

A Comparative the Inhibition Performance of a Newly Synthesized Cationic Surfmer and It's Oligomer Surfactant for Carbon Steel Corrosion in 1M Acid Chloride Solution

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A N-(2-(acryloyloxy)-ethyl)-N,N-bis(2-hydroxyethyl)dodecan aminium bromide (cationic surfmer) obtained by the quaternization reaction of obtained product from the esterification reaction of acrylic acid with triethanolamine. The synthesized cationic surfmer was polymerized in the presence of water and potassium persulfate (KPS) as initiator to give oligomer. The synthetic structure of recently surfactants was attested by basic examination, elemental analysis, FTIR, ¹HNMR and gel permeation chromatography (GPC). The critical micelle concentration (CMC) values for cationic surfmer and its oligomer measured via surface tension and conductivity measurements respectively. Electrochemical impedance spectroscopy and potentiodynamic polarization measurements used to determine the inhibition performance of cationic surfmer and oligomer for carbon steel in 1M HCl. The oligomer exhibited inhibition performance more than the corresponding cationic surfmer. The potentiodynamic polarization studies clarified that, the inhibitors represent a mixed-type inhibitors and the adsorption of inhibitors on the carbon steel followed the Langmuir isotherm. Quantum chemical parameters were also deliberate to explain the adsorption mechanism. Satisfactory connections were gotten between inhibition performance and the obtained quantum chemical parameters.

Keywords: Surfmer, Cationic Surfactants, Corrosion, Quantum, chemical analysis

1. INTRODUCTION

Carbon steel is commonly used as a constructional material as a part of various enterprises due to its extraordinary mechanical properties and insignificant exertion. It is utilized as a part of substantial tonnages in marine applications, synthetic preparing, oil and gas creation (refining development) and metal handling hardware. For acid pickling, aggressive solutions such as

hydrochloric and sulfuric acids are used which leads to corrosive attack [1-3]. More than one technique has been utilized to inhibit the corrosion of carbon steel. Reducing the corrosion of steel in aggressive acid solutions is a great significant for both industrial facilities and theoretical aspects [4]. Using organic inhibitors is one of the most commonsense techniques for reducing the acidic corrosion [5-8]. The adsorbed organic inhibitors reduce corrosion, acting over the anodic or the cathodic surface or both. Containing Organic compounds on heteroatoms (oxygen, nitrogen, and sulphur atoms) makes inhibitor molecules adsorbed on the metal surface in acidic media, forming adsorption film goes about as a boundary isolating the metal from the destructive medium and blocks the active sites [9 –14]. Quaternary ammonium salts (cationic surfactant) used as a representative type of these organic inhibitors. [15–17].

Our objective of this paper was coordinated to synthesize a newly cationic surfumer and its oligomer. The inhibition performance of these surfactants for carbon steel in 1M HCl solution was tested via electrochemical techniques. Values of CMC of the cationic surfmer and its oligomer were calculated from surface tension and conductivity measurements. Obtained surface parameters were discussed about in light of surface tension estimations. Quantum studies were additionally discussed about.

2. EXPERIMENTAL SECTION

2.1. Chemical composition of tested carbon steel specimens

The composition of the used carbon steel specimens in the experiment as follow (wt%): C (0.19%), Si (0.05%), Mn (0.94%), P (0.009%), S (0.004%), Ni (0.014%), Cr (0.009%), Al (0.034%), V (0.016%), Ti (0.003%), Cu (0.022%), and balance Fe.

2.2. Surface treatment of specimens

Preceding every analysis a pre-treatment was done, in which example surface was mechanically pounded with several grades of emery paper (340, 400, 600, 800, 1000 and 1200), washed by distilled water and ethanol, degreased with acetone and dried at 25 °C.

2.3. The used chemicals

Triethanolamine (TEA), acrylic acid (AA) were obtained from Aldrich, and dodecyl bromide from Merck, Germany. The solvents were used as received; they were all of analytical grade. A polymerization inhibitor was added (hydroquinone) at 200 ppm to prevent strong exothermic polymerization of AA when exposed to light or heat.

2.4. Solutions

1M HCl was prepared by the dilution of an analytical grade HCl (37% wt) with distilled water. The concentrations of synthesized inhibitors used ranged from 5×10^{-5} to 5×10^{-3} M. All solutions were prepared in double distilled water.

2.5. Synthesis of a cationic surfmer:

The synthesis of a cationic surfmer was completed in two stages:

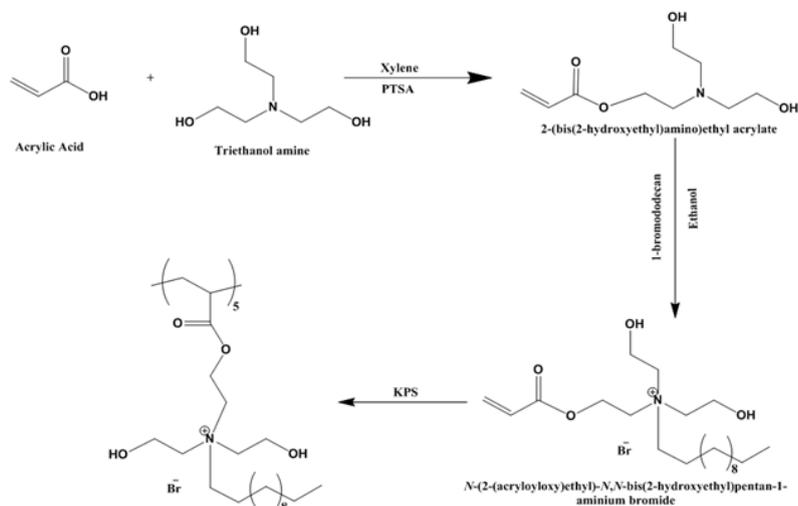
a. Synthesis of a 2-(bis(2-hydroxyethyl)amino)ethyl acrylate

In flat bottom flask fitted by Dean Stark, 0.1 mol of freshly distilled triethanol amine was added to 0.11 mol acrylic acid dissolved in xylene. The reaction mixture was catalyzed with p-toulene sulfonic acid and refluxed until collecting the theoretical amount of water. Product was neutralized by a dilute solution of sodium bicarbonate after the solvent distilled off. The obtained ester was washed out with petroleum ether.

b. Synthesis of a N-(2-(acryloyloxy)ethyl)-N,N-bis(2-hydroxyethyl)dodecan aminium bromide (cationic surfmer)

Quaternization reaction of 0.1 mol 2-(bis(2-hydroxyethyl)amino)ethyl acrylate by 0.12 mol 1-bromododecane in ethanol at 70 °C for 48 h to produce cationic surfmer. Reaction mixture was permitted to cool down. The produced cationic surfmer was further refined by diethyl ether then recrystallized from ethanol.

2.6. Polymerization of a N-(2-(acryloyloxy)ethyl)-N,N-bis(2-hydroxyethyl)dodecan aminium bromide



Scheme 1. Synthesis of the newly cationic surfmer and its oligomer

The amount of N-(2-(acryloyloxy)ethyl)-N,N-bis(2-hydroxyethyl)dodecan-1-aminium bromide in 25 ml water was put into a 250 ml well stoppered conical flask followed by the addition of the required amount of potassium per sulfate (KPS) dissolved in 25 ml water under nitrogen atmosphere. The reaction flask was then placed in an automatically controlled thermostat at 60 °C for 10 h. After cooling, the product was precipitated by methanol. The solid product was dried under vacuum until constant weight. Preparation the cationic surfmer and its oligomer illustrated in scheme 1.

2.7. Structural confirmation of the synthesized products

The chemical structure of the synthesized 2-(bis(2-hydroxyethyl)amino)ethyl acrylate, cationic surfmer and oligomer surfactant was affirmed by elemental analysis using an Elemental C, H, O and N Analyzer Vario Elementar instrument, FT-IR spectra using a Nicolet /100, ¹HNMR spectroscopy was performed using a Varian NMR-400-Mercury 400 MHz spectrometer with TMS as an internal standard in DMSO. Molecular weight of the oligomer was carried out through GPC (gel permeation chromatography). The high pressure GPC consisted of a high pressure pump (type 600E multisolvent delivery system).

2.8. Evaluation of the surface tension

Surface tension (S.T.) measurements for different concentrations of cationic surfmer and oligomer in double distilled water were tested at 25 °C using the Du Nouy method with a Kruss K6 tensiometer (Germany). The critical micelle concentration (CMC) and surface tension (S.T.) at CMC (γ_{cmc}) were determined from the plots and other surface properties such as effectiveness (π_{cmc}), maximum surface excess (Γ_{max}) and minimum surface area per molecule (A_{min}), at the air/solution interface were calculated.

2.9. Evaluation of the conductivity

Specific conductivity was recorded using (522; Crison Instrument, S.A.) with a dip-type cell at 25 °C. All tests were done in a jacketed vessel, which was kept up at the appropriate temperature (± 0.1 °C). Conductance for each dilution was measured thorough mixing and after temperature equilibrium. In every analysis, the conductivity of double distilled water was subtracted from the value indicated by the conductometer.

2.10. Evaluation the cationic surfmer and its oligomer as corrosion inhibitors

The inhibition performance of the cationic surfmer and oligomer was carried out through the electrochemical measurement (polarization and impedance experiment) which was fully described elsewhere [18]. The potentiodynamic polarization examinations were determined by changing the electrode potential automatically from -800 to -200 mV versus SCE with a scan rate 2 mV s⁻¹ at 25 °C.

For EIS a small alternating voltage perturbation (5 mV) was imposed on the cell over the frequency range of 100 kHz to 30 MHz at 298 K.

2.11. Quantum chemical study

The molecular structures of the synthesized inhibitors had been completely geometric enhance by MINDO3 semi-empirical method for organic inhibitors calculation which are performed in Hyperchem 8.0 with considering some parameters [19].

3. RESULTS AND DISCUSSION

3.1. Illustration the chemical structure of the synthesized compounds

The chemical structure of the synthesized 2-(bis(2-hydroxyethyl)amino)ethyl acrylate, cationic surfmer and oligomer was confirmed by elemental analysis, FTIR, ¹HNMR spectroscopy and gel permeation chromatography.

Table 1. The Elemental analysis of the synthesized compounds (acrylate ester, cationic surfmer and its an oligomer).

Compounds code	C %		H %		O%		N %	
	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
Acrylate ester	53.20	52.84	8.37	8.00	31.52	30.99	6.89	6.12
Cationic surfmer	55.75	55.10	9.29	9.32	14.15	14.00	3.09	2.99
Oligomer	55.75	52.91	9.29	8.81	14.15	13.43	3.09	2.89

Data obtained from (C, H, O and N) elemental analysis are listed in Table 1, indicates that, the nitrogen percentage (N%) for cationic surfmer and its oligomer decreases from 2-(bis(2-hydroxyethyl)amino)ethyl acrylate. This observation confirmed the formation of expected compounds. The average molecular weight (M_w) of the synthesized oligomer determines through gel permeation chromatography (GPC). The value of M_w (2381), shows the cationic surfmer (N-(2-(acryloyloxy)ethyl)-N, N-bis(2-hydroxyethyl)dodecan aminium bromide) was polymerized to its oligomer .

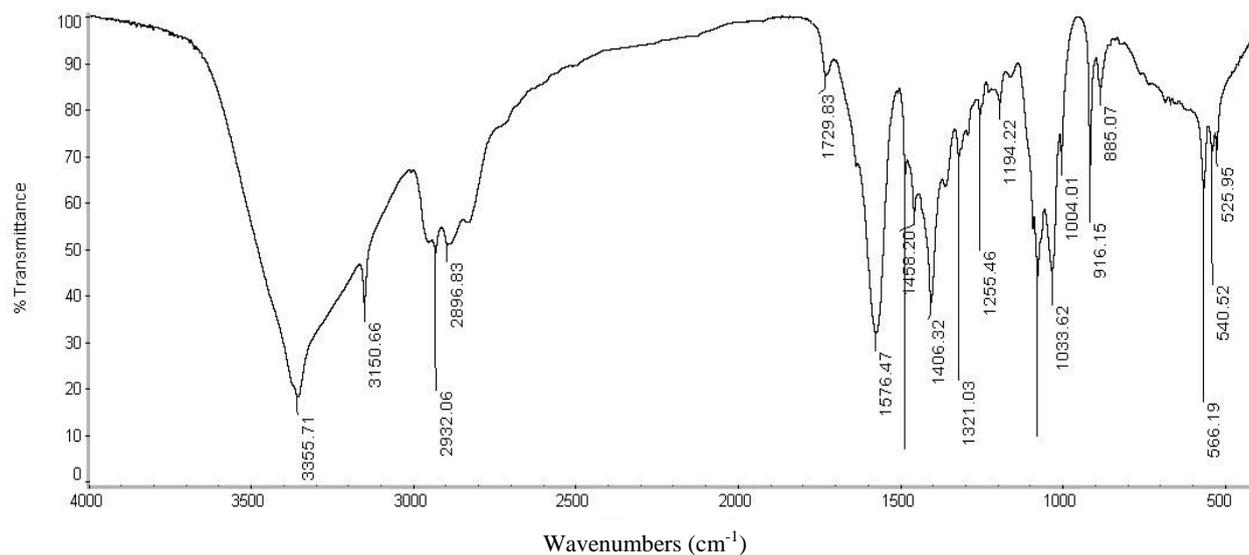


Figure 1. FT-IR spectrum of the prepared 2-(bis(2-hydroxyethyl)amino)ethyl acrylate

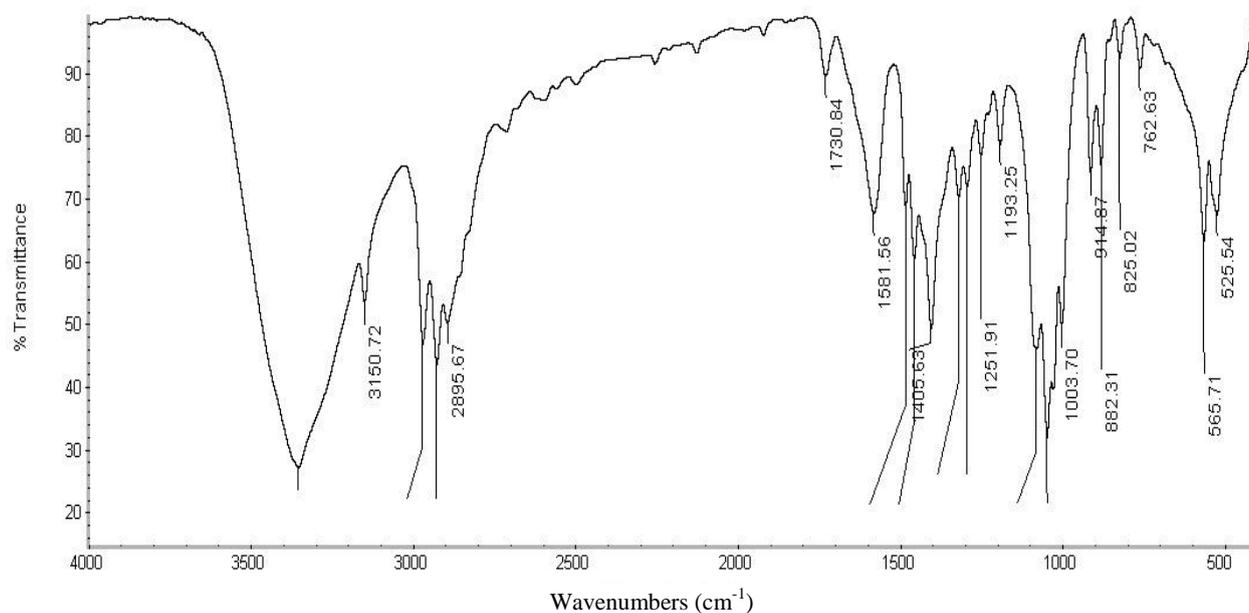


Figure 2. FTIR spectrum of the prepared N-(2-(acryloyloxy)ethyl)-N,N-bis(2-hydroxyethyl)dodecanaminium bromide

The FTIR spectra of the synthesized 2-(bis(2-hydroxyethyl)amino)ethyl acrylate, (N-(2-(acryloyloxy)ethyl)-N,N-bis(2-hydroxyethyl)dodecanaminium bromide) and oligomer shown in Figs. 1, 2, and 3.

The FTIR spectrum of 2-(bis(2-hydroxyethyl)amino)ethyl acrylate is presented in Fig. 1, reveals that the characteristic bands of ester group appeared at 1729.83, 3355.71 cm^{-1} for C=O stretching, OH respectively. However, the observed bands at 2932.06, 2896.83 for C-H stretching

vibration of methylene $-\text{CH}_2-$. Olefinic $\text{C}=\text{C}$, $=\text{CH}$ exhibited an absorption bands at 1574.47 and 3150.66 cm^{-1} respectively.

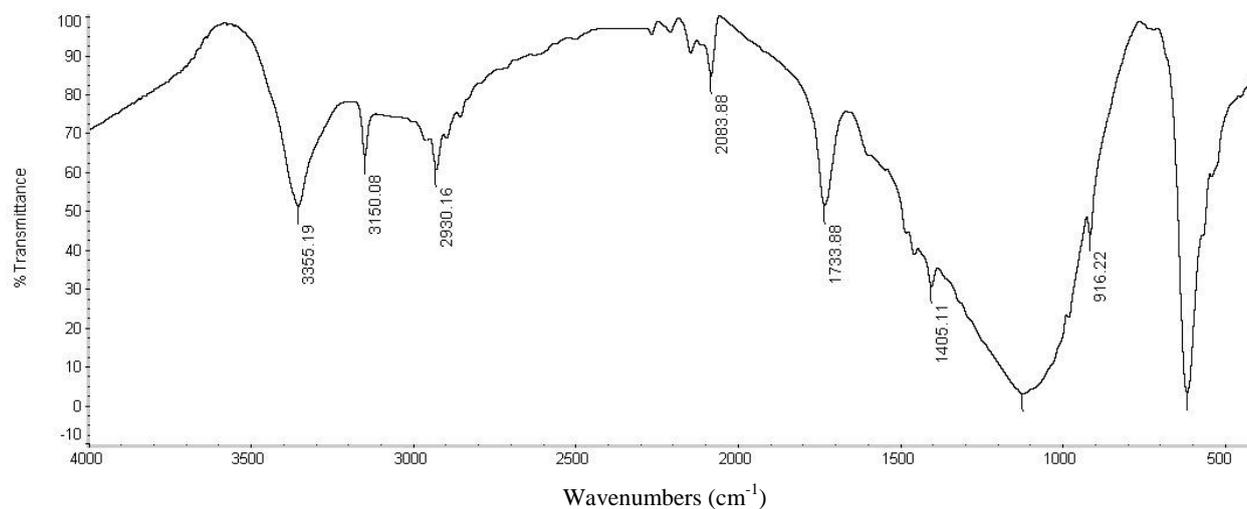


Figure 3. FTIR spectrum of the prepared oligomer

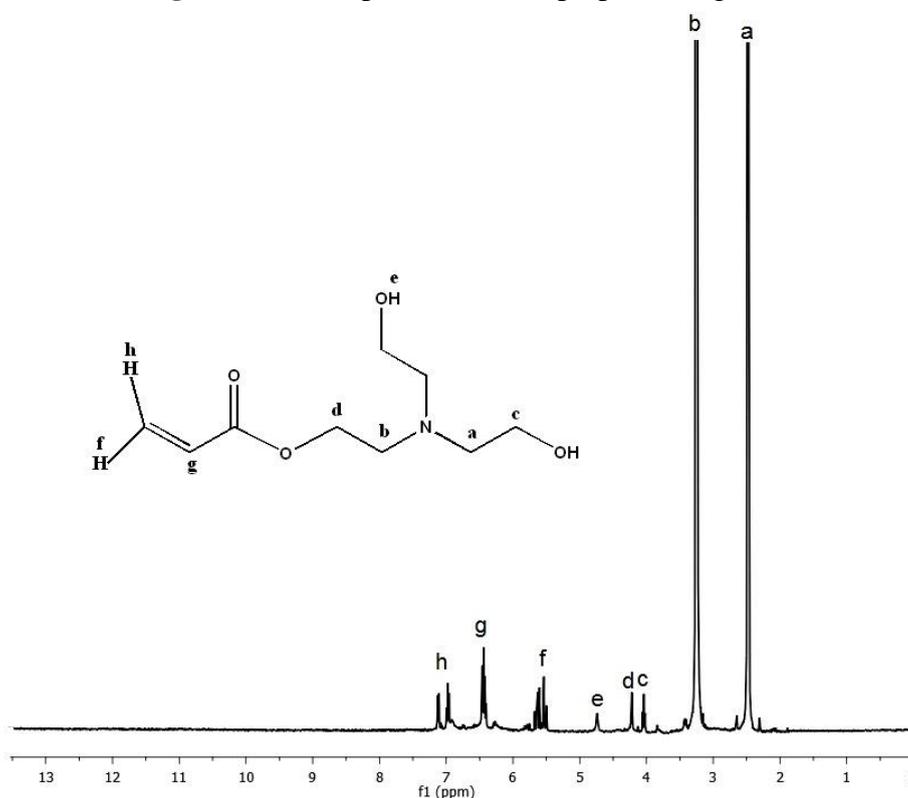


Figure 4. ^1H NMR spectrum of 2-(bis(2-hydroxyethyl)amino) ethyl acrylate

FTIR spectrum of (N-(2-(acryloyloxy)ethyl)-N,N-bis(2-hydroxyethyl)dodecan aminium bromide) in Fig. 2, showed that the absorption bands at 762.63 cm^{-1} for $-(\text{CH}_2)_n-$ rock, 1360 cm^{-1} for symmetric bending (CH_3), 2923 and 2852 cm^{-1} for asymmetric and symmetric stretching (CH), and 1030 cm^{-1} for ($\text{C}-\text{N}^+$).

FTIR spectrum of the synthesized oligomer in Fig. 3, showed that the disappearance of bands for olefinic $\text{C}=\text{C}$, $=\text{CH}$ at 1574.47 and 3150.66 cm^{-1} respectively.

^1H NMR (DMSO) spectrum of (2-(bis(2-hydroxyethyl)amino)ethyl acrylate) represented in Fig. 4, illustrates different peaks at $\delta = 2.5$ ppm for (a, $\text{NCH}_2\text{CH}_2\text{OH}$); $\delta = 4.1$ ppm for (c, $\text{NCH}_2\text{CH}_2\text{OH}$); $\delta = 3.3$ ppm for (b, $\text{NCH}_2\text{CH}_2\text{OCH}$); $\delta = 4.4$ ppm for (d, $\text{NCH}_2\text{CH}_2\text{OCH}$); $\delta = 4.7$ ppm for (a, $\text{NCH}_2\text{CH}_2\text{OH}$); $\delta = 5.6$; 6.4 ; 6.9 ppm for protons of acrylate moiety (h; i; and j respectively).

^1H NMR (DMSO) spectrum of (N-(2-(acryloyloxy)ethyl)-N,N-bis(2-hydroxyethyl)dodecan-1-aminium bromide) in Fig. 5, showed the appearance a new peaks at $\delta = 0.80$ for terminal methyl group (a, CH_3); $\delta = 1.19$ for (b, $((\text{CH}_2)_9)$); $\delta = 1.7$ for (c, $((\text{N}^+\text{CH}_2\text{CH}_2(\text{CH}_2)_9)$); and $\delta = 1.7$ for (d, $((\text{N}^+\text{CH}_2\text{CH}_2(\text{CH}_2)_9)$).

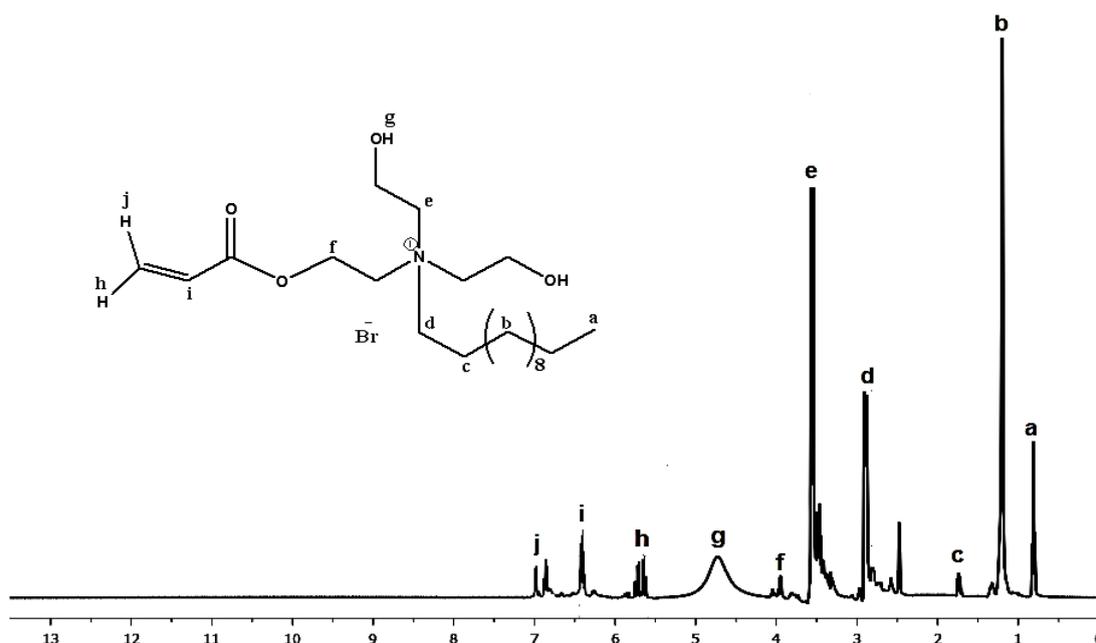


Figure 5. ^1H NMR spectra of N-(2-(acryloyloxy)ethyl)-N,N-bis(2-hydroxyethyl)dodecan-1-aminium bromide

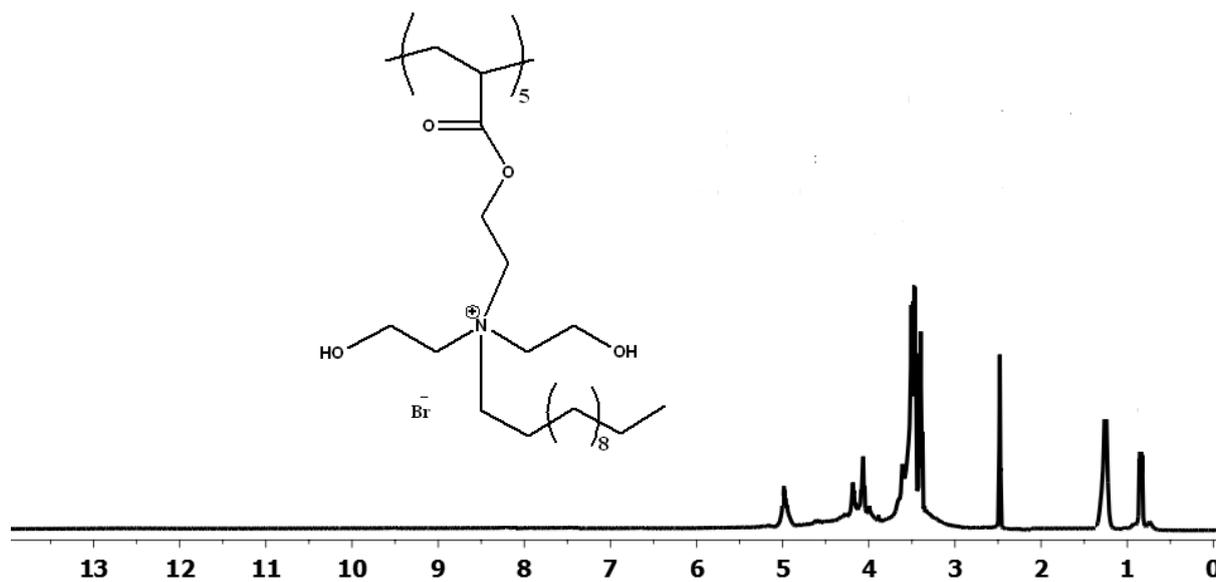


Figure 6. ^1H NMR spectra of the prepared oligomer

¹HNMR spectrum of the oligomer Fig. 6 differs from that of the monomer Fig. 5 in the disappearance of the two olefinic protons =CH at $\delta = 5.6$; 6.4; and 6.9 ppm and the appearance peaks at $\delta = 2.2$; 2.4 ppm for the -CH protons in the polymer backbone. The using analyses were matched with each other and confirmed the chemical structure of cationic surfmer and oligomer.

3.2. Surface active properties

3.2.1. Critical micelle concentration (CMC)

The surface tension of cationic surfmer and its oligomer was evaluated for a range of concentrations above and below the critical micelle concentration. Plot of surface tension values Vs. ln concentration of these surfactants is shown in Fig. 7.

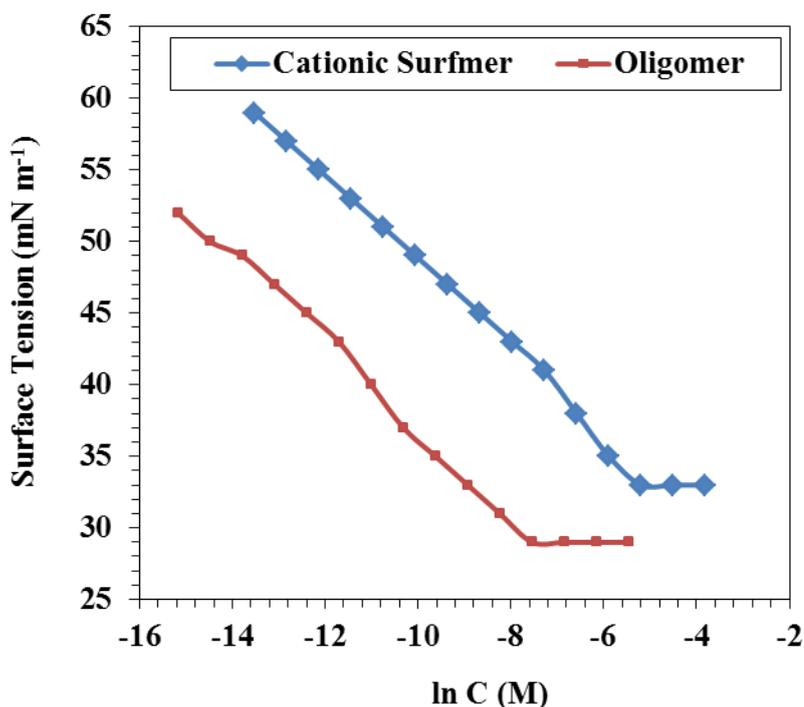


Figure 7. Variation of the surface tension with logarithm concentrations of synthesized cationic surfmer and its oligomer in water at 25°C

From the this figure it can observed that, decrease in surface tension with increasing the surfactants concentrations up to the CMC, beyond which no considerable change was observed. This is a common behavior shown by surfactants in solution and is utilized to determine their purity and CMC's. The values of CMC obtained from the break point in the γ - ln C plots and listed shown Table 2.

Table 2. Surface active parameters for the synthesized surfmer and its oligomer from surface tension measurements at 25 °C

surfactants	CMC (mol L ⁻¹)	γ_{CMC} (mNm ⁻¹)	Π_{CMC} (mNm ⁻¹)	$\Gamma_{max} \times 10^{11}$ (mol cm ⁻²)	A_{min} (Å ²)
Cationic surfmer	0.0055	33	39	6.05	27.41
Oligomer	0.0010	29	43	2.04	81.13

From Table 2 the CMC value for oligomer less than cationic surfmer and this due to there is a strong propensity for an oligomer molecule to self-assemble and form micelles at very low concentrations contrasted with its monomeric partner [20-22]. The γ -ln C plots also provide information about effectiveness, surface excess and area per molecule at air/water interface of the synthesized surfactants. Obtained surface parameters from surface tension estimations are listed in Table 2.

3.2.2. Effectiveness (π_{CMC})

The maximum surface pressure (π_{CMC}) is defined as the effectiveness of a surfactant in reducing surface tension and calculated from the following equation:

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad (1)$$

where γ_0 and γ_{CMC} are the surface tensions of pure distilled water and surface tension at CMC, respectively. It was found that, effectiveness increments with increasing the hydrophobic part and the strong binding ability of the counter ion.

3.2.3. The surface excess (Γ_{max})

Surface excess (Γ_{max}) is the amount of adsorbed surfactant at the air/water interface. The values of the Γ_{max} were computed from the slope of the straight line in the surface tension plot ($d\gamma/d\ln C$) below CMC, by applying the Gibbs adsorption equation [23, 24]:

$$\Gamma_{max} = - (1/nRT) (d\gamma/d \ln C) \quad (2)$$

where Γ_{max} = maximum surface excess concentration of surfactant, R = gas constant, T = absolute temperature, C = surfactants concentration, γ = surface tension at taken concentration and n = number of species ions in solution. The constant (n) takes the value two for an ionic surfactant where the surfactant ion and the counter ion are univalent, and six for an oligomer surfactant made up of a divalent surfactant ion and five univalent counter ions, in the absence of a swamping electrolyte [25-27]. It was found that, surface excess concentration for oligomer surfactant higher than monomeric surfactant by increments the number of carbon chain length, which could be due to the hydrophobic effect of carbon chain.

3.2.4. The Area per Molecule (A_{min})

The occupied area by each molecule in nm^2 at the liquid/air interface can be defined as minimum surface area per adsorbed molecule (A_{min}). A_{min} can be calculated as follows [28]:

$$A_{min} = 10^{16} / N_A \Gamma_{max} \quad (3)$$

where N_A = Avogadro's number and Γ_{max} (mol m^{-2}) = maximum surface excess of adsorbed surfactant molecules at the interface. The value of A_{min} for cationic surfmer was lower than oligomer due to the oligomer molecules packed better at interface than cationic surfmer.

3.3. Conductivity Estimations

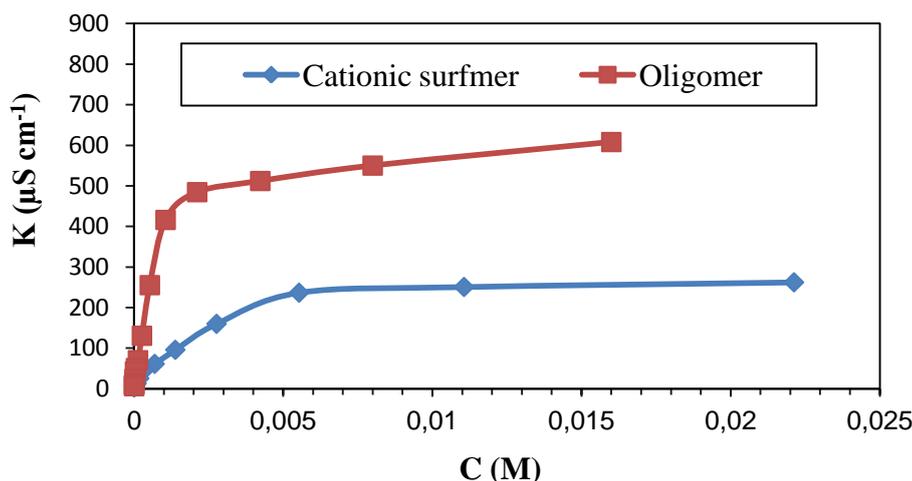


Figure 8. The plots of specific conductivity, K, against concentration for synthesized cationic surfmer and its oligomer in water at 25°C.

Table 3. The critical micelle concentration (CMC), degree of dissociation, and free energy of micellization of the synthesized surfactants from specific conductivity measurements at 25 °C

Compounds	CMC (M)	β	ΔG_{mic} (kJ mol^{-1})
Cationic surfmer	0.0049	0.07	-25.43
Oligomer	0.0011	0.02	-33.35

Specific conductivity (K) estimations were performed for the incorporated cationic surfmer and oligomer surfactants at 25°C in order to evaluate the CMC and the degree of counter ion dissociation, β . It is well known that, the specific conductivity is specifically connected to the concentration of the surfactant in both the premicellar and in the postmicellar regions, and the slope in the premicellar region is higher than in the postmicellar region [29, 30]. The intersection point between

the two straight lines gives the CMC while the ratio between the slopes of the postmicellar region to that in the premicellar region gives the counter ion dissociation, β . Fig. 8 showed the relationship between the specific conductivity and the concentration of the evaluated cationic surfmer and oligomer.

It was found from reported data in Table 3, the β value for oligomer less than the cationic surfmer due to the increase in cation bulkiness. The CMC values, obtained from both electrical conductivity and surface tension are matched with each other.

3.3.1. The standard free energy of micelle formation ΔG_m^o

The standard free energy of micellization (ΔG_m^o), a measure of the tendency of the synthesized surfactants to form micelles, in the charged pseudophase model of micelle formation, the standard free energy of micelle formation per mole of surfactant is given by equation:

$$\Delta G_m^o = (2 - \beta) RT \ln (CMC) \quad (4)$$

where R = gas constant, T = absolute temperature, CMC is expressed in the molarity of the surfactant and β = ionization degree of the micelles. From Table 3, it is clear that, the ΔG_m^o values for oligomer and cationic surfmer are negative value, this means that, micellization process proceeds spontaneously [31, 32].

3.4. Inhibition performance of the synthesized surfactants

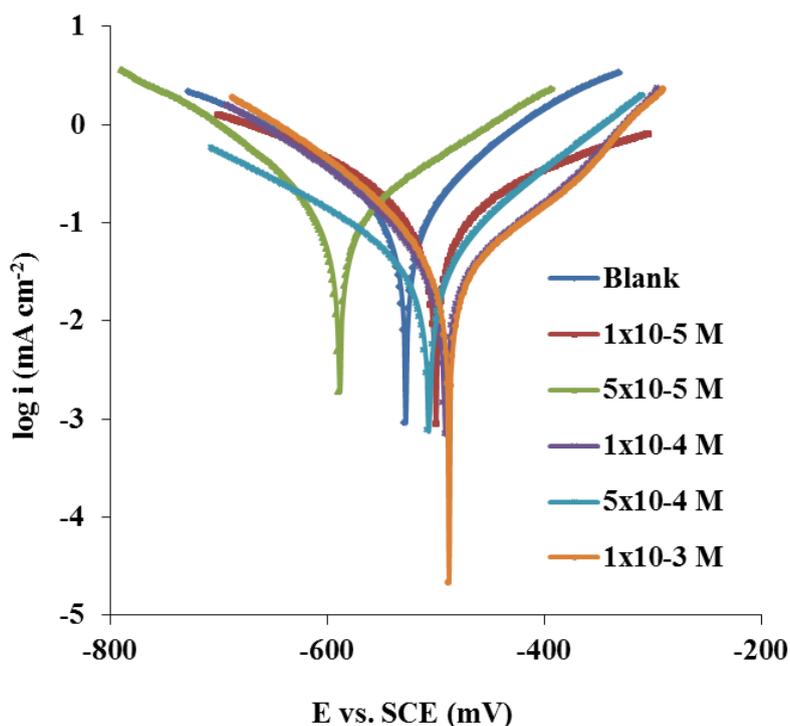


Figure 9. Anodic and cathodic polarization curves for different concentrations of surfmer in 1 M HCl at 25 °C

Electrochemical techniques (polarization and impedance) were carried to evaluate the performance of the prepared cationic surfmer and its oligomer as corrosion inhibitors for tested carbon steel in acidic media (1M HCl). The Potentiodynamic polarization behavior in the Tafel region for tested steel electrode in 1M HCl media in absence and presence of various concentrations of the synthesized surfactants are appeared in Fig. 9 and 10.

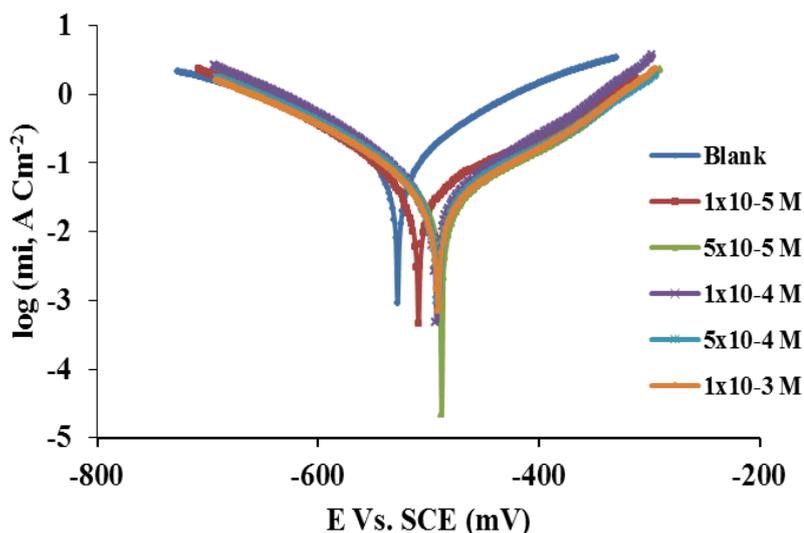


Figure 10. Anodic and cathodic polarization curves for different concentrations of oligomer in 1 M HCl at 25 °C

The corrosion inhibition efficiency ($\eta_p\%$) and surface coverage (θ) of steel corrosion were deliberate using the following equations [33, 34]:

$$\eta_p \% = \left[\frac{i_{corr} - i_{corr}(inh)}{i_{corr}} \right] \times 100 \tag{5}$$

$$\theta = \frac{i_{corr} - i_{corr}(inh)}{i_{corr}} \tag{6}$$

where $i_{corr}(inh)$ and i_{corr} = values of corrosion current density with and without inhibitor respectively. Corrosion current densities were dictated by extrapolation of the cathodic and anodic Tafel slopes to the respective free corrosion potential. The obtained data such as the corrosion potentials (E_{corr}), corrosion current densities (i_{corr}), the anodic and cathodic Tafel slopes (β_a , β_c), surface coverage (θ) and the corrosion inhibition performance percentage ($\eta_p\%$) are given in Table 4.

Table 4. Electrochemical parameters for tested carbon steel electrode in 1M HCl in the absence and presence of different concentrations of synthesized inhibitors at 25 °C

Inhibitors	C (mol L ⁻¹)	E _{corr} (mV)	I _{corr} (mA cm ⁻²)	R _p (ohm.cm ²)	β _a (mV dec ⁻¹)	β _c (mV dec ⁻¹)	θ	η _p (%)
Blank	0.00	-528.8	0.2489	104.02	169.3	-212.0	-	-

Cationic surfmer	1×10^{-5}	-500.2	0.1249	292.25	230.0	-183.3	0.4981	49.81
	5×10^{-5}	-588.9	0.1051	216.55	143.6	-116.3	0.5777	57.77
	1×10^{-4}	-491.4	0.0730	692.08	136.2	-148.6	0.7067	70.67
	5×10^{-4}	-502.5	0.040	755.12	123.4	-185.3	0.8392	83.92
	1×10^{-3}	-488.6	0.0328	640.91	116.4	-138.0	0.8682	86.82
oligomer	1×10^{-5}	-509.3	0.0840	506.27	148.9	-136.0	0.6625	66.25
	5×10^{-5}	-488.0	0.0262	641.74	117.4	-93.7	0.8947	89.47
	1×10^{-4}	-492.6	0.0168	525.47	84.9	-75.9	0.9325	93.25
	5×10^{-4}	-490.4	0.0150	627.98	93.3	-80.9	0.9397	93.97
	1×10^{-3}	-491.4	0.0112	692.08	85.2	-75.2	0.9550	95.50

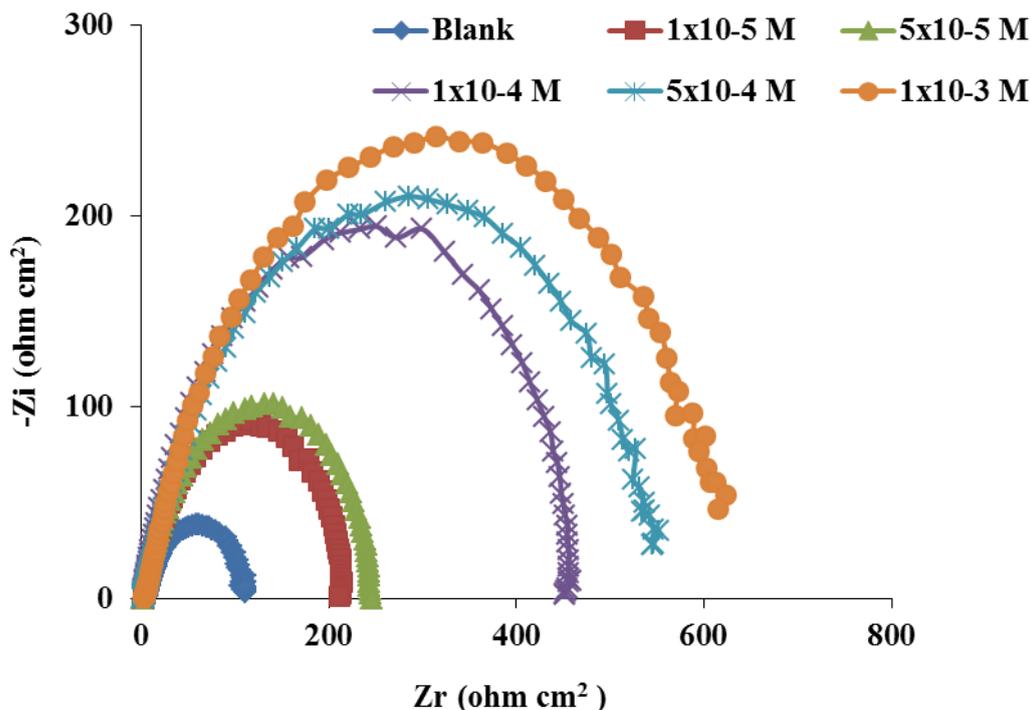


Figure 11. Nyquist plots of carbon steel in 1 M HCl solutions in the absence and presence of different concentrations of surfmer

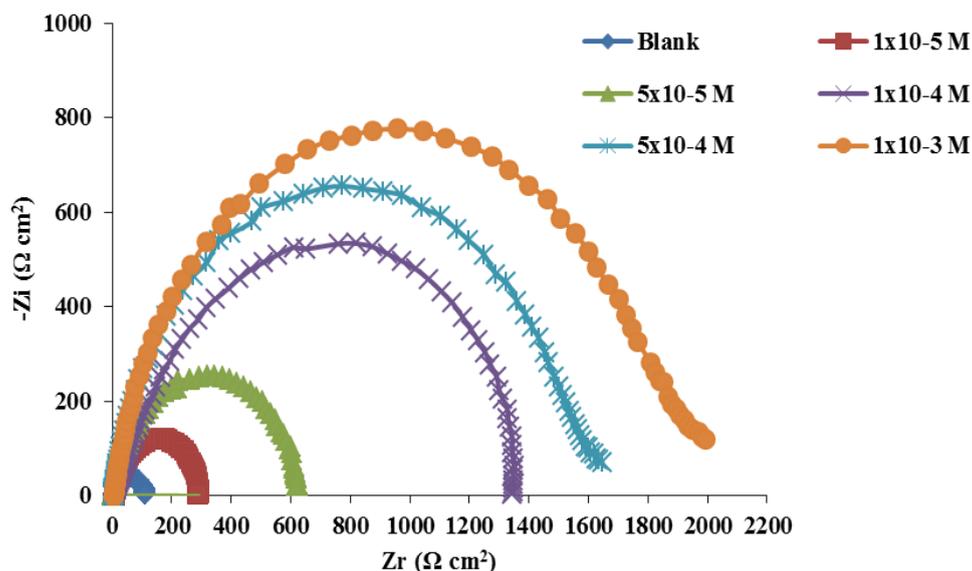


Figure 12. Nyquist plots of carbon steel in 1 M HCl solutions in the absence and presence of different concentrations of oligomer.

Data in Table 4 reveal that, values of β_a and β_c don't indicate evident changes and these outcomes clarify that, the corrosion mechanism for anodic and cathodic reactions doesn't change. It can be observed that, from Fig. 9 and 10, there are the slightly shifted to both positive and negative directions for corrosion potential (E_{corr}) curves in the presence of the cationic and oligomer inhibitors, which mean that, these inhibitors act as a mixed type inhibitor [35-37]. The values of corrosion inhibition efficiencies ($\eta_p\%$) in Table 4 show that, the i_{corr} decreases with increasing surfactant concentrations while η_p increases. This can be related to the adsorption of the inhibitor over both the anodic and cathodic active corroded surfaces.

The electrochemical impedance spectroscopy (EIS) diagrams in the absence and presence of the synthesized surfactants in 1M HCl solution are presented in Figs. 11 and 12, respectively. From Figs. (11, 12), notice that the semicircle diameter in Nyquist plots increased with increasing the inhibitors concentration to confirm the higher protection.

Table 5. EIS parameters for the corrosion of carbon steel in 1 M HCl in the absence and presences of different concentrations of the synthesized cationic surfmer and its oligomer at 25 °C

Inhibitors	C (mol L ⁻¹)	R _s (ohm cm ²)	R _{ct} (ohm cm ²)	C _{dl} (μF cm ⁻²)	η _i (%)
Blank	0.00	6.186	106.9	416.6	-
Cationic Surfmer	1x10 ⁻⁵	4.545	209.7	75.88	49.02
	5x10 ⁻⁵	3.709	242.5	91.84	55.91
	1x10 ⁻⁴	4.543	453.3	55.47	76.14

	5×10^{-4}	4.128	553.5	90.85	80.68
	1×10^{-3}	4.964	626.0	127.1	82.92
	1×10^{-5}	8.77	284.1	44.30	62.22
	5×10^{-5}	4.019	628.7	29.80	83.12
oligomer	1×10^{-4}	17.48	1353	21.04	92.16
	5×10^{-4}	2.07	1609	17.8	93.41
	1×10^{-3}	2.738	1951	15.67	94.56

Table 5 contains on The electrochemical parameters such as double layer capacitance values (C_{dl}), charge transfer resistance values (R_{ct}) and solution resistance (R_s) which obtained from EIS measurements. The corrosion inhibition efficiency (η_I %) in the case of the electrochemical impedance spectroscopy, was calculated from the following equation [38, 39]:

$$\eta_I \% = [\{R_{ct}(inh) - R_{ct}\} / R_{ct}(inh)] \times 100 \quad (7)$$

where $R_{ct}(inh)$ and R_{ct} are the charge transfer resistances in both of presence and absence of inhibitor, respectively. The R_{ct} data of tested carbon steel immersed in aggressive 1M HCl solution containing prepared surfactants increments with increasing the surfactants concentration, which is identified with surface blocking by adsorbed molecules. As clear from Table 5 for all concentrations, charge transfer resistance values (R_{ct}) of oligomer surfactant solutions is higher than cationic surfmer solutions indicating that, the better corrosion inhibition performance obtained by added oligomer surfactant compared to cationic surfmer.

When compared the double layer capacitance values (C_{dl}) of prepared surfactants in HCl solutions by the blank it can noticed that, samples containing synthesized surfactants is lower than ones in blank solution this due to surfactant molecules adsorption on the tested carbon steel surface. Also, the capacitance values in presence of synthesized surfactants decreases with increasing the concentration of cationic surfactants, and this is due to higher replacement of surfactants molecules by water molecules and increasing the thickness of electrical double layer. It can also note that, the values of C_{dl} of oligomer surfactants are less than cationic surfmer.

3.5. Adsorption isotherm

The adsorption of surfactant molecules on metal surface consider the main factor in the corrosion inhibition process in acidic media, which cause block of the metal surface and thus reduce the corrosion process [40]. There are two main types of adsorption, physical adsorption and chemical adsorption. The adsorption process is mainly affected by some factors such as, the type aggressive

solution, charge of the metal, the molecular structure of used inhibitor [41-43]. To describe the adsorption process adsorption isotherms are usually used.

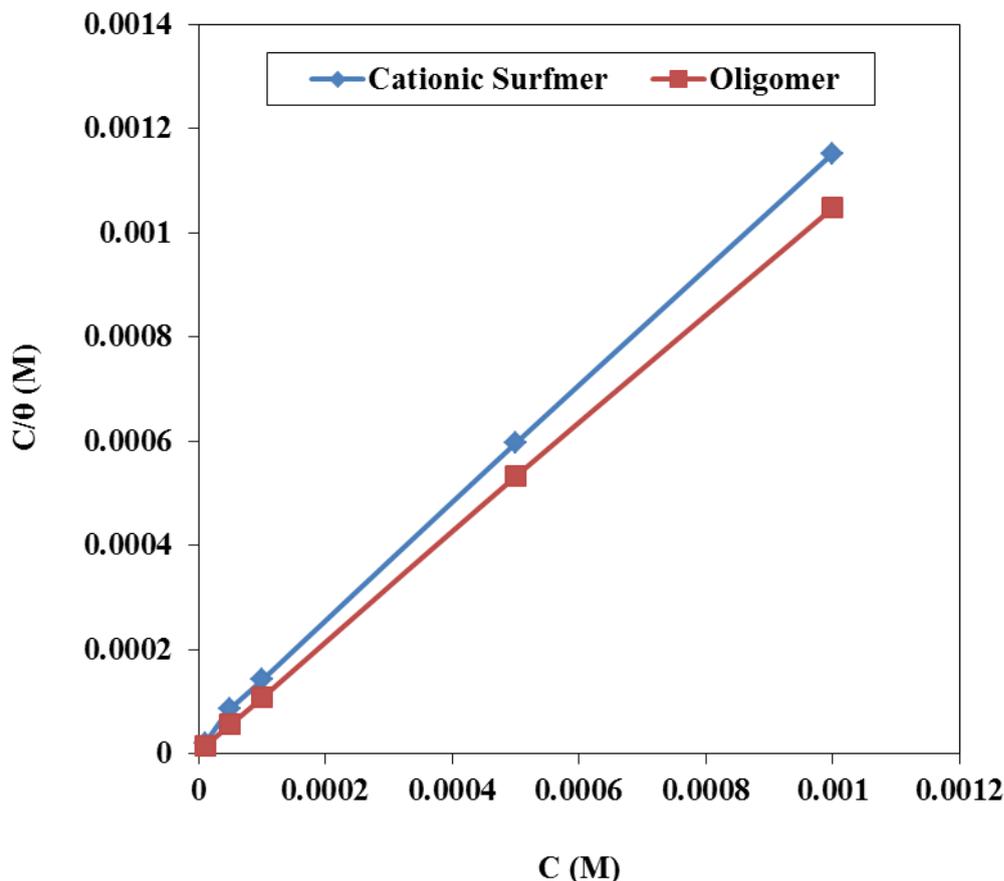


Figure 13. Langmuir isotherm for the adsorption of inhibitors (cationic surfmer and oligomer) on the carbon steel surface in 1 M HCl at 25 °C.

To obtain the adsorption isotherm, the degree of surface coverage (θ) for different concentrations of the synthesized surfactants calculated according to following equation. (8) [44].

The adsorption isotherm relationships of Langmuir [45]:

$$C/\theta = 1/K_{ads} + C \tag{8}$$

where C = inhibitor concentration, θ = degree of surface coverage on the metal surface and K_{ads} = equilibrium constant for adsorption - desorption process related to the standard free energy of adsorption (ΔG_{ads}) by the equation 9 [46]:

$$\Delta G_{ads} = -RT \ln (55.5K_{ads}) \tag{9}$$

where ΔG_{ads} = free energy of adsorption process, K_{ads} = equilibrium constant for adsorption - desorption process, R = gas constant, T = absolute temperature and 55.5 = molar concentration of water. Fig. 13 shows the relationship between C/θ against C of the cationic surfmer and its oligomer. Fig. 13 Plotting yielded a straight line clarify that, the adsorption of cationic surfmer and its oligomer obeys Langmuir isotherm model. The adsorption parameters for studied models were determined, and listed in Table 6.

Table 6. Adsorption isotherm parameters for the synthesized cationic surfmer and its an oligomer in 1 M HCl solution at 293 K.

Inhibitors	R ²	C/θ ~ C, Slope	K (mol ⁻¹)	ΔG _{ads} (kJ mol ⁻¹)
Cationic surfmer	0.9996	1.1326	0.2x10 ⁶	34.48
oligomer	1.0000	1.0448	5.0x10 ⁶	42.46

From this table it can observe that, the value of adsorption equilibrium constant for oligomer is higher than the cationic surfmer this may be due to the easier adsorption of oligomer cationic surfactant on steel. Oligomer surfactant have charge density of head group higher than the cationic surfmer as a result of quaternary cationic head groups in a short distance from each other this lead to increase the electrostatic attraction of surfactant molecules to the solid surface with opposite charges. Because having the oligomer surfactant nearly five alkyl chains in its chemical structure it has difficulty for accommodation in spherical micelle formation and so on, it preferably adsorb at planar surface to a greater extent than its corresponding monomeric counterpart [47]. The higher corrosion inhibition efficiencies of oligomer in comparison to cationic surfmer may be due to the oligomer surfactant easier film formation on steel surface and in much lower concentration.

The large values of ΔG_{ads} around (-33 and -42.46 KJ mol⁻¹) and its negative sign are usually indicate to strong interaction and a high efficient adsorption and adsorption process is spontaneous. When the values of ΔG_{ads} up to 20 kJ mol⁻¹ this mean there are electrostatic interaction between the surfactant molecules and surface (physical adsorption), while those of more negative than -40 KJ mol⁻¹ are associated with chemisorption [48, 49]. Therefore, it can be assumed that, according to value ΔG_{ads} of cationic surfmer (-34.48) and oligomer surfactants (-42.46) the adsorption mechanism on carbon steel surface in 1 M HCl solutions can be described as physical and chemical adsorption but physical adsorption more efficient than chemisorption for cationic surfmer surfactant and chemisorption more efficient than physical adsorption for oligmer surfactant.

3.6. Inhibition mechanism

Steel surface in 1 M HCl is charged with a negative charge because of $E_{\text{corr}} - E_q = 0$ (zero charge potential) < 0, so, it is easy for the positively charged inhibitor to approach the negatively charged carbon steel surface due to the electrostatic attraction [50]. The adsorption of the synthesized surfactants on the metal surface was happen via the quaternary nitrogen atom (N⁺) and counter ion (Br⁻). Quaternary nitrogen atom (N⁺) adsorbed on the cathodic sites to decrease the evolution of hydrogen while the counter ion (Br⁻) adsorbed on the anodic sites to reduce the anodic dissolution. Corrosion performance of the prepared surfactants may be due to presence of more than one adsorption centers, the planarity of compounds and larger molecular size. The oligomer was higher inhibition efficiency than those of the cationic surfmer surfactant at different concentrations; this may be to the higher

molecular size than cationic surfmer surfactant and due to the presence of nearly five quaternary nitrogen atoms and bromide ions in this compound while cationic surfmer has only one quaternary nitrogen atom and one bromide ion [40].

3.7. Quantum calculations

Quantum chemistry has been largely utilized to inhibition mechanism of the metals [51]. There are strong relation between the effectiveness of organic inhibitors and its electronic molecular structure. Some essential quantum parameters, which are directly impact on electronic interaction between the inhibitor and metal surface such as the energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap (ΔE), the number of transferred electrons (ΔN) and dipole moment (μ), are reported in Table 7.

Table 7. Quantum chemical parameters of the investigated cationic surfmer and it are an oligomer.

Compound	$E_{\text{HOMO}}(\text{eV})$	$E_{\text{LUMO}}(\text{eV})$	$\Delta E(\text{eV})$	$\mu(\text{debye})$	ΔN
Cationic Surfmer	-2.85	1.65	4.5	13.54	1.422
oligomer	-1.97	1.12	3.09	2.14	2.127

According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between frontier orbitals (HOMO and LUMO) of reacting species [52]. It has been proved that, higher value of E_{HOMO} (less negative values) of the inhibitor is easy donating electrons to the unoccupied d orbital of metallic iron and lead to higher inhibition performance. From Table 7 the oligomer has high E_{HOMO} value (-1.97) and low E_{LUMO} (1.12) with low energy gap (3.09). In the event that, an inhibitor does not simply offer electrons to the vacant d orbital of metallic iron but however can likewise take the electrons in the d-orbital of metallic iron by using their anti-bonding orbital to form a feedback bond, in this case the inhibitors considered as an excellent inhibitor. It has been exhibited that the lower the E_{LUMO} (E_{LUMO}) level is, the less demanding is the taken of electrons of the d orbital of metallic iron. The inhibiting performance of this inhibitor comes back to their parallel adsorption at the surface of the metal. Presence of one or more active centers in the back bone of inhibitors the main reason for parallel adsorption.

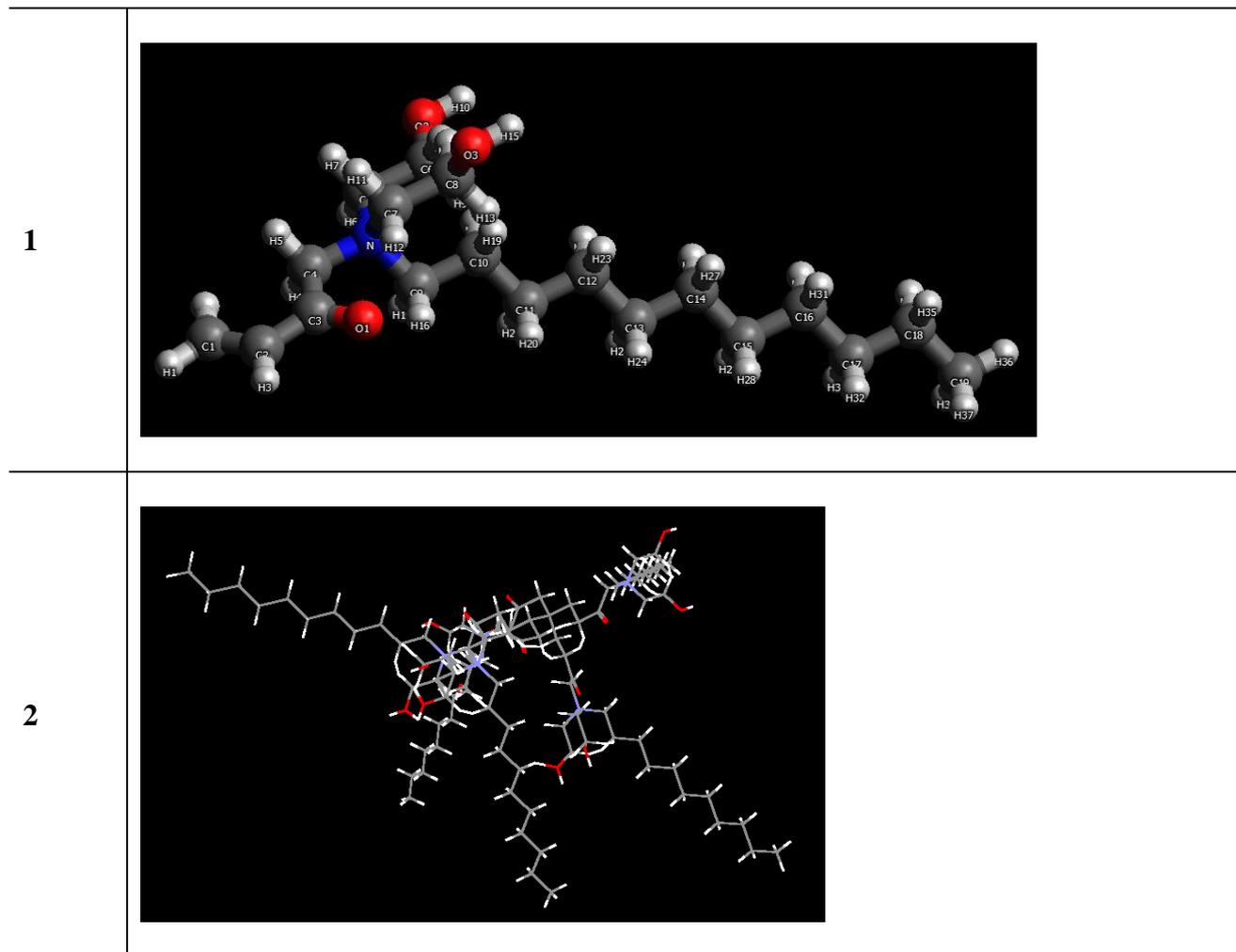


Figure 14. Optimized geometries of the investigated compounds

The molecular adsorption may occur in a manner that, the metal surface and the molecular plane are parallel to each other, and that, in this conformation the interaction is controlled by donation and back donation between the inhibitors and the metal surface. The planar geometry is clear in Fig. 14 and 16. From Fig. 14-16, these molecules have approximately planar structure, which can display the largest contact area between the inhibitor molecules and the steel surface. The number of transferred electrons (ΔN) was also calculated according to Eq. (10)

$$\Delta N = (X_{Fe} - X_{inh}) / [2(\eta_{Fe} - \eta_{inh})] \quad (10)$$

where X_{Fe} and X_{inh} , the absolute electronegativity of iron and the inhibitor molecule, respectively; η_{Fe} and η_{inh} , the absolute hardness of iron and the inhibitor molecule, respectively. These quantities are related to electron affinity (A) and ionization potential

$$X = (I + A) / 2$$

$$n = (I - A) / 2$$

I and A are related in turn to E_{HOMO} and E_{LUMO} . Values of X and η were calculated by using the values of I and A obtained from quantum chemical calculation. The theoretical values of X_{Fe} and η_{Fe} are 7 and 0 eV/mol, respectively.

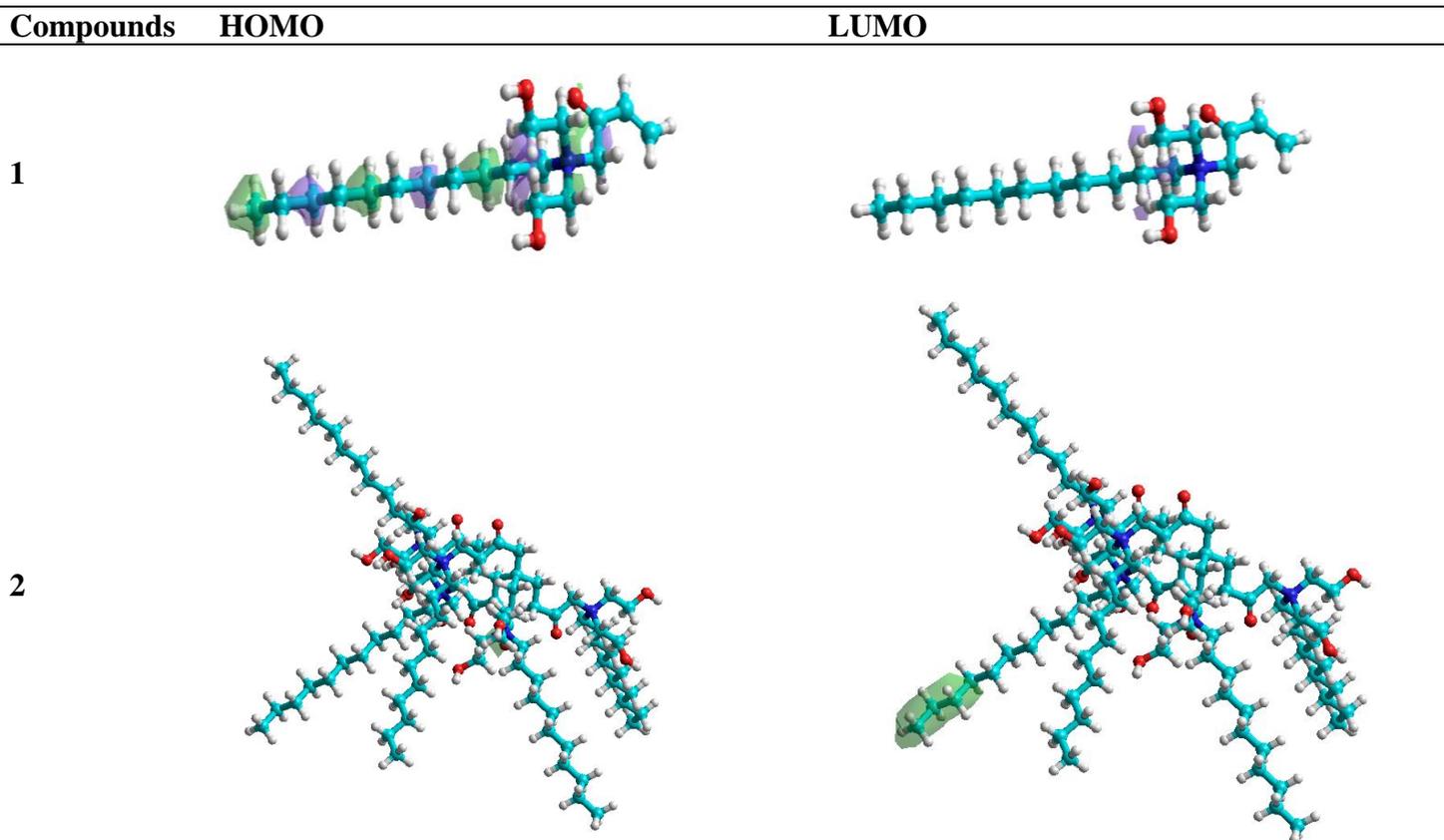
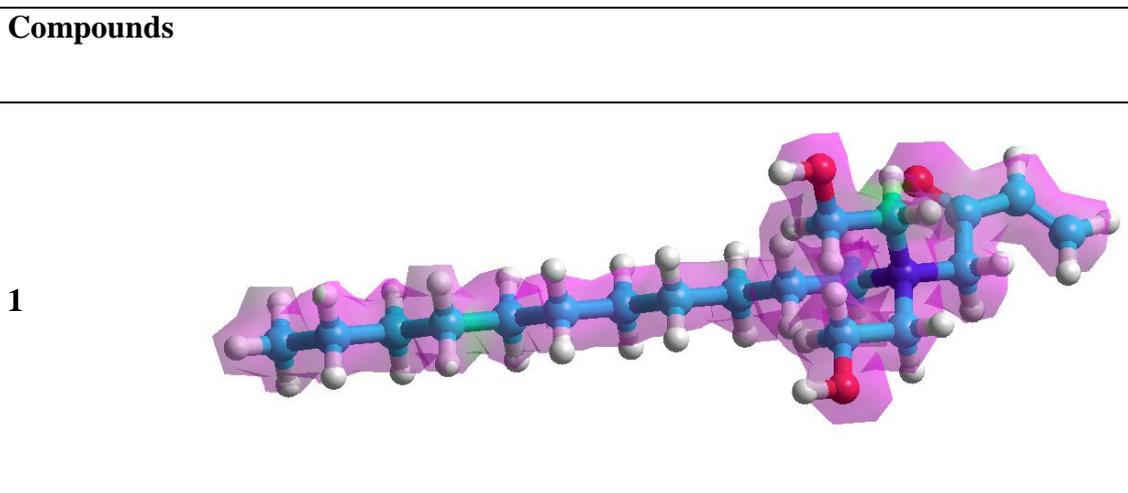


Figure 15. The frontier molecule orbital density distributions of the investigated compounds

According to other reports [52], value of ΔN showed inhibition effect obtained from electrons donation and listed in Table (7). Inhibition performances increment with increasing the values of ΔN . For oligomer surfactants, the greater value of 2.217 indicates the maximum transfer of electrons and hence greater inhibition performance. Another parameter can be used to prognostic the corrosion inhibition mechanism is the dipole moment (μ). Decreases the values of the dipole moment will support the accumulated the surfactant molecules on the metal surface.



2

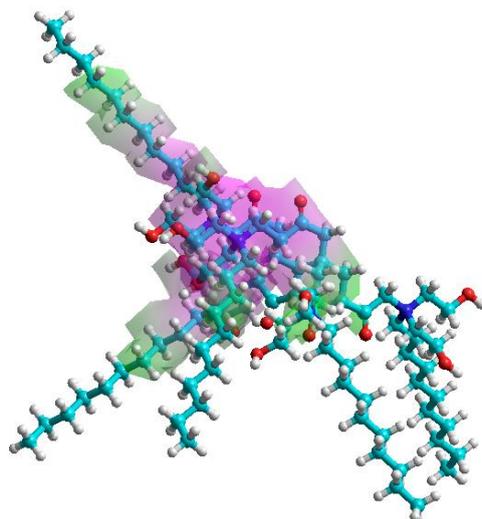


Figure 16. Molecular electrostatic potential map of investigated compounds

4. CONCLUSIONS

1. A Cationic surfmer and its oligomer were synthesized, purified and the chemical structure confirmed by elemental analysis, FT-IR, ^1H NMR and GPC.
2. The newly synthesized surfactants revealed good surface active properties.
3. The inhibition performance of the newly synthesized inhibitors increments with increasing the inhibitors concentration. The high inhibition performance was attributed to adsorption of the compounds on the carbon steel surface.
4. The corrosion inhibition performance of the oligomer surfactant higher than the cationic surfmer surfactant at the same concentration.
5. Polarization measurements show that e the newly synthesized inhibitors acts as a mixed type inhibitor.
6. EIS measurement results indicate that the resistance of the carbon steel electrode greatly increased and its capacitance decreases by increasing the inhibitor concentration.
7. The high inhibition efficiency of the synthesized surfactants against corrosion process is mainly due to both the physical and chemical adsorption. The adsorption is consistent with Langmuir adsorption behavior.

References

1. K. Kerkouche, A. Benchettara and S. Amara, *Mater Chem. Phys.*, 110 (2008) 26.
2. A.M. Al-Sabagh, H.M. Abd-El-Bary, R.A. El-Ghazawy, M.R. Mishrif and B.M. Hussein., *Egypt. J. of Petro.*,20 (2011) 33.

3. M. Khadija Hijazi1, A. M. Abdel-Gaber and G. O. Younes, *Int. J. Electrochem. Sci.*, 10 (2015) 4366 .
4. G. Trabanelli, *Corros.*, 47 (1991) 410.
5. B. Sanyal, *Prog. Org. Coat.*, 9 (1981) 165.
6. S.A.Abd El-Maksoud, *Int. J. Electrochem. Sci.*, 3 (2008) 528.
7. P. Chatterjee, M.K. Benerjee and K.P. Mukherjee, *Ind. J. Technol.* 29 (1991) 191.
8. M. Elachouri, M.S. Hajji, S. Kertit, E.M. Essassi, M. Salem and R. Coudert, *Corros. Sci.*, 37 (1995) 381
9. A. Lgamri, H.A. El Makarimb and A. Guenbour, *Prog. Org. Coat.*, 48 (2003) 63.
10. F. Bentiss, M. Traisnel and N. Chaibi, *Corros. Sci.*, 44 (2002) 2271.
11. A. Popova, M. Christov and S. Raicheva, , *Corros. Sci.* 46 (2004) 1333.
12. M.A. Quraishi and H.K. Sharma, *Mater. Chem. Phys.*, 78 (2002) 18.
13. D. Chebabe, Z.A. Chikh and N. Hajjaji, *Corros. Sci.*, 45 (2003) 309.
14. E. Elayyachy, A. El Idrissi and B. Hammouti, *Corros. Sci.*, 48 (2006) 2470.
15. L. Niu, H. Zhang and F. Wei, et al., *Appl. Surf. Sci.*, 252 (2005) 1634.
16. S. Mohanan, S. Maruthamuthu and N. Kalaiselvi, *Corros. Rev.*, 23(2005) 425.
17. D.P. Schweinsberg and V. Ashworth, *Corros. Sci.*, 28 (1988) 539.
18. A. S. El-Tabei , M. A. Hegazy , A. H. Bedair and M. A. Sadeq, *J Surfact Deterg.*, 17 (2014) 341.
- 19.S. Deng and X. Li, *Corros. Sci.*, 55 (2012) 407.
20. M. Rosen, *J. Colloid Interface Sci.*, 56 (1976) 320.
21. M. Rosen and S. Aronson, *Colloids Surf.*, 3 (1981) 201.
22. M. Rosen, *MittalKL, Plenum Press, New York.* 2(1979) 45.
23. 22. F.K.G. Santos, E.L.B. Neto, M.C.P. Moura, T.N.C. Dantas and A.A.D. Neto, *J. Colloids and Surfaces A: Physicochem. Eng. Aspects*, 333 (2009) 156.
24. T. Azuma, T. Suzuki and K. Hasebe, *US. Pat.*, 6 (2000) 679.
25. R. Zana, *Adv. Colloid Interface Sci.* 97 (2002) 205.
26. Z.X. Li, C.C. Dong and R.K. Thomas, *Langmuir*, 15 (1999) 4392.
27. E. Alami, G. Beinert, P. Marie and R. Zana, *Langmuir*, 9 (1993) 1465.
28. S.M. Hamid and D.C. Sherrington, *J. Brit. Polym.*, 16 (1984) 39.
29. A. M. Badawi, M. A. Hegazy, A. A. El-Sawy, H. M Ahmed and W. M. Kamel, *Mater Chem Phys.*, 124 (2010) 458.
30. A. Samakande, R. Chaghi, G. Derrien, C. Charnay and P.C. Hartmann, *J. Colloid Interface Sci.*, 320(2008) 315.
31. M. A. Hegazy and A. S. El-Tabei, *J Surfact Deterg.*, 16 (2013) 221.
32. M. Stern, *J Electrochem Soc.*, 104(1957) 56.
33. A.M. Al-Sabagh, N.M. Nasser, O. E. El-Azabawy and A. E. El- Tabey, *J. of Molecular Liquids*, 219 (2016) 1078.
34. A.M. AL-Sabagh, M. Elsabee, O.E. Elazabawy and A.E. Eltabey, *J. Dispers. Sci. Technol.*, 31 (2010) 5.
35. A.M. Al-Sabagh , N.Gh. Kandile , N.M. Nasser, M.R. Mishrif and A. E. El-Tabey, *Egypt. J. of Petroleum*, 22 (2013) 351.
36. A.M. Al-Sabagh , N.Gh. Kandile , N.M. Nasser and A. E. El-Tabey, *Chem. Eng. Communications*, 202(2015)1335.
37. Z.B. Stoynov, B.M. Grafov, S. B. Savova and V.V. Elkin, *Electrochemical Impedance.* Nauka, Moscow (1991).
38. A. Popova, M. Christov and A. Vasilev, *Corros Sci.*, 53 (2011) 1770.
39. M . Motamedi, A.R. Tehrani-Bagha and M. Mandavian., *Electrochimica Acta.*, 58 (2011) 488.
40. E.L. Bettini, *Nova Science Publisher, Inc.*, 2007, Chapter 5.
41. F. Bentiss, C. Jama, B. Mernari, H. El Attari, L. El Kadi, M. Lebrini, M. Traisnel and M. Lagrenée, *Corros. Sci.*, 51 (2009) 1628.

42. I.B. Obot, N.O. Obi-Egbedi and S.A. Umoren, *Int. J. Electrochem. Sci.* 4 (2009) 863.
43. M. Mahdavian and S. Ashhari, *Electrochim. Acta.*, 55 (2010) 1720.
44. Zh. Tao, Sh. Zhang and W. Li, B. Hou, *Ind. Eng. Chem. Res.*, 49 (2010) 2593.
45. M. Motamedia, A.R. Tehrani-Baghaa, and M. Mahdavian, *Electrochimica Acta* 58 (2011) 488.
46. O.K. Abiola, *Corros. Sci.*, 48 (2006) 3078.
47. M. Bouklah, B. Hammouti, M. Lagrenee and F. Bentiss, *Corros. Sci.*, 48 (2006) 2831.
48. M.S. Morad, *J. Appl. Electrochem.*, 38 (2008) 1509.
49. M. J. Bahrami, S.M. A. Hosseini and P. Pilvar, *Corros. Sci.*, 52 (2010) 2793.
50. K. Fukui, Theory of orientation and stereo selection, *Springer-Verlag*, New York (1975).
51. E. Scrocco, J. Tomasi, Topics in Current Chemistry, *Springer: Berlin* (1973).
52. P. Politzer, D. G. Truhlar, Chemical Applications of Atomic and Molecular Electrostatic Potentials, *Plenum: New York* (1981).

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