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Protection of Corrosion of Carbon Steel with Core-Shell Inorganic Magnetic Nanogels in Formation Water

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The effectiveness of poly (2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) and copolymers with acrylic acid (AA) and acrylamide (AM) magnetic nanogels as protective corrosion of CS in reaction with water by (EIS), (EFM) and tafel polarization method. Polarization method demonstrated that all the polymers are mixed inhibitor type. (EIS) Electrochemical impedance given that the attendance of these investigated polymers declines the double layer capacitance and improvement the charge transfer resistance. The polymers adsorption on surface of steel was follow isotherm Temkin. The morphology of the CS surface was examining by (EDX) energy dispersive X-ray and (SEM) scanning electron microscope. The data obtain showed improvement in efficiencies for inhibition with raising the dose of inhibitor.

Keywords: CS, Corrosion inhibition, Magnetite core-shell nanogel polymers, Formation water, SEM, EIS, EFM.

1. INTRODUCTION

CS is the common regularly utilized pipeline materials as a part of petroleum creation. In any case, it is exceptionally inclined to corrosion in environments include sulphur [1]. Corrosion of sulfur has been one of the corrosion sorts in gas/oil manufacture, offering ascend to the pipelines failure and equipment's and utilized in biggest economic reduction and accidents. Likewise, spillage of raw petroleum because of endures consumption of pipelines would actuate fire accident, and natural contamination [2–4]. Explored to comprehend its mechanism, decrease the corrosion rate, additionally create experimental models to survey and foresee the parametric effects and the states-of the-art of internal corrosion of pipelines [5–12]. Theoretical approaches provide means of experimental of these reactions and there are many reports connection with this area [13]. Last papers have study the connection between the efficiency and structure of the inhibitor molecule, but low attention has been paid to the reliance of the protection efficiency on the size and electronic distribution of the protective molecule, Relation between chemical structure and inhibition efficiency was not research, The super paramagnetic Fe_3O_4 nanoparticles covered with polymers are usually connected to the magnetic cores to ensure a strong magnetic [14]. Attractive nanogels of regular interest are ferromagnetic magnetite (Fe_3O_4) covered with cross-connected polymer nanogels. The Fe_3O_4 center has solid attractive characteristic and super paramagnetic conduct, is of generally declines danger to the human body when epitomized in the defensive shell of polymer, which is cross-connected hydrogels polymer. The shell keeps the Fe_3O_4 center from total oxidation. In this appreciation, the utilizing of nanogels particles as a part of the field of consumption hindrance insurance for steel rather than ordinary natural inhibitors can deliver uniform flimsy film (with no pine opening because of cross-connected polymers) on the surface of CS to coat all surface with no deformities which give focal points over typical natural inhibitors. A few strategies have been produced to get ready attractive miniaturized scale and nanogels, for example, reverse microemulsion polymerization and emulsion polymerization [15–18]. The target of this paper is to calculation the inhibitive effect of these polymers on carbon steel in formation water by various electrochemical methods.

2. EXPERIMENTAL TECHENIQE

2.1. Materials and Solutions

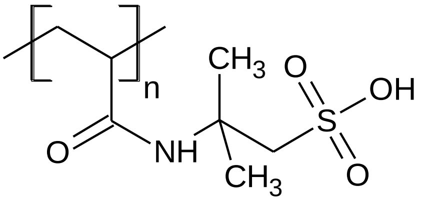
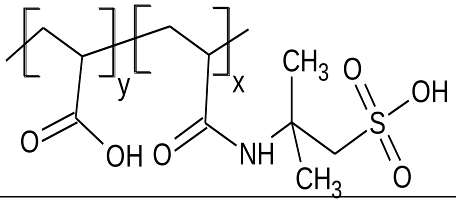
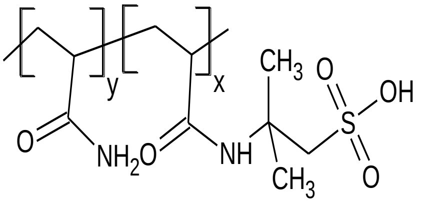
Coupons were obtain from CS sheet with a composition (in weight %) of C0.20, Mn 0.35, P 0.024, Si 0.003 and the rest Fe. Specimens divided into 20 ml X 20 ml X 2 ml dimensions were utilized for mass loss tests. All reagents were analytical-grade obtainable and utilized under further experiment, excluding (AMPS), (AM), and (AA) were purchased from chemicals Aldrich Company and cleaned or recrystallized prior to utilized. N,N-methylene-bis-(acrylamide), which utilized as cross-linker N,N,N0,N0-tetramethylethylenediamine (TEMED) was supplied from Aldrich chemicals Company (KPS) was utilized excluding further purification. Nitrogen (99.99%) was utilized as gas protective. Bidistilled water was utilized throughout the method. The water obtained utilized in this method was given from Company Qarun Petroleum, Egypt Western Desert. The properties of water formation are written in Table 1.

Table 1. Formation of oil field water and Composition

ions	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Conc. (mg/L)	3,5820	1152	7496235	6,9222	288	353	11,3819

2.2. Inhibitors

Investigated inhibitors were synthesized as before [19] and their structures are shown below:

comp	Name	Structure	Formula
1	Poly (2-acrylamido-2-methylpropanesulfonic acid)		$[C_7H_{13}O_4NS]_n$
2	Poly (2-acrylamido-2-methylpropanesulfonic acid)-co-acrylic acid		$[C_{10}H_{17}O_6NS]_n$
3	Poly (2-acrylamido-2-methylpropanesulfonic acid)-co-acrylamide		$[C_{10}H_{18}O_5N_2S]_n$

2.2. Electrochemical techniques

2.2.1 Potentiodynamic polarization method

Electrochemical tests were including three electrodes thermostatic cell assembly utilized a Gamry (model PCI 300/4),a platinum sheet as utilized counter and (SCE) were utilized as electrode reference, the steel electrode was in the form of a square cut from CS electrode of size (10 x10 mm) and was welded to a Cu wire utilized for electrical connection, the electrode C-steel was abraded successively with various of emery grades papers, rinsed with bi-distilled and acetone.

Electrochemical experiments were performed at room temperature. The potentiostatic diagrams were reported from -5 to 5 V at a scan with rate 0.5 mVs^{-1} after reached to the steady state half hours and the (OCP) was observed. (θ) and the % η were measured from Eq. 1

$$\% \eta = 100 \times \theta = [1- (i^{\circ}_{corr} / i_{corr})] \times 100 \qquad (1)$$

Where i_{corr} and i°_{corr} are the current of corrosion in surfactant solutions and in HCl, respectively.

The electrochemical impedance (EIS) spectra were done in the 100 kHz and 0.2 Hz frequency range. The inhibition efficiency (% E) and (θ) of the utilized inhibitors were given from the impedance technique were measured from Eq. 2:

$$\% E = \theta \times 100 = [1-(R^{\circ}_{ct}/R_{ct})] \qquad (2)$$

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

EFM can be utilized as a fast and nondestructive experimental for rate of corrosion technique without prior information of Tafel constants. EFM technique utilized 2.0 to 5.0 Hz. The main frequency was 0.1 Hz. In this work the time which given steady state of the specimens found 30 min [21].

3. RESULTS AND DISCUSSION

3.1 Tafel polarization technique

The effect of investigated derivatives on the reactions of corrosion was investigated by these techniques. The changes measured in the polarization plots after the appending of the polymers are utilized as the criteria to type inhibitors as cathodic, anodic or mixed [22]. Figure 1 given the tafel polarization plots for CS in formation water at inconsistent dose of polymer (1) at 25ºC. Similar plots were given for other but not shown. This Figure shows that the cathodic plots give approximately parallel lines, suggesting that the discharge hydrogen reaction lowers, its activation being controlled [23] by polymer addition in aggressive medium. The kinetic parameters for example corrosion potential (E_{corr}), (β_c and β_a), (i_{corr}), and protective efficiency data (% E) were obtained from Tafel plots and are tabulated in Table 2. The results showed that the addition of these additives at all the studied dose were observed in: i) a decrease in the corrosion rate and hence a decrease in the current density (i_{corr}) ii) An increase in the surface coverage and hence an increase in the % E. There was no observed shift in the corrosion potential (E_{corr}) data with respect to the blank.

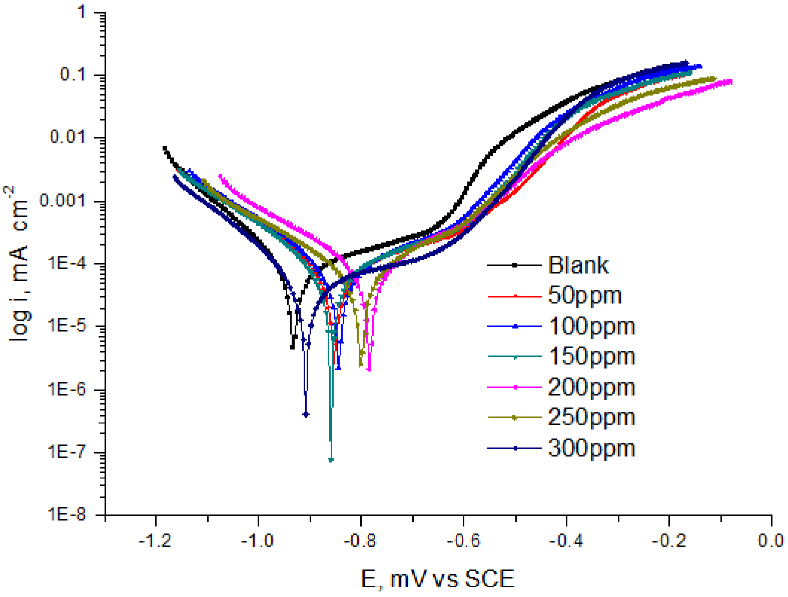


Figure 1. Polarization diagrams for CS in the formation water in attendance and lack various dose of inhibitor 1.

Table 2. Kinetic parameters of CS in the formation water in attendance and lack various dose of studied polymers

Inh.	Conc., ppm	i_{corr} µA cm^{-2}	- E_{corr} mVvs SCE	β_a mV dec^{-1}	β_c mV dec^{-1}	C.R. mpy	ϴ	%E
1	Blank	181	932	462	183	82.57	---	---
	50	121	983	634	223	55.26	0.331	33.1
	100	83.2	984	270	185	38.03	0.540	54.0
	150	63.8	932	417	109	29.15	0.648	64.8
	200	57.7	959	219	135	26.34	0.681	68.1
	250	43.5	984	104	109	19.88	0.760	76.0
	300	34.5	981	106	114	15.65	0.811	81.1
2	50	101.4	958	830	152	46.32	0.439	43.9
	100	68.6	914	848	190	31.36	0.621	62.1
	150	57.4	929	648	122	26.21	0.683	68.3
	200	37.7	965	315	183	17.25	0.792	79.2
	250	32.3	960	329	179	14.77	0.822	82.2
	300	23.4	949	226	173	10.68	0.871	87.1
3	50	87.7	958	855	162	40.1	0.515	51.5
	100	50.7	915	684	121	23.16	0.719	71.9
	150	38.8	965	323	187	17.75	0.785	78.5
	200	29.8	950	264	203	13.62	0.835	83.5
	250	22.3	949	216	171	10.21	0.876	87.6
	300	14.3	948	167	147	6.542	0.921	92.1

Both cathodic and anodic reactions are same effect, which given the influence of these additives on both the cathodic and the anodic reactions. According to what reported in the literature [24], when the shift in (E_{corr}.) is more than -85 mV with respect to the blank. However, the displacement higher in this experiment is lower than -85 mV (50-52 mV). This suggested that these additives a function act as mixed inhibitors type. From this method the % E for the investigated compounds follows the following order: 3 > 2 > 1.

3.2. Adsorption isotherms

The different isotherms such as Langmuir, Frumkin, Freundlich and Temkin may be used, in order to know the adsorption of these polymers on CS surface, by plotting the degree of surface coverage values with maximum regression coefficients. The best fitting of our results was found with Temkin adsorption isotherm, which may express by the Eqs. 3 and 4[25]:

$$\text{Exp}(-f\,\theta) = KC \qquad (3)$$

$$\Theta = 1/f \ln K + 1/f \ln C \qquad (4)$$

Where K = adsorption-desorption equilibrium constant, C = dose (mol/ L) of polymers, θ = coverage surface (θ = E/100), and 'f' = heterogeneous factor of CS surface, given the number of the active surface sites utilized by each polymer molecule.

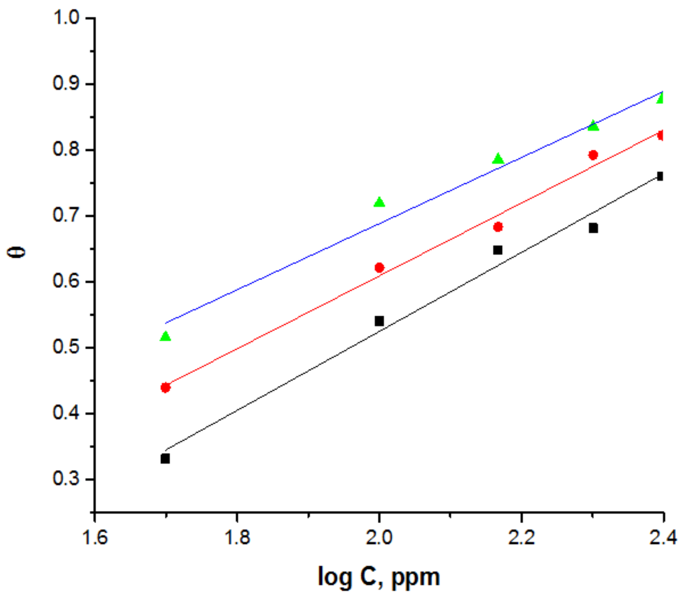


Figure 2. Temkin isotherm for the adsorption of investigated polymers on CS in formation water at 25˚C

It is seen that the data of "f" are positive and more than unity in all cases, meaning that attraction exists in the adsorption layer and a single molecule of polymers disables several active sites on the CS [26]. The standard adsorption free energy (ΔG^o_{ads}) was measured utilized Eq.5 [27]

The adsorption-desorption (K) (equilibrium constant) of was utilized to measure (ΔG^o_{ads}) given in Eq.5 [28]:

$$K = 1/55.5 \exp (\Delta G^o_{ads}) /RT \qquad (5)$$

Where 55.5 = concentration of water in solution by molar, R = universal gas constant (8.31 J/ mol K) and T = temperature absolute (298K).

Straight lines were given from plots θ vs. log C for Temkin with regression coefficient values near unity as shown in Fig. 2. The values of (ΔG^o_{ads}), K and a are given in Table 3. The -ve data of (ΔG^o_{ads}) indicate that the adsorption of the investigated polymer on the CS is spontaneous. It is reported that values of (ΔG^o_{ads}) around 20 kJ mol^{-1} suggests physisorption and around 40 kJ/mol suggests chemisorption. The calculated values of (ΔG^o_{ads}) are in the range -21.0 to -25.4 kJ/mol indicating these polymers adsorbed on CS surface contains physical adsorption [29].

Table 3. Interaction parameter (a), adsorption equilibrium constant (K), free energy (ΔG^o_{ads}) and regression constant (R^2) of CS dissolution in the attendance of polymers at 25°C in formation water

Compounds	a	K M^{-1}	$-\Delta G^o_{ads}$ kJ mol^{-1}	R^2
1	3.8	74.7	21.0	0.98909
2	4.1	126.4	23.0	0.98997
3	4.6	234.3	25.4	0.97985

3.3. EIS measurements

In order to measure the stability of protective layer, EIS tests for CS were observed in formation water containing various concentrations of investigated polymers. Nyquist plots were obtained in without and with of various dose of compound (1), one capacitive loop appears as a semicircle as shown in Figure (3a), the loops diameters increases with the rise in concentration. The same plots were given for other polymers but not shown. Figure (3b) shows the fit of formation water with the equivalent circuit**.** As shown from this Figure that the obtained data fit well the equivalent circuit. The calculation Nyquist diagram from resulting data is utilized the circuit in Fig. (4), in which R_s represents the resistance in solution, R_{ct} is the charge-transfer resistance and (CPE) constant phase element. The EIS parameters tests were measured and listed in Table 4. It was note from the given EIS data that R_{ct} improvement with the rise of additive concentration. The higher in R_{ct} data and inhibition efficiency arrived to a maximum data of 90.6% at 250 ppm of compound 3, due to the gradual change of water molecules by the polymer molecules on the CS surface to form film which coating the CS surface.

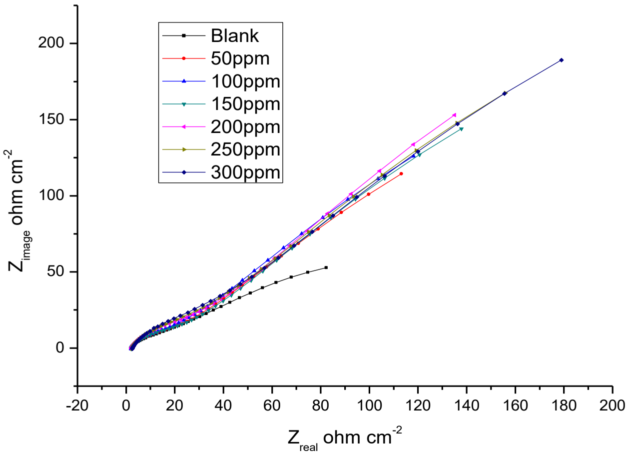


Figure 3a. Nyquist of CS in the formation water in attendance and lack various dose of inhibitor 1.

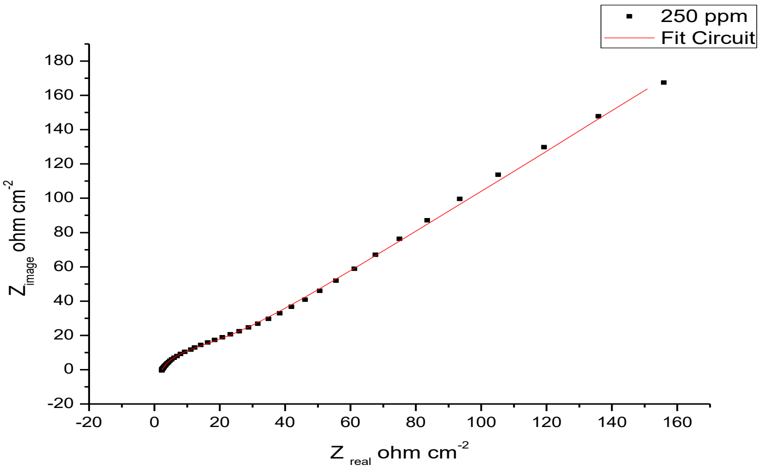


Figure 3b. Fit of formation water inhibited with equivalent circuit

The thickness of film increase by rise adsorbed layer. On the other hand, the lower in C_{dl} could attribute to the lower in the dielectric constant and/or improve in the thickness of the electrical double layer [30]. EIS data confirm the inhibition behavior of the polymers obtained with other techniques. The order of % E of the investigated polymers is the same as in Tafel polarization (1 < 2 < 3).

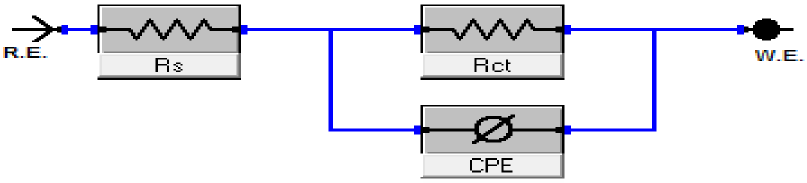


Figure 4. circuit utilized to fit the impedance data

Table 4. EIS parameters of CS in the formation water in attendance and lack various dose of investigated compounds at 298 K

Inhibitor	ppm	R_{ct}, Ω cm^2	C_{dl} μFcm^{-2}	ϴ	% E
Blank	0	23.5	330.1	-----	------
1	50	41.5	300.6	0.434	43.4
	100	56.2	221.4	0.583	58.3
	150	59.6	90.3	0.474	47.4
	200	62.2	82.5	0.623	62.3
	250	128.1	80.1	0.817	81.7
	300	183.8	65.9	0.872	87.2
2	50	110.0	180.2	0.787	78.7
	100	140.0	81.8	0.832	83.2
	150	169.0	50.2	0.861	86.1
	200	189.0	45.5	0.876	87.6
	250	201.0	25.6	0.883	88.3
	300	260.0	24.0	0.910	91.0
3	50	105.0	400.0	0.777	77.7
	100	135.0	230.4	0.826	82.6
	150	200.0	209.5	0.883	88.3
	200	210.0	120.7	0.888	88.8
	250	250.0	82.5	0.906	90.6

3.4. EFM measurements

Table 6. Parameters given by EFM method for CS in the formation water in attendance and lack various dose of the investigated polymers at 25^{o}C

Inh.	Conc., ppm	i_{corr}, μA cm^{-2}	β_a mV dec^{-1}	β_c mVdec^{-1}	CF-2	CF-3	CR mmy^{-1}	ϴ	% E
Blank	0.0	442.4	135	232	2.0	3.04	202.1	------	-----
1	50	276.1	152	209	1.9	3.2	126.2	0.3759	37.5
	100	249.2	149	201	1.9	2.8	113.9	0.4367	43.7

	150	245.5	165	233	2.2	3.1	112.2	0.4450	44.5
	200	225.5	159	214	1.9	3.1	103.0	0.4902	49.2
	250	165.0	132	176	2.0	3.0	75.4	0.6270	62.7
	300	147.1	133	182	2.3	3.2	67.2	0.6674	66.7
2	50	201.6	102	180	2.0	3.4	92.13	0.544	54.4
	100	149.7	157	167	1.9	3.3	68.38	0.662	66.2
	150	134.1	111	139	2.0	2.6	61.28	0.696	69.6
	200	107.6	164	178	2.2	3.0	49.17	0.756	75.6
	250	57.92	186	151	1.9	3.1	26.47	0.869	86.9
	300	49.71	173	120	2.3	3.9	22.71	0.887	88.7
3	50	156.8	156	161	1.7	2.3	71.65	0.645	64.5
	100	143.7	132	215	1.9	2.5	65.65	0.675	67.5
	150	108.5	139	139	1.3	3.0	49.56	0.755	75.5
	200	92.49	108	188	2.2	2.8	42.26	0.791	79.1
	250	42.19	167	105	1.7	2.2	19.28	0.905	90.5
	300	32.42	149	162	2.3	3.5	14.81	0.926	92.6

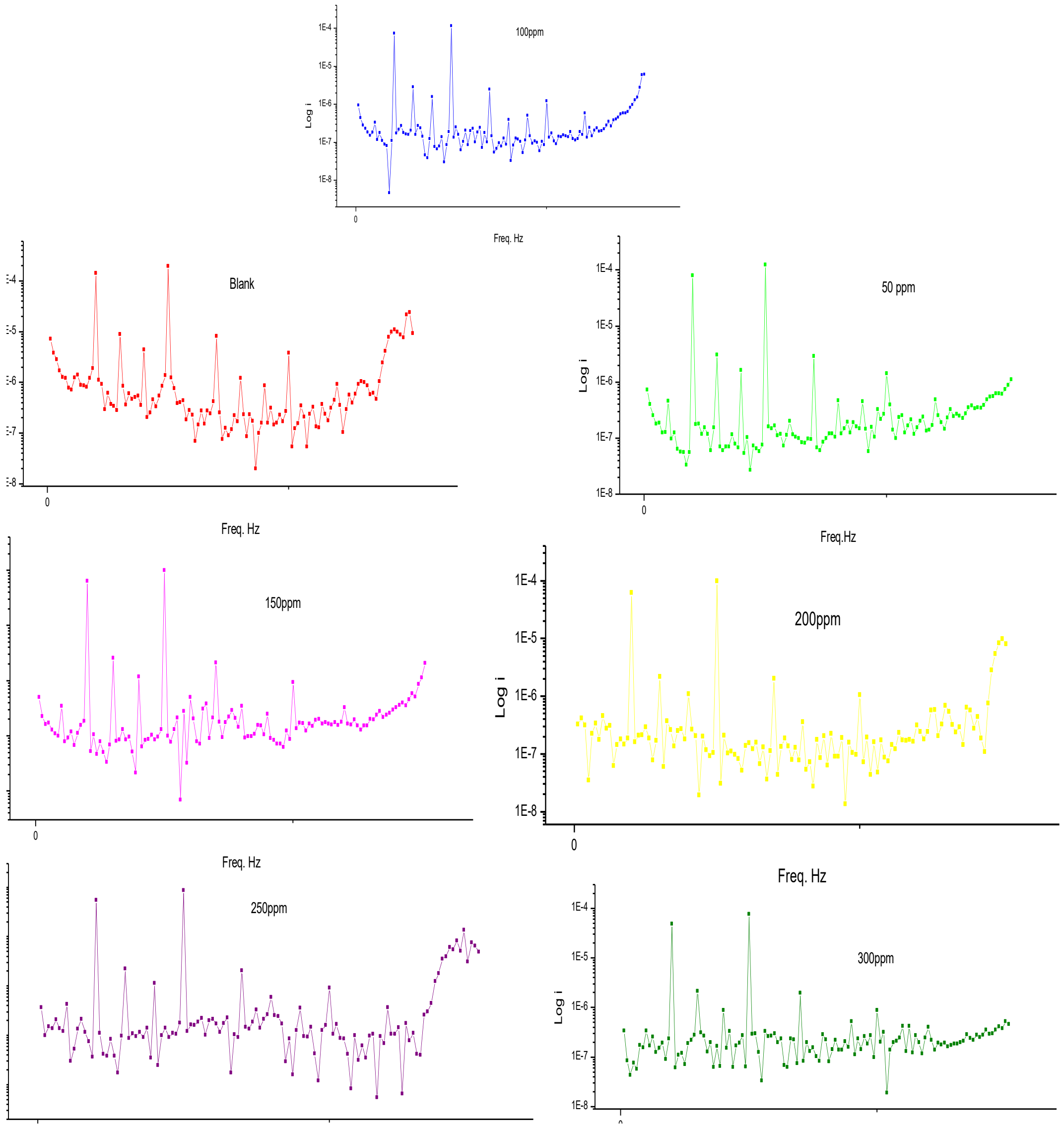


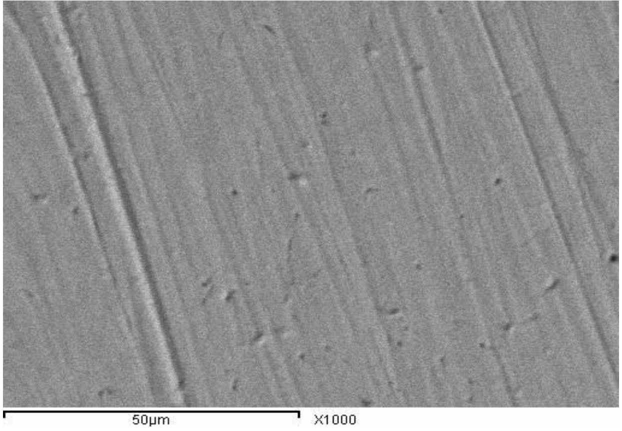
Figure 5. EFM spectra for carbon steel in formation water without and with various dose of compound 1 at 25^0C

EFM is a non-destructive method that can fast and exactly measure the current of corrosion values without prior information of Tafel lines, these advantages of EFM render it an ideal candidate for corrosion determine [31]. The good strength of the EFM is the causality factors which act as an internal check on the validity of EFM tests, (CF-2) and (CF-3) are measured from the frequency of spectrum. The order of % E of the investigated polymers is the same as in Tafel polarization and in EIS measurements (3 > 2 > 1).

3.5. SEM tests

Figure (6) show the micrographic of CS in the formation water and with various dose of inhibitor 1 after exposure for 2 days immersion. It is essential to worry that when the inhibitor is available in the solution the surfaces morphology of CS is quite various from the previous one, and the couins surfaces were smoother. We observed a film found which is arranged in a random way on the whole CS surface. Due to the inhibitor polymers molecules adsorption on the CS surface to form the passive film in order to block the active sites present on the CS, or inhibitor molecules improve interaction with the reaction sites of CS, resulting in a lower in the reaction between acidic medium and CS i.e act as good protective effect .

Pure Sample



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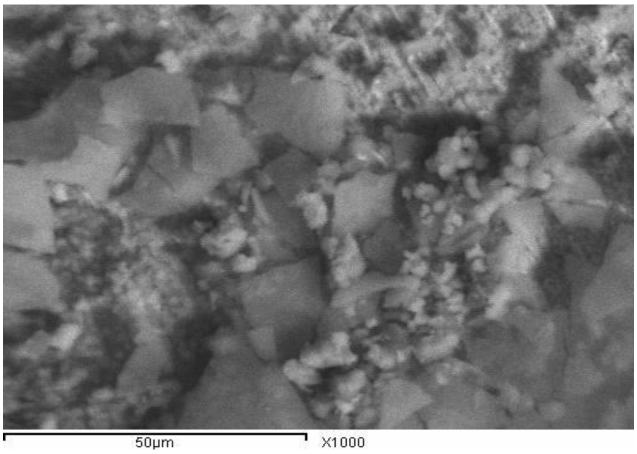


Inhibitor 1

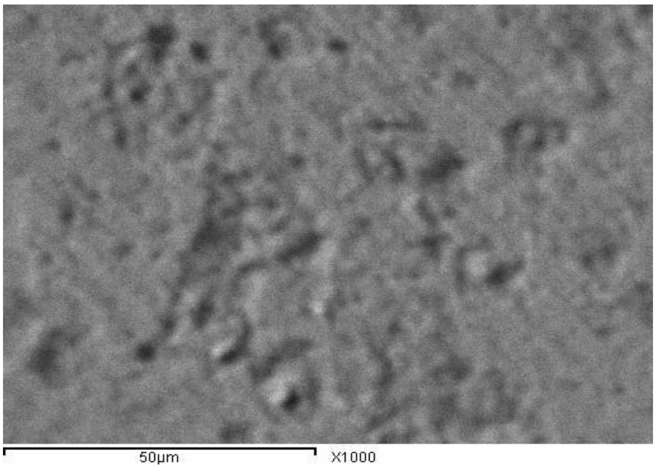
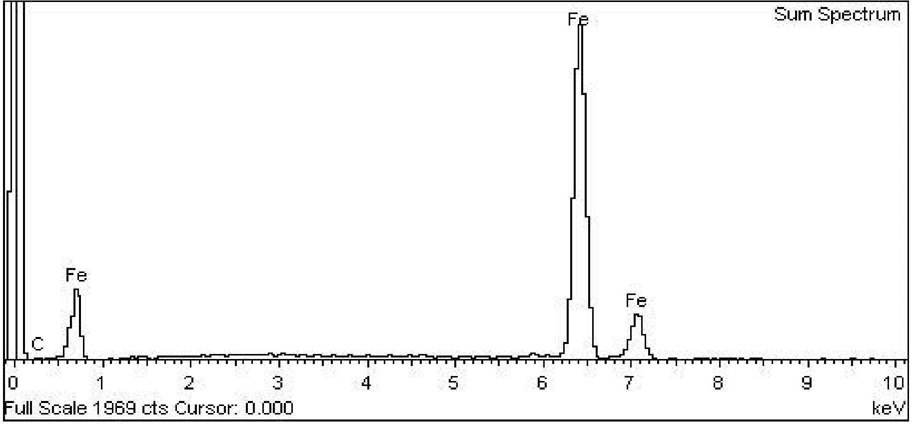


Figure 6. SEM for CS in the formation water and with various dose of inhibitor 1

3.6. Energy dispersion spectroscopy (EDX) studies

Pure sample



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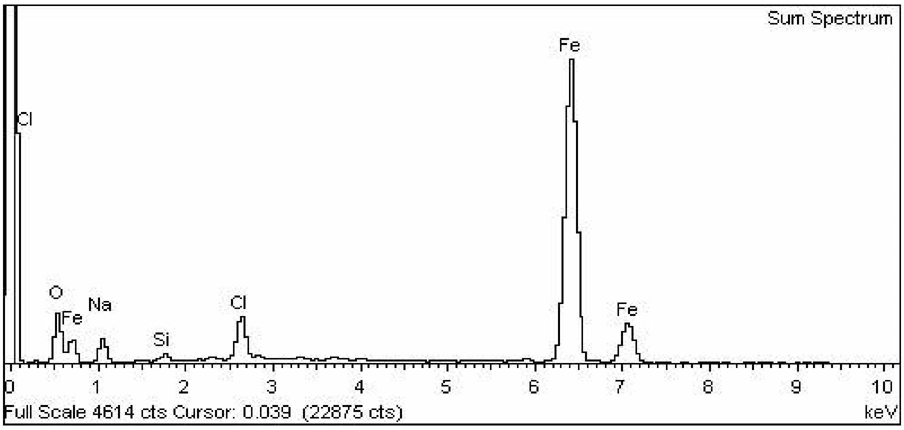

Inhibitor 1

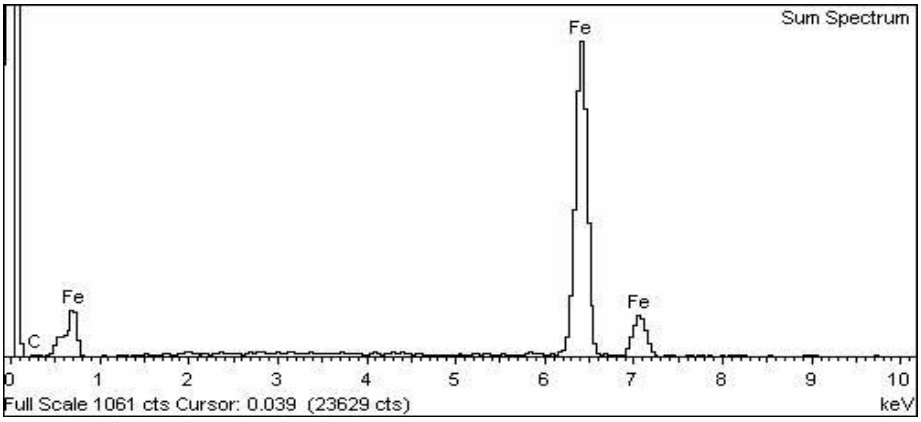

Figure 7. EDX tests on CS without and with compound 1 for immersion two days

The EDX spectra were utilized to measure the elements attendance on the CS surface, after 2 days of putted in the inhibited and lack inhibitor formation water, figure (7) shows the EDX data on the CS without and with the addition of compound 1, the EDX examination illistrated that only iron and O_2 were observed, which given the passive film with only Fe_2O_3, the spectra (Table7) showed additional lines, lead to the precense of carbon (follow to the carbon of compound 1), these value given atoms which coating the CS surface.

Table 7. Portrays the EDX resulted of CS in formation water only and with of compound 1

	Fe	C	O	Cl	Na
Pure sample	93.33	6.67	-----	-----	-----
blank	64.44	----	17.92	5.20	11.33
Inhibitor	88.44	11.56	-----	-----	----

3.7. Mechanism of inhibition

The extent of metal corrosion inhibition by organic inhibitors is dependent upon the capacity of the inhibitor to get adsorbed and found a film on the metal surface. The protective process begins with the replacement of the water adsorbed by the species of inhibitor bring to adsorption of the inhibitor on the surface. However, certain properties such as inhibitor chemical structure, the charge and nature of the metal, and the kind of corrosion inducing environment influenced the adsorption process. As could be seen from Table **1**, the studied polymers have heteroatoms in their functional groups thus justifying their selection as metal corrosion inhibitors. The heteroatoms in these functional groups could serve as the interaction center between the molecule of inhibitor and the metal. As noted before [32], the presence of heteroatoms in functional groups within inhibitor molecule could make bridges between the metal and molecule, as a consequence, decrease corrosion rate. Moreover, attendance of lone pairs of electrons on the heteroatom(s) may enhance the interaction between the molecule and the positive surface of the metal. Two forms of adsorption are consistent with organic inhibitors: physical and chemical. Physisorption is electrostatic consistent with interaction between the charged metal surface and charged molecules while chemisorptions contain charge sharing or transfer from organic molecule to the metal surface to form coordinate kind of bond. Results of most researches [33] showed that most polymers exist as polycations in acid medium (most studied environment). This makes it hard for the polycations to approach the charge metal surface positively. Therefore, Fe_3O_4 particles which were dispersed in the aqueous solution due to the presence SO_3^{-2} group in the structure of the polymers will first adsorb on the metal surface, bringing excess -ve charge close to the interface and favoring further adsorption of polycations *via* electrostatic attraction. Hence, physical adsorption mechanism is mostly proposed for most of the studied polymers studied [34].

The order of % E is: polymer 3 > polymer 2 > polymer 1. This is due to polymer 3 contains one extra N atom but polymer 2 contains one extra O atom and as known N atom can donate more electrons than the O atom, hence, polymer 3 > polymer 2 in % E. Polymer 1 contains less one O and N atoms than the polymers 3 and 2. So it comes the least effective one

4. CONCLUSIONS

The investigated polymers were obtained to be inhibitors effective for CS in formation water at 25°C. These investigated polymers are adsorbed physically on surface of CS followed isotherm Temkin. The polarization value revealed that these investigated polymers play as mixed inhibitors type. The data indicated that the % E improve with higher dose of the polymer. The charge transfer resistance improvement, while lower double layer capacitance by increment the dose of the polymers. The surface analysis indicated attendance of film on the CS surface.

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