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Inhibitive, Adsorption Studies on Carbon Steel Corrosion in Acidic Solutions by New Synthesized Benzene Sulfonamide Derivatives

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The inhibitive action of some organic derivatives, namely (NN- azanediyl bis (ethane-2,1diyl))bis (4-dodecyibenzenesulfonamide), NN- ((ethane-1,2,diylbis (azanediyl)) bis (ethane-2,1-diyl)) bis(4-dodecylbenzenesulfonamide), NN-(((azanediylbis(ethane-2,1diyl))bis(azanediyle))bis(ethane-2,1-diyl))bis(4-dodecylbenzenesulfonamide),NN-(3,6,9,12-tetraazateradecane-1,14-diyl)bis(4-dodecyl benzene sulfonamide) against the corrosion of CS (CS) in 1M HCl solutions has been tested using gravimetric, (EIS) electrochemical spectroscopy impedance, Tafel polarisation, and (EFM) electrochemical modulation frequency methods. The protection efficiency rise with improving inhibitor doses and lower with temperature rising. Potentiodynamic method demonstrated that Benzene sulfonamide Derivatives play as mixed type inhibitors. The molecule adsorb on the surface of CS follow adsorption isotherm Temkin and was adherent on the molecular size and molecules centres which active. Quantum modelling was utilized to gain the electronic and structural effects are related to the efficiencies of inhibition. The data obtain showed improvement in efficiencies for inhibition with raising the dose of inhibitor. All methods employed were in reasonable agreement with protective efficiency values.

Keywords:CS corrosion, HCl, Benzene sulfonamide derivatives, EFM, EIS. Temkin isotherm

1. INTRODUCTION

Carbon steels are the most regularly utilized pipeline materials as a part of petroleum creation, a conductor in electrical by communication as power lines, microelectronic industries, conductors heater, and fabrication of exchanger's heat by its excellent thermal and electrical conductivities, affordable and its good workability mechanical [1-3]. Mineral acids, namely HCl is widely utilized to eliminating oxide films in many industrial such as oil well acidizing, acid cleaning and acid pickling. Acids are indirectly responsible for the failure of the materials. Inhibitors efficient for CS is organic heterocyclic compounds consisting N, S, O atoms and π-electrons in its molecules. It is observed that attendance of these heteroatom and functional groups in the organic structures increase its action as inhibitor for corrosion of CS due to they enable chemisorption's, such as amino acids, azoles , amines [4-14], derivatives from organic also special offer ability to inhibit corrosion of different metals in various acidic medium [15-22]. Derivatives of benzene sulfonamide have showed promising corrosion inhibition for CS properties in one molar hydrochloric acid media. On comparing the percentage protective efficiencies of these derivatives with previously reported % inhibition efficiencies of different organic derivatives in various acidic media, it was found that these Benzene sulfonamide derivatives of the present study could serve as effective on corrosion inhibition.

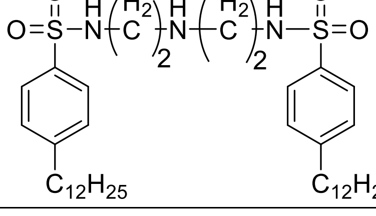
The purpose of this paper is to evaluate the corrosion inhibition behavior of novel Benzene sulfonamide derivatives in 1M HCl solution on CS at different temperatures and correlating these properties with their chemical structure. The study was performed by chemical and electrochemical analysis. The surface morphology was done utilized by (EDX) energy dispersive X-ray and scanning electron microscope (SEM).

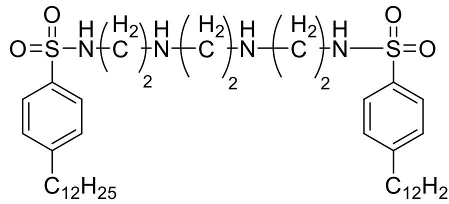
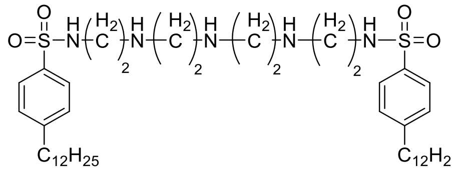
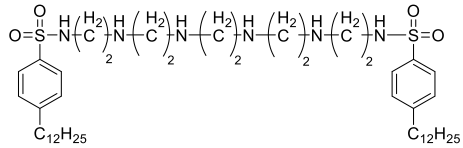
2. EXPERIMENTAL DETAIL

The composition of CS sample in weight %: 0.20 C, 0.35 Mn, 0.024 P, 0.003 Si, and balance Fe.

The test solution of 1 M hydrochloric acid (BDH grade) was prepared by diluting 37% analytical grade HCl with bi-distilled water. The investigated organic derivatives were synthesized according to the laboratory procedure reported previously [23]. The chemical structure and IUPAC names are given in Table (1).

Table 1. Chemical composition of benzene sulfonamide derivatives

inhibitors	Names, Molecular formula, Molecular weight	Structures
1	***N,N'*-(2,2'-azanediylbis(ethane-2,1-diyl))bis(4-dodecylbenzenesulfonamide)** Chemical Formula**:** $\mathbf{C_{40}H_{69}N_3O_4S_2}$ Exact Mass**: 719.47**	

2	***N,N'*-(2,2'-(ethane-1,2-diylbis(azanediyl))bis(ethane-2,1-diyl))bis(4-dodecylbenzenesulfonamide)** Chemical Formula**:** $\mathbf{C_{42}H_{74}N_4O_4S_2}$ Exact Mass**: 762.52**	
3	***N,N'*-(2,2'-(2,2'-azanediylbis(ethane-2,1-diyl)bis(azanediyl))bis(ethane-2,1-diyl))bis(4-dodecylbenzenesulfonamide)** Chemical Formula**:** $\mathbf{C_{44}H_{79}N_5O_4S_2}$ Exact Mass**: 805.56**	
4	***N,N'*-(3,6,9,12-tetraazatetradecane-1,14-diyl)bis(4-dodecylbenzenesulfonamide)** Chemical Formula**:** $\mathbf{C_{46}H_{84}N_6O_4S_2}$ Exact Mass**: 848.60**	

2.1. Techniques utilized for measurements

2.1.1. Mass reduction method

Coupons were obtain from carbon steel sheet with a composition (in weight %) of C 0.20, Mn 0.35, P 0.024, Si 0.003 and Fe is the rest. Specimens divided into 20.0 mm x 20.0 mm x 2 mm dimensions were utilized for mass reduction methods. All chemicals reagents were analytical-grade commercially available and utilized without further experiment. The mass loss method was done in a 100 ml glass beaker put in water thermostat. The coupon was putted in the solution test in presence and absence desired dose of the benzene sulfonamide derivatives. Triplicate Coupons were museum for same behaviors and the average mass reduction were obtained. The corrosion rate (υ) was measured using the following Eq.:

$$\upsilon = W/St \qquad (1)$$

where W is the average mass reduction of the three parallel CS coupons, S is the surface area of the CS coupons and t is the time of exposure. The protection efficiency IE_w% of tested compounds on the corrosion of CS was calculated using Eq. 2:

$$IE_w\% = (\upsilon_o - \upsilon) / \upsilon_o \times 100 \qquad (2)$$

Where υ_o and υ are the values of the corrosion rate without and with the inhibitor.

2.1.2. Tafel method

“Electrochemical technique were done in three electrodes thermostatic cell conventional assembly utilized a Gamry Galvanostat/ZRA/Potentiostat (model PCI 300/4),a sheet of platinum is a counter and saturated calomel electrode (SCE) were utilized as reference electrodes, the steel electrode was in the form of a cut square from CS electrode of size (1 x1 cm) and was welded by one side to a copper wire utilized for connection electrical, the C-steel electrode was abraded successively with different emery papers grades , rinsed with bi-distilled water and then degreased with $(CH_3)_2CO$”.

Electrochemical testes were done at 25^{o}C. The diagrams for potentiostatic were occurred from -5 to 5 V at a scan with rate 0.5 mVs^{-1} after reached to the steady state (30 minutes).

2.1.3. EIS measurements

The equivalent electrical circuit model utilized for this system where R_{ct} = charge transfer resistance, R = resistor and R_s=resistance of solution, and C_{dl} represents the double layer capacitance. Gamry applications contain software EIS300 for EIS measurement; computer was utilized for summation of data. Echem Analysis 5.5 software was utilized for fitting plotting, and graphing data.

2.1.4. EFM measurements

EFM can be utilized as a fast technique and nondestructive experimental for measure rate of corrosion technique without prior information of Tafel constants. EFM performed by utilized 2 frequencies (2.0 to 5.0 Hz). The time in this work which given steady state of the specimens was found half-hour, the Intermodulation spectra include current responses form corrosion density ($i_{corr.}$)and harmonical intermodulation peaks of current. The larger peaks were utilized to measure the current, the Tafel slopes (β_a and β_c) and the causality factors (CF2 & CF3) [24-25]. All the experiments were conducted at 25±1°C.

2.1.5. Surface morphology

The steel analysis had a scratching first with different emery papers grades and then dipped 12 hrs in one molar hydrochloric acid with and without optimum dose of investigated inhibitors. The coin's rinsed gently with water bi-distilled, dried and subjected to the examination of surface. “The morphology of surface experiments of the CS surface were performed by utilized (SEM)scanning electron microscopy into the spectrometer (pw-1390) Philips by (Cu kal, 1= 1.54051A°) tube of cupper, (EDX)Emission dispersive X -ray analysis Model HITACHI S-3000H and (SEM, JOEL, JSM-T20, Japan) a scanning electron microscope”.

2.1.6. Quantum chemical study

These four molecules have been fully optimized using B3LYP Density Function Theory formalism (DFT) with 6-31G (d,p) basis set using Gaussian-03 [26]. The following quantum chemical parameters were studied: Energy of the Highest Occupied Molecular Orbital (EHOMO), Energy of the Lowest Unoccupied Molecular Orbital (ELOMO), Energy gap between HOMO and LUMO (ΔE) and dipole moment (μ).

3. RESULTS AND DISCUSSION

3.1 EFM methods

EFM is a nondestructive and linear corrosion test method that can directly measure the current data of corrosion with only a littile polarizing signal and without earlier knowledge Tafel slopes, these EFM technique advantages lead to ideal technique for corrosion monitoring online [27], the best EFM strength is causality factors, which play as an internal check on the truth of the EFM method Fig. (1) given EFM spectra for CS with and without various dose of compound (1). Similar diagram were given for the rest investigated derivatives. The experimental EFM values were process utilized two different models: “complete diffusion control of the cathodic reaction and the activation model. For the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to the polarization of the working electrode” [26].The parameters of kinetic from EFM such as the (CF-2 and CF-3) causality factors, the(icorr) corrosion density current and (β_a and β_c) Tafel slopes are write in Table 2. The protection efficiency % IE increments by expanding the investigated concentrations of inhibitors. The causality factors CF-2 and CF-3 are near to their theoretical data, showing that the calculated data are quality good [25]. The inhibition efficiencies %IE and was calculated from Eq. 3:

$$\% \, IE_{EFM} = [1-(i_{corr} / i^{o}_{corr})] \times 100 \qquad (3)$$

Where i^{o}_{corr} and i_{corr} = corrosion current densities without and with benzene sulfonamide derivatives, respectively. The protective efficiency given from this experimental is in the order: (4) > (3) > (2) > (1)

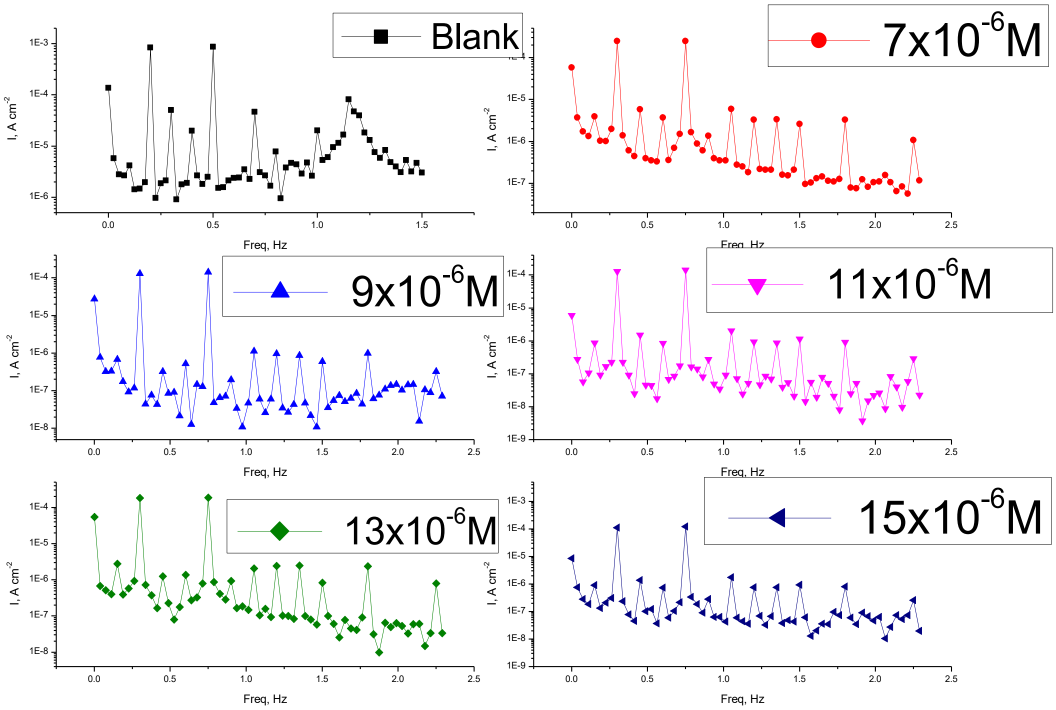


Figure1. EFM spectra for CS in 1 M HCl with and without doses of compound (4)

Table 2. Parameters form electrochemical kinetic obtained by EFM method for CS in 1M HCl with and without doses of investigated compounds

Comp	Conc., x10^6M	i_{corr} μA cm^{-2}	β_c mV dec^{-1}	β_a mV dec^{-1}	CF-2	CF-3	CR mpy	θ	IE_{EFM} %
	Blank	1231	81	112	2.4	5.1	562.0	---	---
(4)	7	248.0	129	108	1.889	2.856	113.7	0.798	79.8
	9	211.0	214	140	1.932	3.635	96.55	0.828	82.8
	11	203.5	131	111	1.830	3.264	93.00	0.835	83.5
	13	185.3	153	125	1.90	3.057	84.65	0.849	84.9
	15	174.3	118	114	1.083	3.663	97.73	0.858	85.8
(3)	7	289.1	122	101	1.930	3.320	132.1	0.765	76.5
	9	232.6	121	103	1.846	3.080	106.3	0.811	81.1
	11	224.4	126	106	1.945	2.982	102.5	0.817	81.7
	13	208.1	118	110	1.583	2.836	95.09	0.831	83.1
	15	204.7	127	121	1.494	3.61	67.93	0.834	83.4
(2)	7	348.1	135	147	1.865	2.982	159.1	0.717	71.7
	9	318.9	111	118	1.528	3.510	145.7	0.741	74.1
	11	317.4	133	135	1.573	2.582	145	0.742	74.2
	13	283.2	166	174	1.882	3.631	129.4	0.770	77
	15	238.1	113	127	1.572	3.539	108	0.806	80.6
(1)	7	375.1	92	106	1.8	2.8	124.5	0.695	69.5
	9	304.9	148	141	1.292	3.366	101.2	0.752	75.2
	11	295.4	150	134	1.779	3.187	98.05	0.759	75.9
	13	283.7	102	96	1.497	2.923	94.15	0.769	76.9
	15	250.4	147	131	1.867	2.990	83.09	0.796	79.6

3.2 EIS measurements

EIS is powerful and well-established test in the process of corrosion. Mechanistic information, surface properties and kinetics electrode can be given from impedance curves [28-32]. Figure (2) illustrate the (a) Nyquist and (b) Bode plots given from open-circuit potential without and with improving dose of benzene sulfonamide derivatives at room temperature. The rise in the size of the loop capacitive with the appending of benzene sulfonamide derivatives lead to a barrier gradually forms on the surface of CS. The improving in the size of loop capacitive (Figure 2a) related to a fixed inhibitor dose, obeyed the order: (4) > (3) > (2)> (1), affirmation the upper inhibitive influence of (4). Bode curves (Figure 2b), given the summation of impedance rise with improving benzene sulfonamide derivatives dose (log Z against log f). But (log f against phase), also Bode curve lead to the permanent rise in the shift angle phase, obviously relation with the higher of adsorbed benzene sulfonamide derivatives inhibitor on surface of CS. The Nyquist data not give semicircles perfect as anticipating from the theory of EIS. The variation from ideal semicircle was generally lead to the dispersion of frequency [33] EIS spectra of the benzene sulfonamide derivatives appending were measure utilized the circuit equivalent, Figure (3), which represents a single charge transfer reaction and fits well with our experimental data [34]. C_{dl}, for a circuit containing a CPE parameter (Y_0 and n) were measured from equation 4 [35]:

$$C_{dl} = Y_0\omega^{n-1}/ \sin [n (\pi/2)] \qquad (4)$$

whereY_0 = magnitude of the CPE, $\omega = 2\pi f_{max}$, f_{max} = the frequency at which the imaginary component of the impedance is maximal. After experimental the Nyquist curves for corrosion process was mainly controlled on charged-transfer [36, 37].

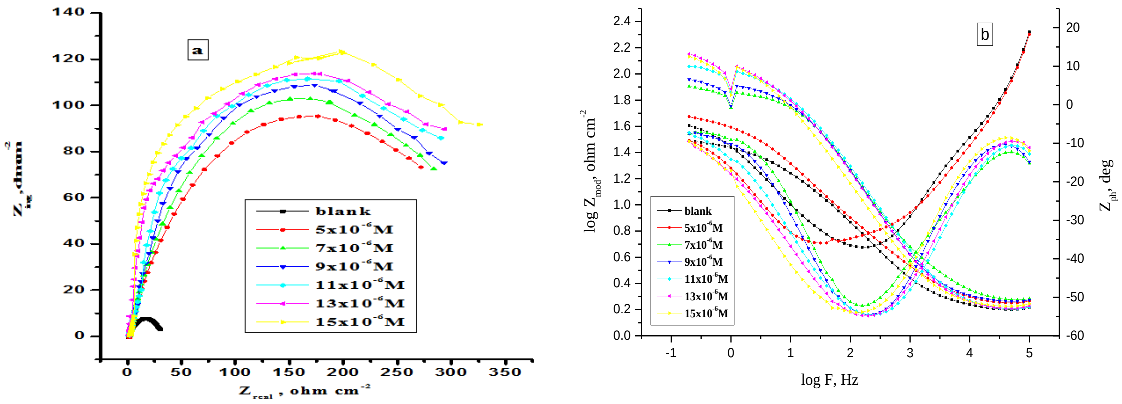


Figure 2. EIS diagrams Nyquist plots (a) and Bode plots (b) for CS in 1 M HCl without and with various dose of compound (4)

EIS data in (Table 3) show that the R_{ct} data rise and the C_{dl} data lower with raise the inhibitor concentrations. This is due to the gradual water molecules replacement by the adsorption of the molecules of benzene sulfonamide derivatives inhibitor on the CS surface, lowering the extent of dissolution reaction. The rise R_{ct} data, are generally, combine with lower corroding system [38]. The lower in the C_{dl} can obtained from the low of the local dielectric constant and/or from the rise of electrical double layer thickness [39,40], suggested that the benzene sulfonamide derivatives inhibitor molecules function by adsorption at the solution/metal interface. The inhibition efficiency was measured from equation 5 [41]:

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

R^{o}_{ct} and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor, respectively. The order of % E of the investigated polymers is the same as in Tafel polarization (4 > 3 > 2 >1).

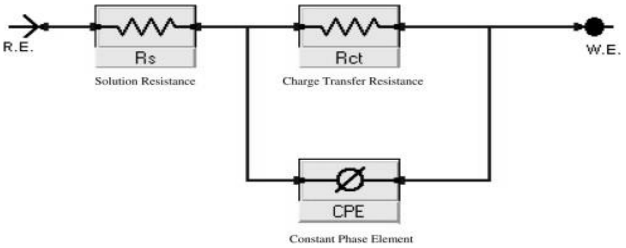


Figure 3. Equivalent circuit model utilized to fit data spectra

Table 3. EIS data given from EIS technique for CS in 1M HCl without and with varios doses of investigated compounds

Comp.	Conc., 10^6 M	R_S, Ωcm^2	Y, x 10^{-3} $\mu\Omega^{-1} s^n cm^{-2}$	n	R_{ct}, $\Omega\ cm^2$	C_{dl}, $\mu F\ cm^{-2}$	θ	IE %
Blank	Blank	1.501	2.602	0.624	29.76	14.24	----	-------
4	5	1.790	534.0	0.743	289.1	46964.4	0.897	89.7
	7	1.855	652.3	0.727	300	85582.7	0.900	90.0
	9	1.645	559.2	0.707	303.5	22313.08	0.901	90.1
	11	1.660	707.8	0.714	307.7	31048.54	0.903	90.3
	13	1.627	705.4	0.676	319.1	26205.81	0.906	90.6
	15	1.877	568.4	0.709	346.5	95934.2	0.914	91.4
3	5	1.887	954.4	0.679	200.5	10151.25	0.851	85.1
	7	1.599	827.4	0.734	203.9	20001.21	85.4	85.4
	9	1.601	830.7	0.718	213.2	20847.08	0.860	86.0
	11	1.661	396.9	0.746	235.2	14662.27	0.873	87.3
	13	1.559	466.1	0.749	285	10389.02	0.884	88.4
	15	1.808	544.9	0.721	284.1	525326.4	0.895	89.5
2	5	1.629	847.6	0.699	141.3	19082.28	0.800	80.0
	7	1.626	985.0	0.687	148.9	22577.11	0.810	81.0
	9	1.884	926.1	0.747	157.2	81060.62	0.825	825
	11	1.956	1011	0.659	170.2	137.2614	0.833	83.3
	13	1.878	553.4	0.724	178.9	52581.27	0.838	83.8
	15	1.725	752.6	0.701	184.3	33042.29	0.789	78.9
1	5	1,650	3.601	0.565	52.57	47.300	0.433	43.3
	7	1.774	5.028	714.2	75.31	142.58	0.604	60.4
	9	1.720	413.9	752.8	81.24	9813.521	0.634	63.4
	11	1.450	488.9	718.7	108.4	4027.016	0.725	72.5
	13	1.457	601.3	706.9	125.7	5476.303	0.763	76.3
	15	1.535	764.6	704.8	127.0	10208.67	0.789	78.9

3.3. Tafel polarization measurements

The effect of investigated derivatives on the reactions by corrosion was investigated by polarization method. The changes measured in the polarization plots after the appending of the benzene sulfonamide derivatives inhibitor are usually utilized as the criteria to classify inhibitors as cathodic, anodic or mixed [42-44]. Figure 4 shows the Tafel polarization plots for CS for various dose of benzene sulfonamide (4) at 25ºC. Same plots were given for other benzene sulfonamide derivatives but not shown. This Figure shows that the cathodic curves give approximately parallel lines, suggesting that the hydrogen discharge reaction lowers, its activation being controlled [45] by organic addition in aggressive medium. The kinetic parameters for example corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c and β_a), corrosion current density (i_{corr}), and inhibition efficiency values (%IE_p) were obtained from Tafel plots and are tabulated in Table 4. The results showed that the addition of these additives at all the studied concentrations resulted in: i) a decrease in the corrosion rate and hence a decrease in the current density (i_{corr}) ii) An improvement on the coverage surface and hence an rise in the % IE_p. There was no observed shift in the corrosion potential (E_{corr}) data with respect to the blank. The inhibition efficiency was measured utilized equation 4:

$$\%IE_p = [(i^o_{corr} - i_{corr}) / i^o_{corr}] \times 100 \quad (4)$$

Where i^o_{corr} and i_{corr} = current corrosion densities without and with benzene sulfonamide derivatives inhibitors, respectively.

From Table (4) that the slopes of the (β_c) cathodic and (β_a) anodic Tafel lines contain almost unchanged upon appending of organic derivatives, giving improving to a nearly parallel set of anodic lines, and almost parallel cathodic plots results too. Thus the adsorbed benzene sulfonamide derivatives inhibitors play by simple blocking active sites for both cathodic and anodic method.

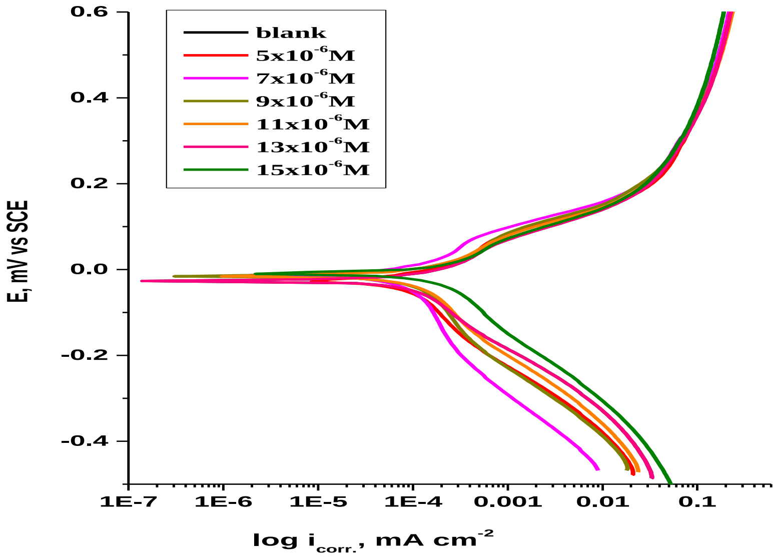


Figure 4. Polarization diagrams for CS without and with various dose of inhibitor (4).

Table 4. Kinetic parameters of CS in the presence and absence of various doses of studied compounds

Conc., x10^6 M		$i_{corr.}$ mA cm^{-2}	-$E_{corr.}$ mV vs SCE	β_a mV dec^{-1}	β_c mV dec^{-1}	θ	IE_p (%)
1M HCl		9.60	268	82	167	---	---
4	5	1.3	261	90	339	0.865	86.5
	7	1.28	231	128	477	0.867	86.7

	9	1.2	255	96	266	0.875	87.5
	11	1.1	246	103	347	0.885	88.5
	13	1.07	268	95	130	0.889	88.9
	15	1.03	203	81	129	0.893	89.3
3	5	1.77	209	93	163	0.816	81.6
	7	1.61	221	84	283	0.832	83.2
	9	1.66	240	52	100	0.827	82.7
	11	1.55	278	99	65	0.839	83.9
	13	1.4	691	44	73	0.854	85.4
	15	1.37	233	110.9	343	0.857	85.7
2	5	3.9	638	96	192	0.594	59.4
	7	3.89	263	129	313	0.595	59.5
	9	3.27	367	117	198	0.659	65.9
	11	3.21	566	65	100	0.666	66.6
	13	2.3	648	101	209	0.760	76.0
	15	2.21	952	111	184	0.770	77.0
1	5	4.97	287	149	247	0.482	48.2
	7	4.48	235	153	227	0.533	53.3
	9	4.33	222	96	175	0.548	54.8
	11	4.27	319	110	267	0.555	55.5

The adsorbedbenzene sulfonamide derivatives inhibitors lower the area of surface for corrosion without impressive the mechanism of corrosion on CS in 1M HCl solution, and only reason inactivation of a part of the surface with respect to the corrosive process [46,47].

The efficiency of inhibition of these organic inhibitors follows the sequence: (4) > (3) > (2) > (1). The improved ability of compound (4) to inhibit corrosion of CS in acid medium compared to benzene sulfonamide (1). This is clearly showed from the biggest efficiency given form benzene sulfonamide (4).

3.4. Mass reduction method

The mass reduction of CS in one malar HCl is nearly different linearly with flooding period without and with different dose of the four tested benzene sulfonamide derivatives compounds at 303 K, Same diagrams was given for each inhibitor. The linearity of the time with mass reduction from the starting was illustrated by El-Hosary et al [48] as the breakdown of the oxide film at the first of the attack (not shown)**.** As shown in Figure (5), the effect of time flooding (2 days) against rate of corrosion, R_{corr}, (mg cm^{-2} h^{-1}) without and with different optimum dose of the benzene sulfonamide derivatives inhibitors tested. The data draw give the dissolution of CS improved by time and arrive to maximum data at two days and the appending of benzene sulfonamide derivatives inhibitors limits the dissolution of CS by blocking its sites of CS corrosion and hence lowering the mass reduction and hence the rate of corrosion in comparison with the without of them, the mass reduction (W) data are listed in Table (5). IE_w % is measured according to equation 5:

$$IE_w \% = 100 \text{ x } [1- (C.R_{corr}/ C.R°_{corr})] \qquad (5)$$

$C.R^{\circ}_{corr}$ = corrosion rates without benzene sulfonamide derivatives inhibitor, $C.R_{corr}$ = corrosion rates with benzene sulfonamide derivatives inhibitor. The ($\%IE_w$) of the organic inhibitor derivatives obeyed the sequence: (4) > (3) > (2) > (1).The same manner was record [49, 50] the rate of corrosion lower until stable lead to a formation of the film protect on the CS surface.

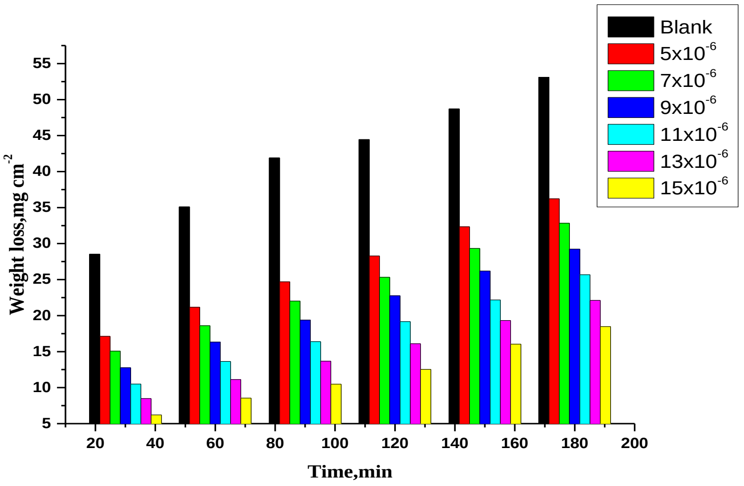


Figure 5. Time mass reduction diagrams for the dissolving of CS without and with various dose of compound (4) at 30°C

Table 5. Variation of %IE of various compounds with different temperature at 13x10^{-6}M from mass reduction measure in 1 M HCl.

Comp.	Temp., °C	C.R. mg cm^{-2} min^{-1}	% IE
Blank	1 M	0.549	98.88
4	30	0.13	63.78
	35	0.17	51.64
	40	0.20	44.30
	45	0.22	38.37
	50	0.23	37.58
3	30	0.13	62.48
	35	0.16	55.17
	40	0.21	40.04
	45	0.22	39.35
	50	0.23	36.03
2	30	0.32	52.01
	35	0.41	42.6
	40	0.43	42.7
	45	0.46	38.53
	50	0.47	38.47
1	30	0.16	43.34
	35	0.17	41.25
	40	0.18	36.66
	45	0.19	31.02
	50	0.20	24.11

The protective efficiencies, measured from EIS, EFM given the same behavior as those given from polarization tafel and mass reduction calculation. Various on protective efficiency from the four technique may be adherent to the surface status various by the electrode in the four method. Due to the various between the area of electrode actually undergoing polarization and the total area [51].

3.5. Kinetic results

The temperature effect on the corrosion rate of steel in acid with various concentrations from organic was measure by mass reduction tests at temperature different. The raising temperature effect on the rate of corrosion and %IE was done by utilized mass reduction tests. The results showed that, by raising the temperature the rate of corrosion rises. The value of the Arrhenius activation energy (E_a^*) can be obtained from (Figure 6), The Arrhenius- equation is:

$$C.R = A \exp(-E_a^* / RT) \tag{7}$$

Where T = the absolute temperature, A = the Arrhenius constant, k = the rate of corrosionand R = the universal gas constant. The energy of activation for the CS corrosion in 1 M HCl was given to be 32 kJ mol^{-1} which is in best agreement with the data obtain by Fouda et al [58] and others [53-54] the transition state were given from equation 8 [55]:

$$C.R = R\,T / N\,h\, e^{(\Delta S^*/ R)} e^{(-\Delta H^* / R\,T)} \tag{8}$$

The draw between 1/T against log k/T lead to lines straight, from its intercept and slope, ΔS^* and ΔH^* can be computed, respectively (Figure 7). Table 6 exhibits the activation parameters data for dissolution of steel in one molar hydrochloric acid solution.

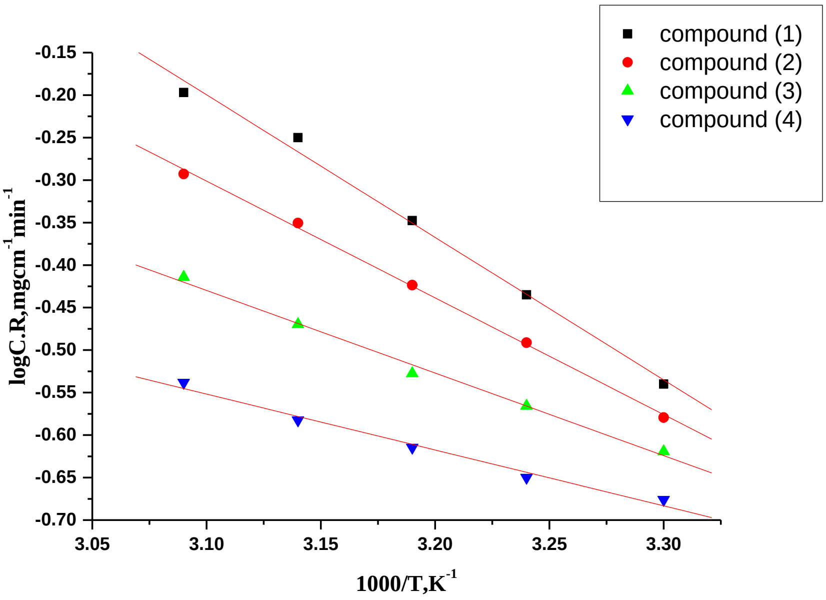


Figure 6. 1/T against log k, for CS corrosion in 1M HCl in the without and with different doses of compounds

Table 6. Kinetic parameters for the dissolution of CS in 1 M HCl without and with various doses of investigated inhibitors

Compounds	$-E_a^*$ kJ mol^{-1}	ΔH_a^* kJ mol^{-1}	$-\Delta S_a^*$ J mol^{-1} K^{-1}
(4)	9.0	3.74	94.9
(3)	5.8	6.81	70.8
(2)	5.7	10.5	41.5
(1)	5.2	13.2	20.4

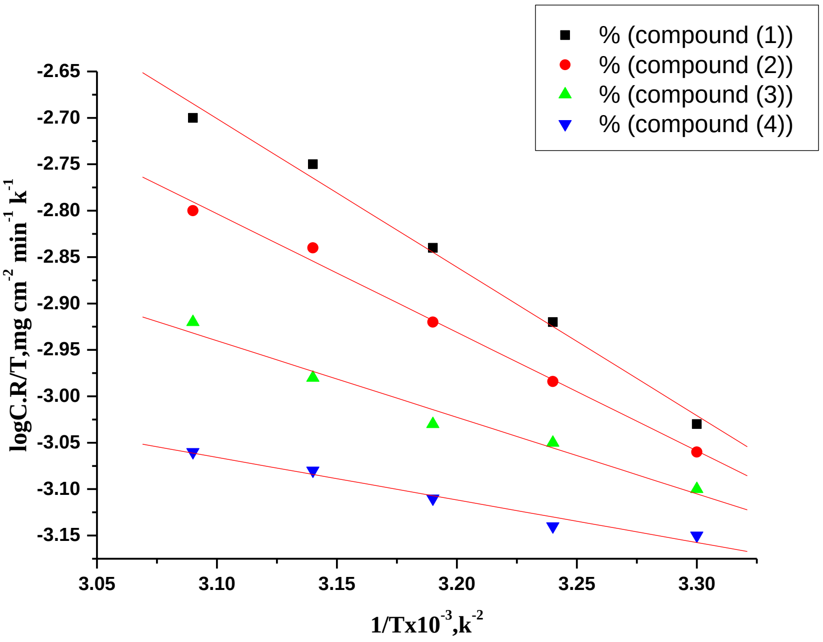


Figure 7. Plots of (log k/T) vs.1/T for corrosion of CS in 1 M HCl without and with various doses of investigated inhibitors

It is clear that the E^*_a data with organic inhibitors is upper than that in its absence. “The higher data of E^*_a with organic inhibitors lead to adsorption physical or lower chemical bonding between the C-steel surface and molecules of inhibitors ,accordingly the increment data of E^*_a lead to the lower rate of corrosion, therefor the lower in rate of corrosion is mostly decided by the apparent activation energy, this is due to the a film formation on the surface of carbon steel act as an energy barrier for the corrosion of carbon steel, enthalpy and entropy of activation (ΔH^*, ΔS^*) of the corrosion process were calculated from the theory of transition state, maximum and -ve ΔS^* signs imply that the activated complex in the rate-determining step represents an association rather than dissociation step which given that lower in disordering carried out on going from reactants to the activated complex, the +ve ΔH^*signs of reflect the nature endothermic of the metal dissolution process” [56-57].

3.6. Adsorption isotherms

Adsorption isotherms were utilized to express the inhibitors adsorbed on the metal surfaces quantitatively. Corrosion protection of metal in one molar hydrochloric acid by surfactant is commonly due to the surfactant adsorbed on metal surface. The corrosion protection mechanism may be expounding on the basis of inhibitor adsorption behavior. The (θ) of CS electrode by adsorption of organic was measured utilized the following equation:

$$\Theta = [1 - (R_{corr} / R^{o}_{corr})] \qquad (9)$$

R and R^{o} were defined before. The data of (θ) for various doses of the studied of benzene sulfonamide derivatives inhibitor at 30°C have been utilized to illustrated the good isotherm to measure the process adsorption. The adsorption of the of benzene sulfonamide derivatives inhibitor, on the electrode of CS surface may regarded as a replacement adsorption process between water molecules adsorbed on surface of CS and (H_2O_{ads}) and benzene sulfonamide derivatives in aqueous phase (org_{aq}) [57]:

$$Org_{(sol)} + x\,(H_2O)_{ads} \leftrightarrow x\,H_2O_{(\,sol\,)} + (Org_{(ads)} \quad 10)$$

where x = water molecules number which replacement by organic molecule. Attempts were done to fit (θ) data to different isotherms, contain Temkin, Frumkin, and Langmuir [58: 61]. In this work, adsorption Temkin isotherm was given the best data findings. This isotherm is illustrated by equation (10).

$$2\,a\,\Theta = \ln (C\,K_{ads}) \qquad (11)$$

where a = factor heterogeneous of surface of metal, C = dose of benzene sulfonamide derivatives inhibitor and K_{ads} = constant adsorption equilibrium. Equilibrium constant (K_{ads}.) of adsorption process given utilized (11) could be further utilized to measured (ΔG^{o}_{ads}) as follows:

$$\Delta G^{o}_{ads} = - RT \ln (55.5\,K_{ads}) \qquad (12)$$

From these data the higher efficient inhibitor has higher –ve ΔG°_{ads} data, so the order of protective efficiency (4) > (3) > (2) > (1). Values of K_{ads} and ΔG^{o}_{ads} for of benzene sulfonamide derivatives inhibitors are record in Table (9). The higher -ve data of ΔG^{o}_{ads} lead to these of benzene sulfonamide derivatives are chemisorption on CS surface. The -ve sign ensures that adsorption spontaneity for process. The data of K_{ads} were obtain to parallel run to the % IE [$K_{(4)} > K_{(3)} > K_{(2)} > K_{(1)}$].

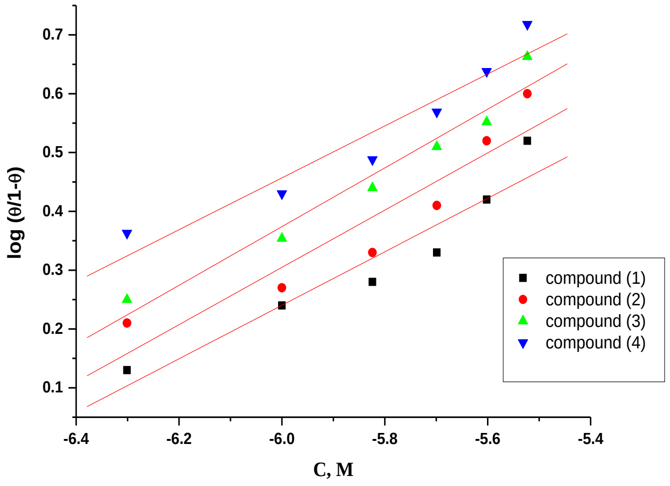


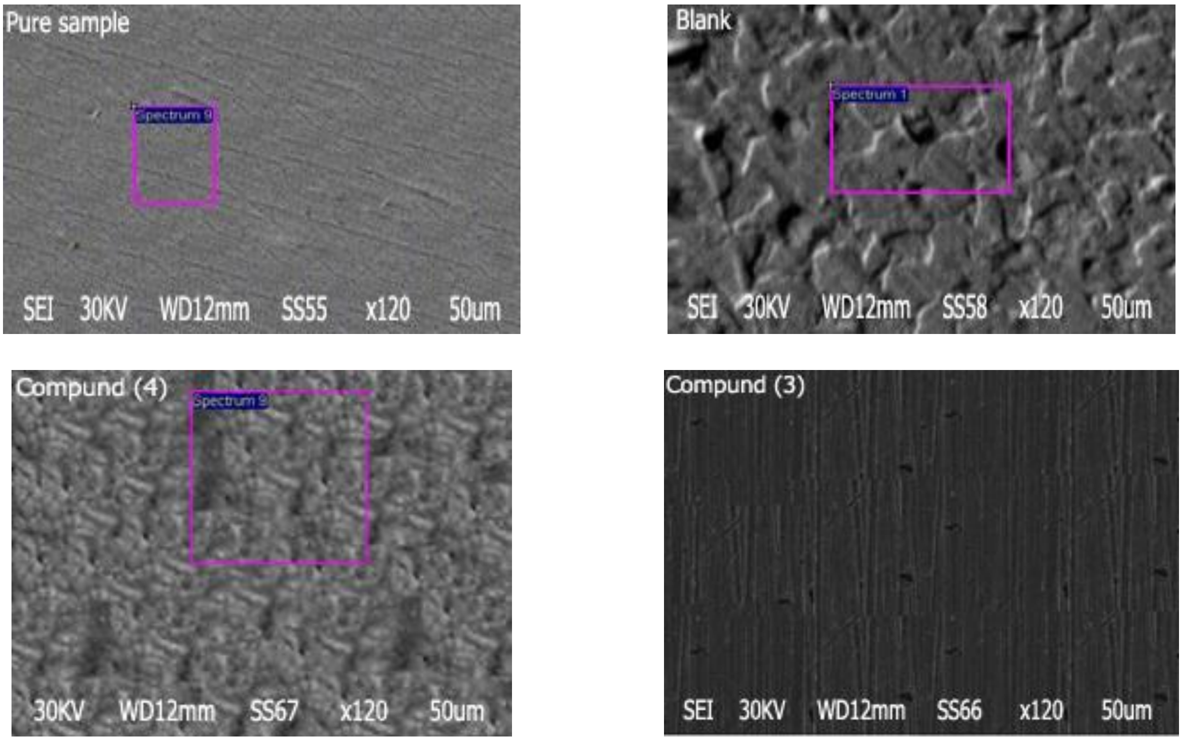
Figure 8. Curve fitting of corrosion resulted for CS with various dose of benzene sulfonamide derivatives inhibitor to isotherm kinetic adsorption at 30°C

Table 7. kinetic adsorption isotherm parameter for the of benzene sulfonamide derivatives after 120 min

compound	Kinetic model		
	1 / y	K_{ads} x 10^{-4} M^{-1}	$-\Delta G°_{ads}$ kJ mol^{-1}
(4)	1.254	80.35	44.35
(3)	1.078	55.59	43.42
(2)	1.025	42.65	42.74
(1)	0.98	29.64	41.84

3.7. SEM and EDX test

In order to see whether the benzene sulfonamide derivatives molecules are adsorbed on the CS or not, both SEM and EDX test were measured. The scanning electron microscopies of CS before and after corrosion are shown in Fig.10. These images give a comparison about the surface microstructures on CS before corrosion and after corrosion in 1 M HCl without and with of 15 x 10^{-6} M inhibitors. The SEM results show that the addition of inhibitors to HCl has significant effect on the morphology of CS. The formation of film which improvement in the surface morphology of CS and protective was given by SEM measurement



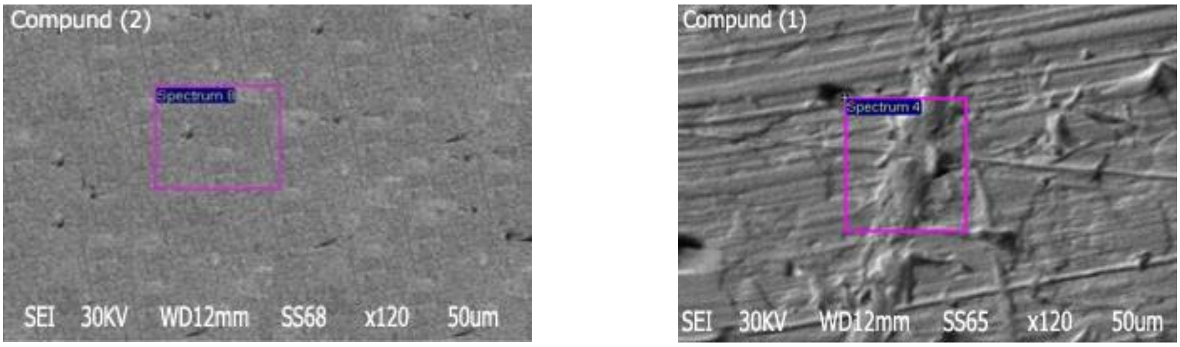
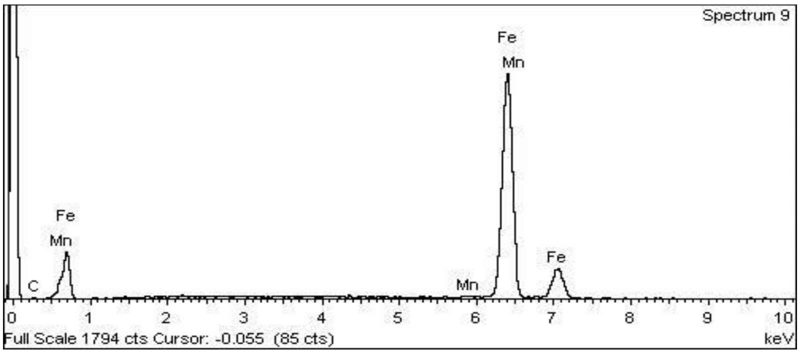


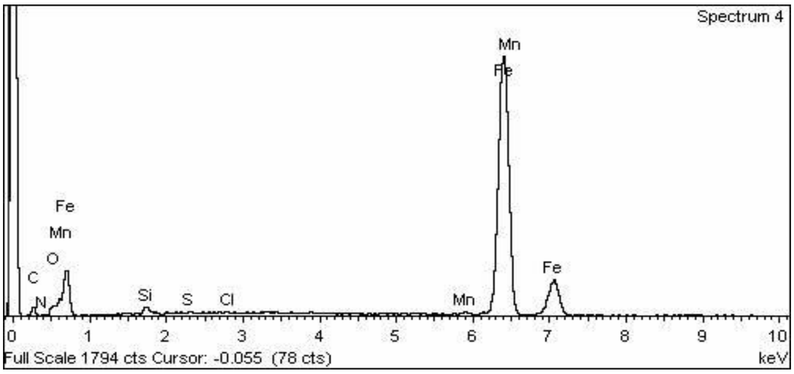
Figure 10. Micrographs SEM for CS without and with 15x10^{-6}M of organic investigated inhibitors.

The EDX spectra were utilized to calculated the elements present on the of CS surface. Figure (11) shows EDX spectra of the CS surface. “It is important to notice the existence of the nitrogen and carbon atoms in the EDX spectra of the CS corresponding to solutions containing the 15x10^{-6} M of the benzene sulfonamide derivatives; this indicates that the benzene sulfonamide derivatives are adsorbed on the surface of CS.

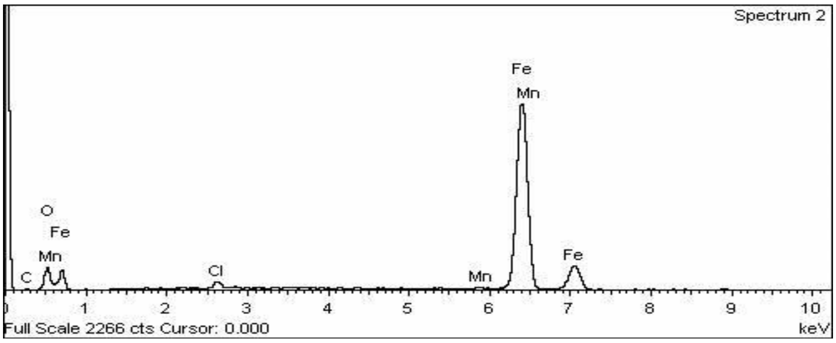
Free sample



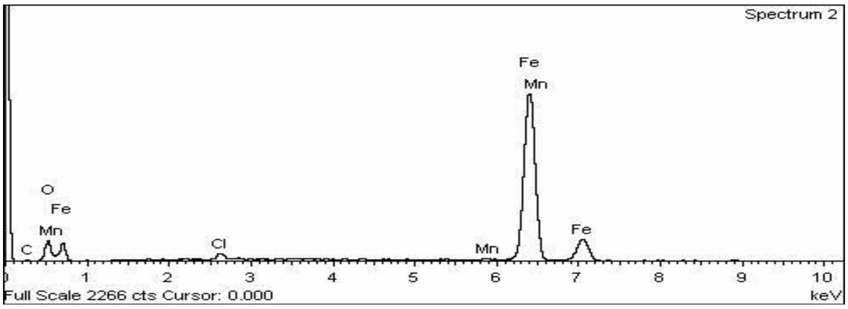
Blank



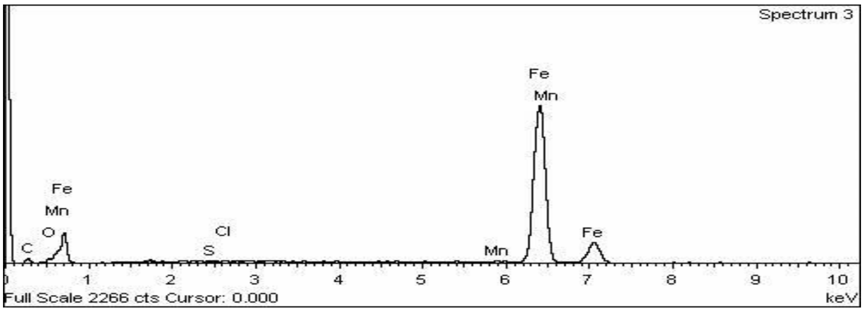
Compound 4



Compound 3



Compound2



Compound 1

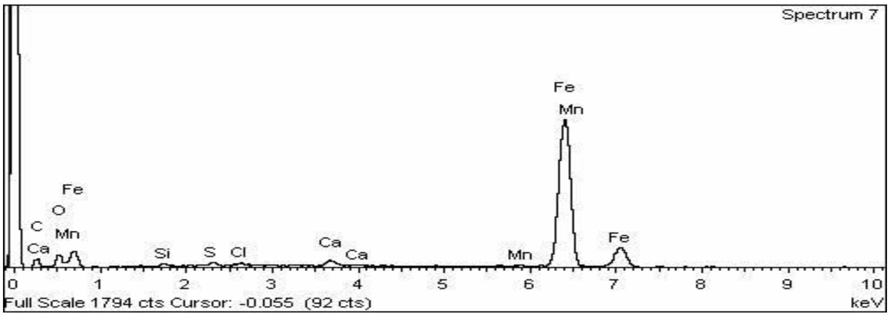


Figure 11.EDX analysis on CS without and with benzene sulfonamide derivatives inhibitor for 3 days immersion

Table 8. Composition of surface (weight %) of CS after three day without and with the optimum dose of the benzene sulfonamide derivatives inhibitor

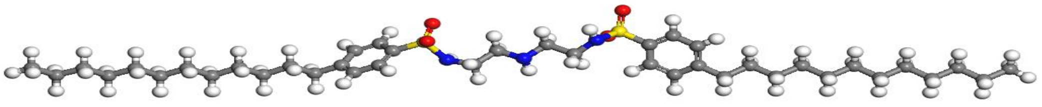
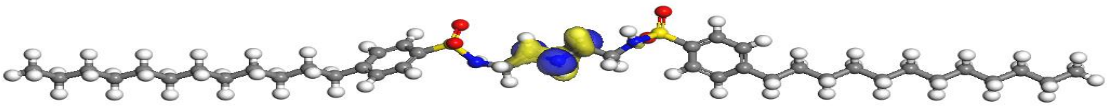
Mass %	Fe	Mn	C	O	N	S	P
Pure sample	98.16	0.64	1.13	--	--	0.03	0.04
Blank	66.71	0.60	1.12	30.33	1.18	0.02	0.04
4	52.23	0.59	25.14	14.21	8.81	0.03	0.03
3	60.83	0.52	19.32	12.13	7.11	0.04	0.05
2	62.51	0.63	16.88	10.21	9.71	0.04	0.02
1	66.49	0.54	14.56	16.34	5.86	0.18	0.06

3.8. Quantum chemistry method

All quantum parameters are recorded in Table (9) for the four investigated compounds in their neutral forms. The optimized geometries (with Mulliken charges), HOMO and LUMO distribution of investigated compounds in their non-protonated form are shown in Fig.12 So, higher the HOMO energy, more possible the electrons can be donated by the benzene sulfonamide derivatives to the unoccupied d-orbitals of the CS. However, lower the LUMO energy; more easily benzene sulfonamide derivatives molecule can accept electrons from the CS. Consequently, the data of energy gap, $\Delta E = E_{LUMO} - E_{HOMO}$, i.e. the decrease its data, improvement of the inhibition efficiency. The dipole moment (μ) is also an important parameter [25]. The E_{HOMO} data is in the order: 4 > 3 > 2 > 1, which is due to the find of donor electron of the Nitrogen atom in the molecule framework of compound (4). So, compound (4) has higher electron-donating tendency. Also, the value of E_{LUMO} is deacrease in case of compound (4). The value of ΔE is lower in case of compound (4), which further supports its more inclination to adsorb onto the Cs surface. This is in best agreement with the experimentally resultes.

Table 9. Quantum chemical parameters of investigated compounds

Inhibitor	μ	$-E_{HOMO}$	$-E_{LUMO}$	ΔE
(1)	**14.237**	**9.781**	**0.811**	**8.970**
(2)	**10.601**	**9.592**	**0.723**	**8.769**
(3)	**9.013**	**9.528**	**0.845**	**8.683**
(4)	**8.891**	**9.509**	**0.89**	**8.619**

Compound 1	
Mulliken charge	
HOMO	

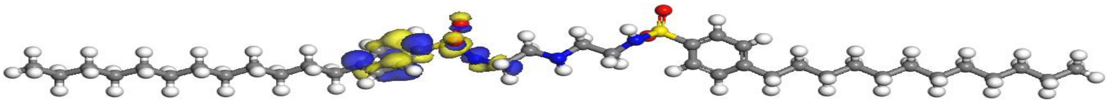
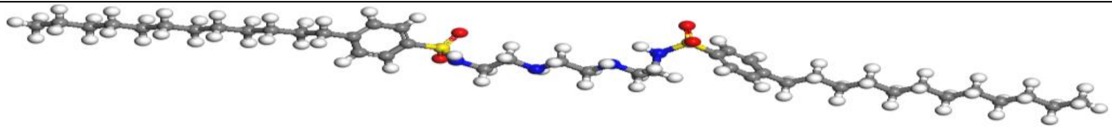
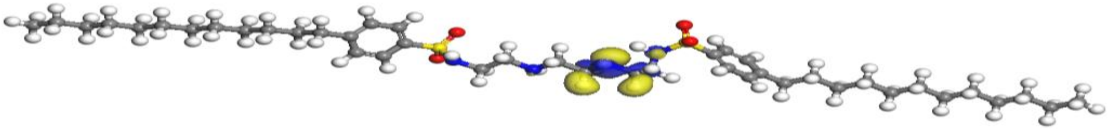
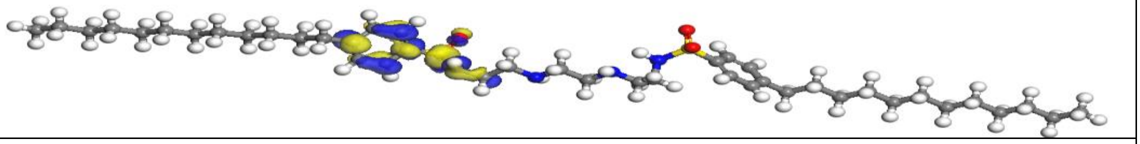
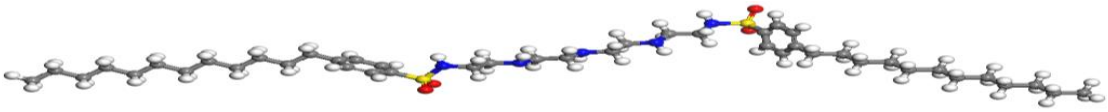
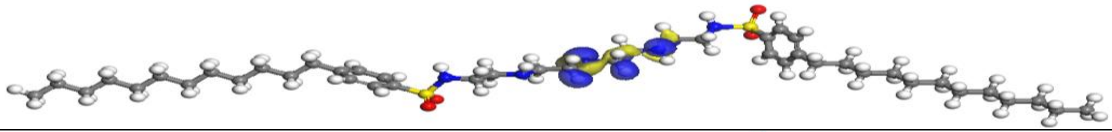
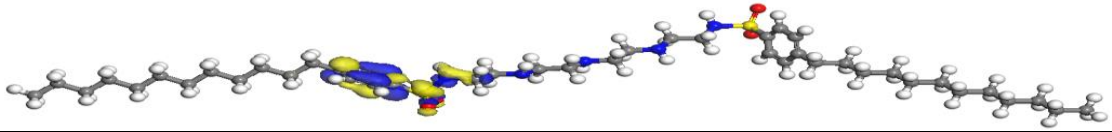
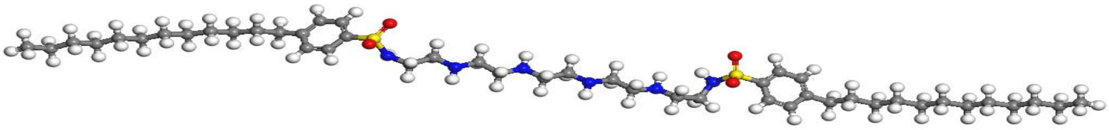
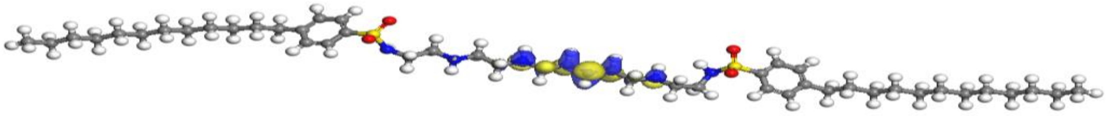
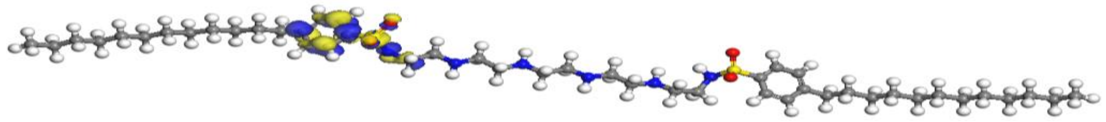
LUMO	
Compound 2	
Mulliken charge	
HOMO	
LUMO	
Compound 3	
Mulliken charge	
HOMO	
LUMO	
Compound 4	
Mulliken charge	
HOMO	
LUMO	

Figure 11. Optimized Mulliken charge, HOMO and LUMO.

3.9. Mechanism of Inhibition

The inhibition efficiency from chemical and electrochremical experimental depends on dose, nature of CS, the kind of adsorption and surface morphology, the number of adsorption of benzene sulfonamide derivatives inhibitor on active centers in CS and their density of charge. Transfer electrons of lone pairs on the nitrogen atoms to the CS surface to form a coordinate kind of linkage are best by the found a vacant orbital in iron atom of slow energy. Polar characters of substituents in the changing part of the inhibitor molecule have important effect on the electron charge density of the molecule. It was observed that the type of adsorption due to the affinity of the CS towards the π-electron clouds of the ring system. Metals such as C and Fe which have a higher affinity towards aromatic moieties were obtain to adsorb benzene rings in a flat orientation. The order of lowering the IE% of the benzene sulfonamide derivatives inhibitor in the corrosive solution was as follows: 4 > 3 >2 > 1. Inhibitor (4) is good power because: (i) it has higher molecular size (848) that may easily best surface coverage and bigest molecular area (ii) its adsorption through 12 active centers (4-O, 6-N and 2-S atoms). Compound (3) the second inhibitor because it has lower in active centers(4-O, 5-N and 2-S atoms) and molecular size(805), compound (2) third in inhibition efficiency due to, it has lesser molecular size (762) and also has lesser active centers (4-O, 4-N and 2-S atoms. Compound (1) is the least one in inhibition efficiency, this due to lesser molecular size (719) and lesser active centers (4-O, 3-N and 2-S atoms).

4. CONCLUSIONS

All the benzene sulfonamide derivatives inhibitors are good corrosion inhibitors for CS in 1 M HCL solution. The chang in IE% depends on the nature and kind of the substituent found in the molecule. The data obtain from EIS illustrate that the rise in the charge transfer resistance, a lower in double layer capacitances and hence improvement in % IE. Results given from potentiodynamic polarization lead to the inhibitor act as mixed-type. The inhibitors are adsorbed on CS surface follow the Temkin isotherm. SEM-EDX images results with benzene sulfonamide derivatives inhibitors due to the formation of thin film on the surface of CS. The orders of % IE of these inhibitors are: (4) > (3) > (2) > (1).

References

1. G. Kane Jennings, P.E. Laibins, *Colloids and Surfaces A*:, 116 (1996) 105.
2. H.Y. Ma, C.Yang, B.S.Yin, G.Y.Li, S.H.Chen, J.L.Luo, *Appl.Surf.Sci.*, 218 (2003) 143.
3. 3- E.I.Sayed and M.Sherif, *Appl.Surf.Sci,* 252 (2006) 8615.
4. E.M.Sherif, Su-Moon Park, *Corros.Sci.*, 48 (2006) 4065.
5. E.Szocs, Gy. Vastag, A. Shabanand E. Kalman, *Corros.Sci.*, 47 (2005) 893.
6. R.Subramanian, V.Lakshminarayanan, *Corros.Sci*., 44 (2002) 535.
7. S.Ramesh and S.Rajeswari, *Corros.Sci.*, 47 (2005) 151.
8. M.M.El-Naggar, *Corros.Sci.*, 42 (2002) 773.
9. Da-quanZhong ,Li-xinGao, Guo-ding Zhou, *Corros.Sci*., 46 (2004)3031.
10. J.Baartly, N.Huynh, S.E.Bottle, H.Flitt, T.Notoya, and D.P.Schweinsberg, *Corros.Sci.*, 45 (2003) 81
11. S. Muralidharan, S.V.K. Iyer, *Anti-Corros.Meth.Mater*., 44 (1997) 100.
12. M.A. Quraishi, M.A.W. Khan, M. Ajmal, *Anti-Corros.Meth.Mater.*, 43 (1996) 5.
13. Bentiss, M. Traisnel, M. Lagrenee, *J. Appl. Electrochem*., 31 (2001) 41.
14. M. Sahin, S. Bilgic, *Anti-Corros.Meth.Mater*., 50 (2003) 34.
15. L. Larabi, Y. Harek, M. Traisnel, A. Mansri, *J. Appl. Electrochem*.,34 (2004) 833.
16. K. Aramaki, M. Hagiwara, H. Nishihara, *Corros. Sci*., 27 (1987) 487.

17. K. Aramaki, *Corros. Sci.*, 44 (2002) 871.
18. N. Ochoa, F. Moran, N. Pebere, *J. Appl. Electrochem.*, 34 (2004) 487.
19. F. Bentiss, M. Bouanis, B. Mernar, M. Traisnel, M. Lagrenee, *J. Appl. Electrochem.*, 32 (2002) 671.
20. K. Aramaki, N. Hackerman, *J. Electrochem. Soc*, 116 (1969) 568.
21. Y.A. El- Awady, and A.I.Ahmed, *J. Ind. Chem*, , 24 (1985) 601.
22. F. Bensajjay, S. Alehyen, M. El Achouri, S. Kertit, *Anti-Corros. Meth.Mater.*, 50 (2003) 402.
23. R. W. Bosch, J. Hubrecht, W. F. Bogaerts, B. C. Syrett, *Corros.Sci.*,57 (2001) 60.
24. S. S. Abdel–Rehim, K. F. Khaled, N. S. Abd–Elshafi, *Electrochim. Acta*, 51 (2006) 3269.
25. M.J.Frisch, G.W.Trucks, H.B.Schlegel, G.E.Scuseria, M.A.Robb, J.R.CheesemmanJ.A.Pople *Gaussian 03, Revision E.01, Wallingford, CT:Gaussian.*
26. S.S. Abd El-Rehim, S.A.M. Refaey, F. Taha, M.B. Saleh, R.A. Ahmed, *J. Appl. Electrochem.*, 31(2001) 429.
27. K.K. Al-Neami, A.K. Mohamed, I.M. Kenawy, A.S. Fouda, *Monatsh Chem.*, 126 (1995) 369.
28. S.S. Abd El-Rehim, M.A.M. Ibrahim, K.F. Khaled*, J. Appl. Electrochem.*, 29(1999) 593.
29. A.S. Fouda, A.A. Al-Sarawy, M.S. Radwan, *Ann. Chim.*, 96 (2006) 85
30. A.K. Mohamed, H.A. Mostafa, G.Y. El-Awady, A.S. Fouda, *Port. Electrchim.Acta,* 18 (2000) 99.
31. A. El-Ouafi, B. Hammouti, H. Oudda, S. Kerit, R. Touzani, A. Ramdani, *Anti-Corros. Meth. Mater.*, 49 (2002) 199.
32. F. Mansfeld, M.W. Kendig, S. Tsai, *Corrosion*, 38 (1982) 570.
33. F. Mansfeld, *Eletrochim. Acta*, 35 (1990) 1533.
34. E. McCafferty, N Hackerman, *J. Electrochem. Soc.*, 119 (1972) 146.
35. E. Kus, F. Mansfeld, *Corros.Sci.*, 48 (2006) 965.
36. G. A. Caigman, S. K. Metcalf, E. M. Holt, *J.Chem. Cryst.*, 30 (2000) 415
37. D.C. Silverman and J.E. Carrico*, National Association of Corrosion Engineers*, 44 (1988) 280 38
38. R.A., Prabhu, T.V., Venkatesha, A.V., Shanbhag, G.M., Kulkarni, R.G, Kalkhambkar, *Corros.Sci.*, 50 (2008) 3356.
39. G., Moretti, G., Quartanone, A., Tassan, A., Zingales, ,*Wekst. Korros.*, 45(1994) 641.
40. C. Lee, W. Yang and R. G. Parr., *Phys. Rev. B.Development of the Colle-Salvetti*, 37 (1988) 785.
41. R. M. Issa, M. K. Awad and F. M. Atlam, *Appl. Surf.Sci.*, 255 (2008) 2433.
42. M. Farady, *Experimental Researches in Electricity*, 2 (1844) 243.
43. F.K. Crundwell, *Electrochim. Acta,* , 37 (1992) 2101.
44. R. Ravichandran and N. Rajendran, *Appl. Surface Sci.*, 241 (2005) 449.
45. R. Ravichandran and N. Rajendran, *Appl. Surface Sci*, 239 (2005) 182.
46. M. Mihit, S. El Issarni, M. Bouklah, L. Bazzi, B. Harnmouti , E. AitAddi. R. Salghi, S. Kertit, *Appl. Surf. Sci.*., 252 (2006) 2389.
47. ManjulaSpah, Dal Chand Spah, BalrajDeshwal, Seungrnoon Lee, Yoon-KeunChae, Jin Won Park, *Corros. Sci.*., 51 (2009) 1298.
48. M.B. Valcarce , M. V'zquez, *Corros. Sci.* , 52 (2010) 1413.
49. M.A. Deyab, *Corros. Sci.*, 49 (2007) 2315.
50. S.A. Abd El-Maksoud A.S. Fouda, *Mater.Chem.phys.*، 93 (2005) 84.
51. K.F.Khaled, *Mater. Chem. phys.*, 122(2008) 290.
52. E.Machnikova,K.H. Whitmire and N Hackeman, *Electrochim. Acta* , 53 (2008) 6024.
53. H Ashassi-sorkhabi, M.R. Magidi and K. Seyyedi, *Appt. Surf. Sci.*, 225 (2004) 176.
54. M.A. Migahed and I.F. Nasser, *Electrochim. Acta* , 53 (2008) 2877.
55. G.Avci, *Colloids Surf. A,* 317 (2008)730.
56. K.C.Pillali and R.Narayan, *Corros.Sci.*, 23 (1985) 151.
57. A.B.Tadros and B.A.Abdel-Naby, *J.Electroanal.Chem.*, 224(1988) 433.
58. JO'M.Bockris and B.Yang, *J.Electrochem.Soc* , 138(1991) 2237.
59. V.Jovancicevic, B.Yang and JO'M.Bockris, *J.Electrochem.Soc.*, 135(1989) 94.
60. J.Uhera and K.Aramaki, *J.Electrochem.Soc.A*, 138(1991)3245.

61. A.A.Akust, W.J.Lorenz and F.Mansfeld, *Corros.Sci*., 22(1982) 611.
62. M. Abdallah, E. A. Helal and A. S. Fouda, *Corros.Sci*. 48 (2006) 1639.
63. O.Benali, L. Larabi, M Traisnel, L. Gengembra, Y. Harwk, *Appl. Surf.Sci*,.253(2007)6130.
64. M.A. Khalifa,M.El-Batouti, F.Mhgoub,A.BakrAknish,*Mater.Corrps*.,54 (2003) 251.
65. Y.Abboud, A.Abourriche, T.Saffag, M.Berrada, M. Charrouf, A.Bennamara, N.Al Himidi and H.Hannache, *Mater.Chem.phy*., 105 (2007) 1.
66. K. FKhaled, *Electrochim. Acta*, 48 (2003) 2493.
67. A. Popova M. Chistov, S. Raicheva and E. Sokolova, *Corros. Sci*., 46(2004)1333.