured data are of good quality, the standard values for CF-2 and CF-3, the deviation of causality factors from their ideal values might be due to the perturbation amplitude was too small or that the resolution of the frequency spectrum is not high enough, another possible explanation is that the inhibitor is not performing very well". The obtained data showed good agreement of kinetic corrosion parameters from the EFM, EIS and Tafel extrapolation methods.

3.8 SEM experimental

To identify the investigated thiosemicarbazide derivatives compound molecules are in fact adsorbed on surface of C-Steel, SEM experiment was done. The micrographs SEM for C-Steel surface single and after one day immersion in 1 molar hydrochloric acid with and without the addition of higher concentration 21x 10⁻⁶ of thiosemicarbazide derivatives are given in Figures (9a-c). As expected, Figure 9a given clear surface metallic, while without investigated thiosemicarbazide derivatives compound, the damaged surface of C-Steel by HCl corrosion (Figure9b). In contrast, with the investigated thiosemicarbazide derivatives compound Figure 9c, the no affected by corrosion for metallic surface. It is clear from the adsorption of investigated thiosemicarbazide derivatives compounds on the C-Steel surface and confirms the formation of a thin film of investigated thiosemicarbazide derivatives compounds resulted in micrograph SEM, thus protecting Carbon steel surface verses corrosion.





Figure 9 (a-c): micrographs SEM of surface C-Steel (a) after24h immersion in 1 molar hydrochloric acid and ethyl derivative, (b) after 24 h of immersion in acidic medium and allyl, (c) after 24 h of immersion in 1 molar hydrochloric acid + 21x10⁻⁶ of phenyl at 25±1 °C

4. Corrosion Inhibition Mechanism

Results of the present paper have shown that these the investigated thiosemicarbazide derivatives compound (inhibitors) resist the acid corrosion of C-Steel by adsorption the investigated thiosemicarbazide derivatives compound onto the surface of metal. "The result shows that the inhibition efficiency of thiosemicarbazide derivatives rise with rise in inhibitor concentration suggests that some of the molecules of the inhibitor are adsorbed on the metal surface thereby protecting the covered" surface from further corrodes attack". Raising the inhibitor concentration rises the Θ surface coverage degree for surface of metal.

CONCLUSION

1- Thiosemicarbazide derivatives acts as an corrosion inhibitor for of metal in acidic solution

2- The inhibition efficiency rise with rise in the concentration of the investigated thiosemicarbazide derivatives inhibitor

3- The inhibition is due to the inhibitor molecule adsorption on the surface of metal by charge transfer by the diffusion of the inhibitor molecules

4- The adsorption of these compounds on the metal surface follows Langmuir adsorption isotherm

5-Results obtained from potentiodynamic polarization is mixed-type inhibitor.

6- Reasonably good agreement was observed between the data obtained from the mass reduction and electrochemical measurements were in good agreement.

REFERENCES

[1]Dawood. K.M, Shabana Y.M., Fayzalla E.A. and EL-SherbinyE.A,..Agri J c.Sci.Mans, (2003) 5335.

[2]Mu, G.N., Zhao, T.P., Liu, M., Gu, T., Corrosion 52 (1996) 853.

[3]Stern, M., Geary, A. L., J. Electrochem. Soc. 104 (1957) 56.

[4] Abdel-Rehim, S.S., Khaled, K.F., Abd-Elshafi, N.S., Electrochim. Acta 51 (2006) 3269.

[5]Bosch, R.W., Hubrecht, J., Bogaerts, W.F., Syrett, B.C., Corrosion, 57 (2001) 60.

[6] Dinnappa, R. K., Mayanna, S. M., J. Appl. Elcreochem. 11 (1982) 111.

[7] Patel, N., Rawat, A., Jauhari, S., Mehta, G., European J. Chem. 1 (2010) 129.

[8] Langmuir, I., J. Am. Chem. Soc. 39 (1947) 1848.

[9] Aramaki, K., Hackerman, N., J. Electrochem. Soc., 116 (1969) 568.

[10] Tang, L., Li, X., Li, L., Mu, G., Liu, G., Mater. Chem. Phys. 97 (2006) 301.

[11] Banerjee G & Malhotra S N, Corrosion, 48 (1992) 10.

[12] Hour T P & Holliday R D, J ApplChem, 3 (1953) 502.

[13] Riggs L O (Jr) & Hurd T J, Corrosion, 23 (1967) 252.

[14]Aljourani, J., Raeissi, K., Golozar, M.A., Corros. Sci. 51 (2009)1836.

[15]Amar, H., Tounsi, A., Makayssi, A., Derja, A., Benzakour, J., Outzourhit, A., Corros. Sci. 49 (2007) 2936.

[16]Migahed, M.A., Azzam, E.M.S., Morsy, S.M.I., Corros. Sci. 51 (2009) 1636.

[17]Moussa, M.N.H., El-Far, A.A., El-Shafei, A.A., Mater. Chem. Phys. 105 (2007) 105.

[18]Benabdellah, M., Touzan, R., Aouniti, A., Dafali, A.S., El-Kadiri, S., Hammouti, B., Benkaddour, M., Mater. Chem. Phys., 105 (2007) 373.

- [19]Bayol, E., Kayakirilmaz, K., Erbil, M., Mater. Chem. Phys. 104 (2007) 74.
- [20]Benalli, O., Larabi, L., Traisnel, M., Gengembra, L., Harek, Y., Appl. Surf. Sci. 253 (2007) 6130.
- [21]Hsu, C.S., Mansbitfeld, F., Corrosion 57 (2001) 747.
- [22]Epelboin, I., Keddam, M., Takenouti, H., J. Appl. Electrochem. 2 (1972) 71.
- [23]Mayer, B.J.C., Tuttner, K., lorenz, W. J., *Electrochim. Acta* 28 (1983)171.
- [24]Kus, E., Mansfeld, F., Corros. Sci. 48 (2006) 965.
- [25]GamryEchem Analyst Manual, (2003).