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Evaluation of Cationic Surfactant Benzalkonium Chloride as inhibitor of Corrosion of Steel in presence of Hydrochloric Acid Solution

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Article Info

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Abstract

Cationic surfactant Benzalkonium chloride was evaluated as inhibitor for carbon steel in presence of 1.0 M HCl by different methods like Chemical Method (Weight loss) or Electrochemical Impedance Spectroscopy (EIS), Potentiodynamic polarization and Electrochemical Frequency Modulation (EFM). The effect of temperature on the corrosion rate was evaluated. Tafel polarization proofed that the surfactant act as mixed type inhibitor. Langmuir's adsorption isotherm was the preferable fitted isotherm. The results showed that the efficiency of the investigated surfactant increases with raising both concentration and temperature. The thermodynamic parameters of activation and adsorption were calculated and discussed. The surfactant's adsorption led to a reduction of the double layer capacitance (C_{dl}) and an increase in the charge transfer resistance (R_{ct}). Quantum Chemical Technique has been employed to discuss the inhibition efficiency by effectiveness of molecular structure of investigated surfactant. The various techniques which used have inhibition efficiency (IE) with the same trend.

Keywords: Corrosion Inhibition; Carbon Steel; HCl; Cationic Surfactant; Benzalkonium Chloride.

Introduction

Carbon steel is a material which has several applications in various directions according to its advantages in low cost and availability. But the challenge which is faced by researchers is its ability to destructive (corroded) easily which costs high financial burden to avoid or treatment it in industry, according to its important role in national economic development [1-3]. Corrosion operation is natural and costly process which destruct the metal via several reasons either chemical, electrochemical or biological agents between the metal and its medium, such as corrosion of iron in presence of moist air, will oxidize into metal oxide, corrosion of zinc when reacts with dilute sulfuric acid, and corrosion of magnesium in the presence of alcohols [4]. Corrosion of metals occurs usually in presence of many factors such as oxygen, aggressive medium and moisture, where two electrochemical reactions occur oxidation at anodic site and hydrogen evolution at the cathodic site [5-7]. There are different forms of corrosion such as general (uniform), atmospheric, galvanic, differential aeration, pitting, stress-corrosion cracking, intergranular, and erosion corrosion [8-11]. Also there are factors that influence the corrosion of metal such as reactivity of the metal, nature of surrounding environment, existence of impurities, nature of oxide, presence of CO_2 in nature water, aeration and pressure [12]. Methods of prevention based on metal, environment, coating and cathodic protection [13] from the effective protection methods for corrosion of metals is using surfactants anionic, cationic or non-anionic

surfactants [14,15]. This category of organic corrosion inhibitors characterized by their high ability to absorb on the metal surface or interface which lead to its inhibition efficiency [16,17]. In our study, we investigate the effect of a novel cationic surfactant Benzalkonium chloride on the corrosion of carbon steel in presence of 1 M-HCl by several methods either chemical (weight loss) method, electrochemical method (Potentiodynamic Polarization, Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Frequency Modulation (EFM), and also estimated it via quantum calculations, the adsorption isotherm of the investigated surfactant was appreciated.

Materials and Methods

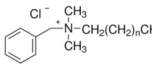
Materials

Tests were performed on carbon steel of the following composition (weight %): 0.15–0.20% C, 0.60–0.90% Mn, 0.04% P, 0.05% S, and the remainder Fe.

Surfactant: Surfactant which used in this research obtained from Fluka product of pure quality (97%), the chemical structure, molecular formula, and systematic name of the investigated surfactant are listed in table 1.

Solution: 1M hydrochloric acid solution used as corrosive medium which was prepared using double distillated water and was standardized by sodium carbonate. All chemicals used were of analytical grade reagents. All experiments were carried out under unstirred and aerated conditions.

Table 1. The name and molecular structure of the investigated surfactant.

Name of Surfactant	Chemical structure	Molecular Formula	Systematic name
Benzalkonium Chloride		$C_6H_5CH_2N(CH_3)_2RCl$ (R=C_8H_{17} to $C_{18}H_{37}$)	Benzyldimethyldode cylammonium chloride

Different experimental methods were used to calculate the inhibition efficiency of these surfactants these are:

Chemical method (weight loss)

Weight loss experiments carried out by Seven rectangular specimens bar of carbon steel of dimensions 2 cm × 2 cm × 2 cm were abraded using successive grades of sand papers (80-1200) before each test, then degreased using acetone, rinsed by double distilled water, dried through two filter papers and precisely weighed, then were totally immersed in blank and different concentrations (50,100,150,200,250,300) ppm. After equal time intervals, the samples were taken out of the solutions and washed out with double distillated water, dried through filter papers and reweighed, then average weight loss at a certain time was determined. The inhibition efficiency (IE) and degree of surface coverage (θ) can be calculated from Eq.1 [18].

- $\%IE=[1-(\Delta W_{inh}/\Delta W_{free})] \times 100=\theta \times 100$ Eq.1
- Where ΔW_{inh}, ΔW_{free} are weight losses in presence and absence of inhibitor, respectively.

Electrochemical methods

Glass cell consists of three electrodes used (Figure 1), the working electrode made of squared carbon steel (10 × 10) mm cut from the original bar used in weight loss method, the exposed surface area to the test solution was 1.0 cm^2 (Figure 2). The reference electrode was a saturated calomel electrode (SCE) and the counter electrode used was platinum sheet (1 cm^2). Luggin capillary is connected to a reference electrode to diminish the effect of potential drop (IR drop) and the tip of Luggin capillary to be very close to the surface of the electrode. All potential values were evaluated versus saturated calomel electrode (SCE), in open air at 25°C ± 1°C. The electrode must be prepared before every experiment as well as weight loss method, and then leave it for 30 min before starting measurements to stabilization; the measurements were carried out using Gamry instrument PC14G750 potentiostat/Galvanostat/ZRA which includes Gamry frame work system which based on ESA400. Gamry applications contain DC105 software for DC corrosion measurements, EIS 300 Software for electrochemical impedance spectroscopy and EFM140 software for electrochemical frequency modulation measurements a long with a computer for collecting data Echem analyst 6.03 software was utilized for plotting, graphing and fitting data [19].

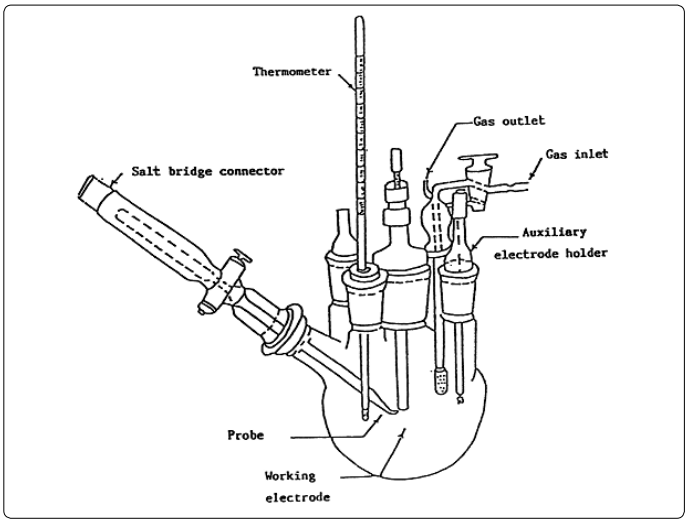


Figure 1. The electrochemical cell.

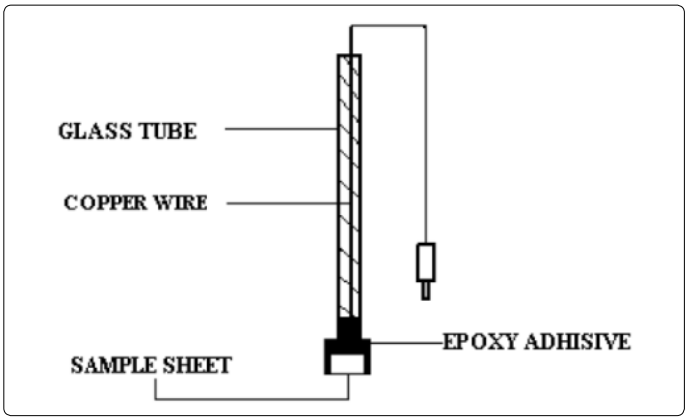


Figure 2. The Working electrode used in the electrochemical techniques.

Potentiodynamic polarization: The electrode potential scanning from (-1000 to 0.0 mV_{SCE}) was done spontaneously to get Tafel polarization graphs at open circuit potential at scan rate of 1 mVS^{-1}. By using Stern-Geary method corrosion current was calculated via extrapolation of anodic and

cathodic Tafel lines of charge transfer controlled corrosion reactions to a point which gives log i_{corr} and the corrosion potential (E_{corr}) for the free acid and for each concentration of surfactant from which surface coverage (θ) and inhibition efficiency (%IE) can be calculated [20].

$$\%IE=[1-(i_{corr(inh)}/i_{corr\ (free)}] \times 100=\theta \times 100 \quad \text{Eq.2}$$

Where $i_{corr(free)}$ and $i_{corr\ (inh)}$ are the corrosion current densities in absence and presence of surfactant, respectively.

Electrochemical impedance spectroscopy (EIS): These measurements were carried out using ac signals at open circuit potential in the frequency range 10 kHz to 0.5 kHz with amplitude of 5 mV peak to peak. The main parameters obtained from the analysis of Nyquist diagram are the charge transfer resistance R_{ct} (diameter of high frequency loop) and double layer capacity C_{dl} which calculated as the following

$$C_{dl}= 1/ (2\pi f_{max} R_{ct}) \quad \text{Eq.3}$$

Where f_{max} is maximum frequency. So the surface coverage can be calculated from eq.4.

$$\%\ IE=1-(R^1_{ct}-R_{ct}) \times 100=\theta \times 100 \quad \text{Eq. 4}$$

Where R_{ct}^1 and $_{ct}R$ are the value of charge transfer resistance in absence and presence of inhibitor surfactant [21].

Electrochemical frequency modulation (EFM): By applying two various frequencies 2 and 5 Hz in electrochemical frequency modulation technique. The base frequency was set to be 0.1 Hz, so that one second is elapsed time for the current wave form. The designated current responses for harmonically and inter modulation current peaks can be obtained from the intermodulation spectra. Via larger peaks, the corrosion current density (i_{corr}), was calculated the Tafel slope (βc and βa) and the causality factors CF2 & CF3 [22].

Quantum calculations

Molecules investigated by using DMol3 module in materials studio version 7.0. Inside DMol3 module, where a basis set of double number polarization (DNP) plus the exchange correlation functions of Becke one parameter (BOP) with generalized gradient approximation (GGA) were performed and the solvent effects were treated using COSMO controls [23].

Results and Discussion

Weight loss measurements

Weight loss measurement is effective method to measure the attitude of inhibitor on corrosion of different metals in aqueous environment by using aggressive electrolyte and different time of exposure. From which corrosion rate can be estimated according to Eq.1. The effect of addition of different surfactants on the dissolution rate of carbon steel in 1 M HCl was studied at 25–40°C by plotting the weight loss (mg cm^{-2}) versus time (min). It can been seen from the resultant linear curves shown in figure 3, which represent that the weight loss curves in case of the solutions containing investigated surfactant, curve fall below in case of the free acid, which can be explained by formation of insoluble layer resulting from the adsorption of surfactant compounds on the carbon surface. In the investigated surfactant the inhibition efficiency increases with increasing its concentration reach to 96.7% at 300 ppm at 25°C the results of surface coverage and inhibition efficiency of the concentrations of studied surfactant at 25°C are listed in table 2, which result from the fact that the adsorption of surfactant on mild steel increases with increase of this surfactant. Thus the carbon steel surface is separated from the surrounding by high efficiency via formation of a film on its surface.

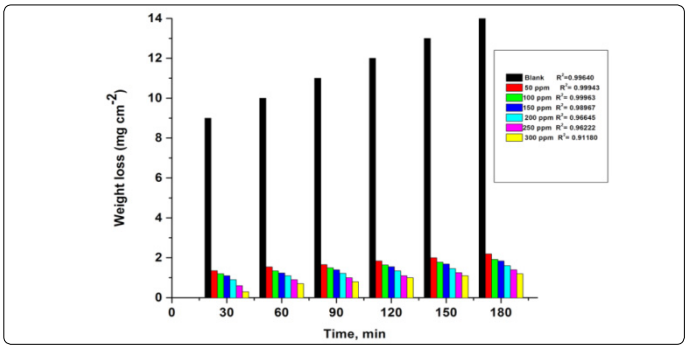


Figure 3. Plots of weight-loss vs time for carbon steel in 1 M HCl in case of the free acid and in presence of with different concentrations of Benzalkonium Chloride at 25 ± 2°C.

Table 2. List of surface coverage (θ) and inhibition efficiency (%IE) values obtained from weight loss experiment after 180 min immersion in presence of various concentrations of surfactants for carbon steel 1M HCl at 25ºC.

C[inh]. ppm	Benzalkonuim chloride	
	θ	%IE
50	0.850	85.0
100	0.867	86.7
150	0.878	87.8
200	0.900	90.0
250	0.933	93.3
300	0.967	96.7

Potentiodynamic polarization measurements

Electrochemical corrosion measurements are very useful method for measuring the corrosion of metals in corrosive mediums. A plot of current potential of an electrode can be measured quickly in a few minutes and accurately. In immersing a carbon steel electrode in a corrosive acid medium, redox reaction will take place on its surface. The carbon steel oxidizes (corroded) and the medium is reduced. So the hydrogen ions are reduced. The electrode of carbon steel (working electrode) could act as both anode and cathode, and both anodic and cathodic currents flow on its surface. The electrode considers as a potential (relative reference electrode) termed as the corrosion potential (E_{corr}) when immersed in a corrosive medium without connection to any instrumentation. The carbon steel electrode at E_{corr} has both anodic and cathodic currents occurs on its surface when these currents are exactly equal in magnitude so there is no net current to be measured hence the carbon steel electrode is at equilibrium with medium. So the definition of E_{corr} is the potential at which the rate of oxidation is exactly equal to the rate of reduction. By plotting the external current response as

a function of the applied potential the polarization characteristics can be measured experimentally. So the calculated current can differ over several orders of magnitude, the log current function is plotted vs. potential on a semi–log chart which called potentiodynamic polarization plot, in which Tafel plot was used and can provide a direct measure of corrosion current and corrosion rate. Figure 4 represents the polarization curve for corrosion of carbon steel in 1 M HCl in the absence and present of surfactant A at 25°C which indicated that the presence of surfactants shift the anodic polarization to more positive and the cathodic polarization to more negative values. By using the potentiodynamic polarization measurements, the values of the surface coverage (θ) and inhibition efficiency (%IE) can be calculated by using Eq.2, The values of the electrochemical polarization parameters and the inhibition efficiency (% IE) percentage are given in table 3 from which deduced that; the resultant anodic and cathodic curves apply to Tafel type behavior. In presence of surfactants there is an increase in both cathodic and anodic over voltage and caused parallel displacement to the more negative and positive values, respectively. The parallel cathodic and anodic Tafel curves confirmed the evolution of hydrogen gas is activation controlled and the reduction and dissolution mechanism experienced constant in presence of surfactant. From which it can conclude that they behave as mixed mode inhibitors for corrosion of carbon steel in 1 M HCl solutions, as it may be adsorbed on the cathodic sites of carbon steel and reduce the evolution of hydrogen. Also these surfactants adsorbed on the anodic sites through the lone pairs of electrons of hetero atoms which could reduce the anodic dissolution of carbon steel. The value of corrosion current density (i_{corr}) decreases as the surfactant concentration increases, so the dissolution rate of carbon steel in 1 M HCl solution decreases in investigated surfactant and the inhibition efficiency is dependent on the concentration and the type of surfactant present, while no definite trend was observed in the shift of E_{corr} values, but the Tafel slopes (βa, βc) are approximately constant indicating that the retardation of the two reactions (cathodic hydrogen reduction and anodic metal dissolution) were affected without changing the dissolution mechanism. By using this method the inhibition efficiency of the studied surfactant reached to 90.4% at 300 ppm.

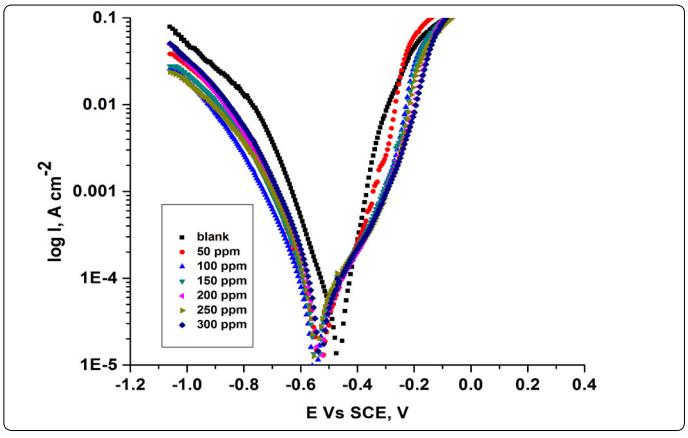


Figure 4. Polarization curves for corrosion of carbon steel in 1 M HCl in the absence and presence of Benzalkonium Chloride at 25°C.

Table 3. Influence of Benzalkonium Chloride concentrations on corrosion parameters of carbon steel in 1M HCl at 25°C.

Conc	i_{corr}	E_{corr}	β_a	β_c	k_{corr}	θ	I.E%
	μA cm^{-2}	mV	mV dec^{-1}	mV dec^{-1}	mpy		
Blank	20.0	510	95	132	102.00		
50	3.5	489	69	92	17.03	0.841	84.1
100	3.3	500	75	102	15.14	0.850	85.0
150	3.0	506	82	116	14.32	0.863	86.3
200	2.8	497	96	104	13.53	0.869	87.9
250	2.5	506	86	100	12.90	0.878	88.8
300	2.2	494	87	113	11.49	0.904	90.4

Electrochemical impedance spectroscopy (eis) measurements

Electrochemical impedance spectroscopy (EIS) or AC impedance method is a measure of the ability of a circle to resist the flow of electrical current, which is measured by applying an AC potential to an electrochemical cell and to evaluate the current through the cell. The AC impedance instrument can record the real (resistance) and imaginary (Capacitance and inductance) components of the impedance response of the system. This method can give information which cannot be obtained from DC techniques also can be used in multiple electrochemical reactions so it had seen wide increase in last recent years. Electrochemical impedance can be analyzed by measuring an equivalent circuit model as shown in figure 5 for carbon steel, which consists of solution resistance R_s and soluble layer capacitance C_{dl} which is placed in parallel to the charge transfer resistance. According to the shape of the EIS spectrum, a circuit model or circuit description code and initial circuit parameters are evaluated and input by the operator. The type of electrical components in the circuit model and their interconnections control are the factors which govern the shape of the model's impedance spectrums but the model's parameter (resistance value of resistor) effect on the size of each feature in the spectrum both of these factors influence on the degree to which the model's impedance spectrum confirm with the measured EIS spectrum. By using EIS method the corrosion behavior of carbon steel in 1 M HCl solution in absence and presence of different concentrations of studied surfactants are investigated at 25°C. For example figure 6 shows the Nyquist plots (A) and Bode plots (B) for corrosion of carbon steel for investigated surfactant. The Bode diagrams characterized by two time constants consisting of large capacitive loop at high to medium frequency and inductive loop at low frequency. The high frequencies of capacitive loop represent the double layer electric layer. The large capacitive loop makes an angle with the real axis and its interaction gives a resistance of solution (Rs) between the working electrode and the counter electrode a relaxation process obtained by adsorption species onto the electrode surface may be attributed by the presence of inductive loop. In 1 M HCl with the presence of different concentrations of inhibitors (surfactants), the impedance diagrams showed the same trend (one capacitive loop), but the diameter of this capacitive loop increases with increasing concentration. Nyquist plots include various electrochemical parameters such as; the diameter of high frequency loop

(charge transfer resistance R_{ct}), the double layer capacity C_{dl} which can be calculated by using Eq.3. The inhibition efficiency and surface the values of impedance data in table 4, it can be conclude that; R_{ct} directly proportional to the concentration of surfactant used but inversely proportional to the corrosion rate, by increasing the concentration of surfactant, the value of C_{dl} be very small, due to formation of a thin protective layer on the metal surface which lead to decrease in the local dielectric constant of the metal solution interface. The %IE obtained from EIS close to the results obtained from the potentio dynamic measurements for this surfactant reached to 88.2% at 300 ppm.

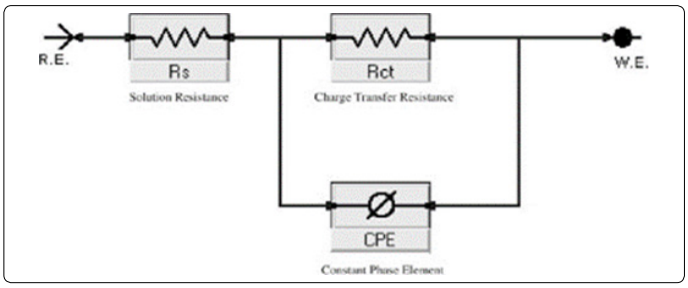


Figure 5. The electrical circuit model used to fit experimental EIS data which obtained from carbon steel electrode in 1 M HCl.

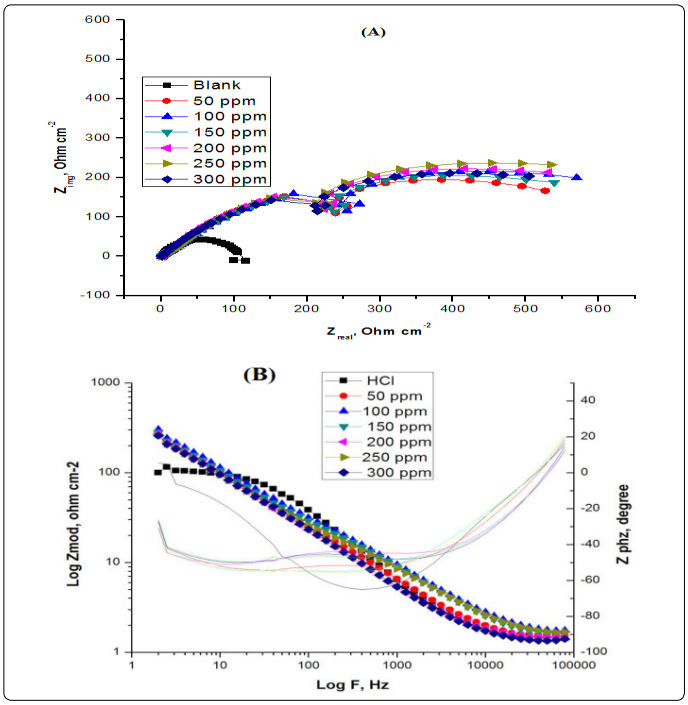


Figure 6. EIS Nyquist plots (a) and Bode plots (b) of carbon steel in 1 M HCl in absence and presence of Benzalkonium chloride at 25°C.

Table 4. EIS parameters for the corrosion of carbon steel in 1M HCl in the absence and presence of different concentrations of Benzalkonium Chloride at 25°C.

Conc	R_{ct}	C_{dl}	θ	%I.E
ppm	Ohm cm^2	μF cm^{-2}		
Blank	104.7	19.4		
50	598.2	0.6	0.825	82.5
100	631.9	0.4	0.834	83.4
150	716.5	0.4	0.854	85.4
200	737.0	0.3	0.858	85.8
250	886.1	0.2	0.882	88.2
300	888.9	0.4	0.882	88.2

Electrochemical frequency modulation (EFM)

EFM or electrochemical frequency modulation can be defined as non–destructive corrosion method which directly gives values of corrosion current without prior knowledge of Tafel constants, by applying one or more sine waves a potential perturbation occurs and the current responses at higher frequencies than the frequency of the applied signal such as at zero harmonic and intermodulation frequencies. By using the resultant spectrum of current responses, EFM measurements can be explained as current response considered as a function of frequency [intermodulation spectrum] and examples for the effect of addition of various concentrations of surfactant (50–300 ppm) to 1 M HCl solution for carbon steel are shown in figure 7, also the EFM spectrum for carbon steel in 1 M HCl at 25°C is shown in figure 8. The spectrum includes current responses refers to harmonically and intermodulation current peaks, the corrosion current density (i_{corr}) calculated from the larger peaks the Tafel slopes (βc and βa) and the causality factors (CF–2 and CF–3), all these electrochemical parameters were determined and listed in table 5, which showed that the corrosion current densities of carbon steel decrease with increasing of the investigated surfactants, and the highest value of current density was recorded in the free acid.

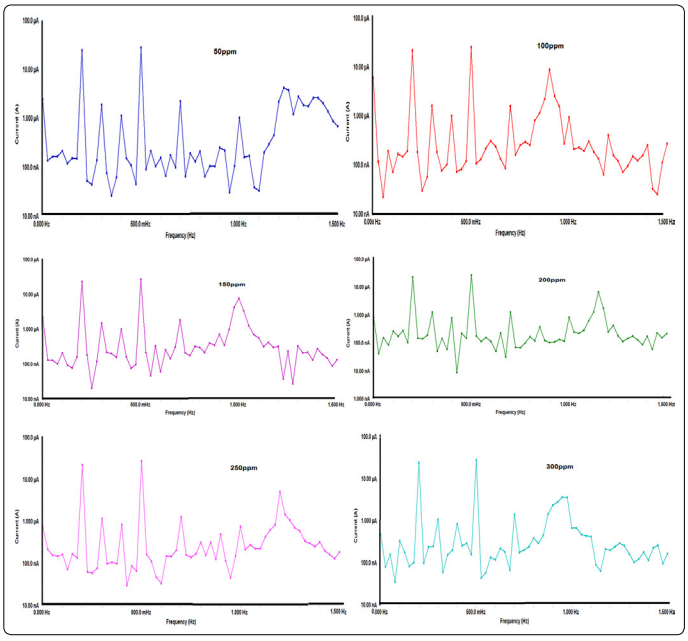


Figure 7. EFM spectra of carbon steel immersed in test solution of 1 M HCl and treated with different concentrations of Benzalkonium chloride at 25°C.

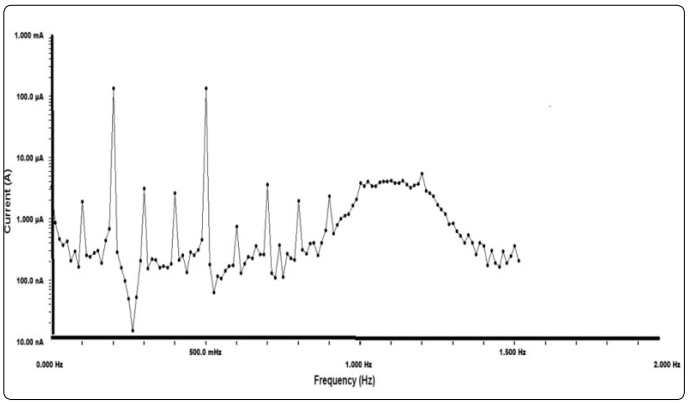


Figure 8. EFM spectrum for carbon steel in 1 M HCl at 25°C.

Table 5. EFM data for corrosion of carbon steel in 1M HCl solutions containing different concentration of Benzalkonium Chloride at 25°C.

Conc	i_{corr}	Ba	Bc	CF 2	CF 3	C.R	θ	%I.E
ppm	μA cm^{-2}	mV dec^{-1}	mV dec^{-1}			Mpy		
Blank	159	73	80	1.05	5.21	72.64		
50	14.14	62	89	1.92	1.68	25.53	0.911	91.1
100	13.88	34	40	1.64	8.23	17.89	0.913	91.3
150	13.16	82	123	1.88	3.96	13.77	0.917	91.7
200	13	11	179	1.57	1.19	12.60	0.918	91.8
250	12	44	503	1.53	14.37	8.36	0.926	92.6
300	11	61	730	1.65	5.83	6.34	0.933	93.3

Adsorption isotherm

Addition of inhibitors to corrosive solutions, they can form protective layer on the metal's surface (metal/solution) interface. Adsorption of inhibitor molecules can be categorized into four classes; Electrostatic attraction between charged inhibitor molecules and changed metal surface, Interaction of unshared electron pairs on the inhibitor molecules in the vacant orbital of metal, Interaction of electrons with the metal, Combination of them.

In the present work, the adsorption process obeys Langmuir adsorption isotherm;

$$(C_{inh}/\theta) = (1/K_{ads}) + C_{inh} \quad \text{(Eq. 5)}$$

Where C_{inh} is the inhibitor concentration, θ is the surface coverage fraction, K_{ads} is modified adsorption equilibrium constant.

$$K_{ads} = [1/C_{solvent}] \exp [-\Delta G^{\circ}_{ads}/RT] \quad \text{(Eq. 6)}$$

Where $C_{solvent}$ is the molar concentration of solvent which in the case of the water 55.5 $mol.L^{-1}$.

Graphical representation of (C/θ) as a function of the concentration of surfactant are shown in figure 9, from which ΔG°_{ads} can be calculated from equation (Eq.6).

The degree of surface coverage (θ) was calculated from weight loss experiments by using Eq. 5. The regression coefficient R^2 is greater than 0.9 which apply to the obtained results in table 6 which show the values of K_{ads} and ΔG°_{ads} obtained from Langmuir isotherm and all results thermodynamic parameters, the heat of adsorption (ΔH°_{ads}) can be calculated by using Van't Hoff equation.

$$\text{Log } K_{ads} = (-\Delta H^{\circ}_{ads}/2.303RT) + \text{Constant} \quad \text{(Eq. 7)}$$

To calculate the value of (ΔH°_{ads}), log K_{ads} was plotted against 1/T as shown in figure 10, the slope of the obtained straight lines equivalent to ($-H^{\circ}_{ads}$/ 2.303R).

Hence, (ΔS°_{ads}) the entropy of adsorption can be evaluated at all temperatures by using equation.

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \quad \text{(Eq. 8)}$$

The negative values of ΔG°_{ads} represented in indicated that the adsorption of surfactants are spontaneously proceed on the surface of carbon steel, as when the values of ΔG°_{ads} of order –20 $kjmol^{-1}$ or less indicates that the adsorption is physicorption but on the other hand, when the values of ΔG°_{ads} reaches –40 $kjmol^{-1}$ or greater this indicates to be chemisorption.

In this study as listed in table 6, ΔG°_{ads} has negative sign and less than –20 $kjmol^{-1}$, which indicated that the mechanism of adsorption of surfactants on carbon steel in 1M HCl at the studied temperatures may proceed by electrostatic attraction (physisorption), by increasing temperature of the test solution, the free energy change (ΔG°_{ads}) become less negative and the inhibitor molecules desorbed from the metal surface as the reaction temperature increases.

The negative sign of ΔH°_{ads} suggests that, the adsorption of surfactants accompanies by exothermic process but exothermic adsorption process can be physisorption or chemisorption, while endothermic process is typical to chemisorption. So the value of ΔH°_{ads} must be calculated to differentiate between physisorption and chemisorption as if the value of ΔH°_{ads} up to 41.9 kj mol^{-1}, is correlated to the electrostatic attraction between the charged molecules and charged metal (physisorption), but if the values of ΔH°_{ads} approach or greater than 100 kj mol^{-1} are correlated to be (chemisorption). In case of studied surfactants, the obtained values of enthalpy ΔH°_{ads} is correlated to physisorption mechanism. The negative values of (ΔS°_{ads}) indicate the ordered of inhibitor molecules on carbon steel surface in presence of investigated surfactants.

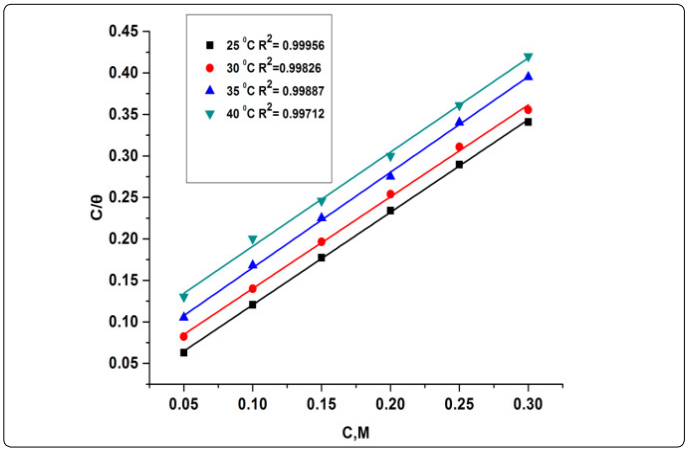


Figure 9. Plots of adsorption isotherm of Langmuir as C/θ versus C of Benzalkonium Chloride on carbon steel surface in 1 M HCl at different temperatures.

Table 6. List of thermodynamic adsorption parameters of Benzalkonium Chloride on carbon steel surface in 1 M HCl at different temperatures.

Temp. K	K ads M^{-1}	$-\Delta G_{ads}$ kj mol^{-1}	$-\Delta H_{ads}$ kj mol^{-1}	$-\Delta S_{ads}$ J mol^{-1} K^{-1}
298	11.4	16.0	20.1	13.7
303	17.6	17.0	20.9	12.8
308	33.9	18.7	22.1	11.2
313	12.9	16.3	21.7	17.4

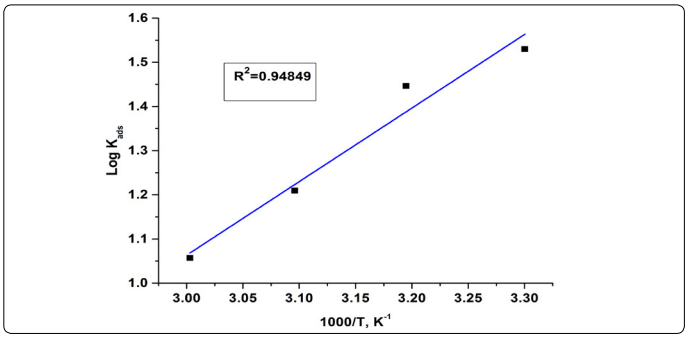


Figure 10. (log K_{ads}) versus (1000/T) curve for the dissolution of carbon steel in 1 M HCl in the presence of Benzalkonium Chloride.

Effect of temperature

The effect of temperature on inhibition efficiency of this surfactant on carbon steel in 1M HCl was studied firstly by using weight loss methods on range (25-40)°C, the results showed that the inhibition efficiency of the surfactant decreases by increase the temperature. Figure 11 shows the wt-loss and time relation plot of the studied surfactant at 40°C as example. The values of inhibition efficiency at different temperatures of the three surfactants are listed in table 7. From which the corrosion rate can be measured at different temperatures according to Eq.9, the results listed in table 8 indicated that the corrosion rate increase by increasing the temperature.

$$k_{corr} = (W1–W2)/a.t. \quad \text{(Eq.9)}$$

Where W1 and W2 are initial and final weight value of the specimens, respectively, a is the exposed surface area of carbon steel specimen (cm^2) and t is time immersion (min) (Table 6). List of corrosion rate values at different temperatures for carbon steel in 1 M HCl in the absence and presence of various concentrations of the three surfactants.

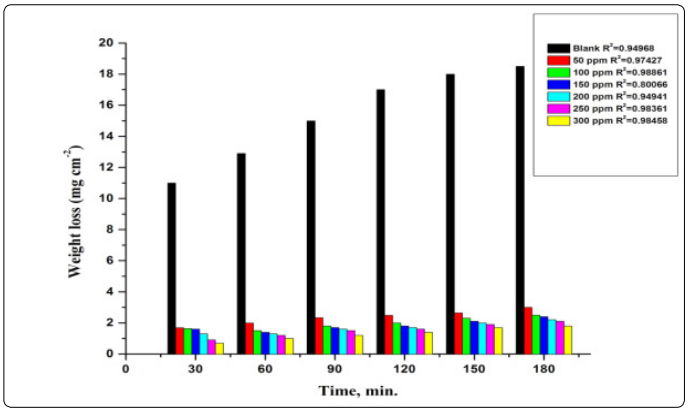


Figure 11. Plots of weight loss vs time for carbon steel in 1 M HCl in case of the free acid and in presence of different concentrations of Benzalkonium Chloride at 40 ± 2°C.

Table 7. The effect of addition of different concentrations of the studied surfactant on the surface coverage (**θ**) and inhibition efficiency values (%IE) at different temperatures.

Temp °C	Conc. ppm	Benzalkonium chloride	
		θ	%IE
30°C	50	0.848	84.8
	100	0.856	85.6
	150	0.875	87.5
	200	0.898	89.8
	250	0.929	92.9
	300	0.959	95.9
35°C	50	0.847	84.7
	100	0.855	85.5
	150	0.877	87.7
	200	0.887	88.7
	250	0.927	92.7
	300	0.955	95.5
40°C	50	0.846	84.6
	100	0.851	85.1
	150	0.855	85.5
	200	0.882	88.2
	250	0.918	91.8
	300	0.936	93.6

Table 8. List of corrosion rate values at different temperatures for carbon steel in 1M HCl in absence and presence of various concentrations of Benzalkonium Chloride.

$C_{[inh],}$ ppm	k_{corr} (mg cm^{-2} min^{-1}) × 10^{-3}			
	25°C	30°C	35°C	40°C
0	100	117	142	143
50	15	18	18	21
100	14	15	16	17
150	13	15	15	15
200	11	12	12	14
250	9	11	11	13
300	8	9	9	12

Activation parameters of corrosion process

Activation parameters of corrosion process, activation energy E^*_a, enthalpy of activation ΔH^* and entropy of activation ΔS^* can be calculated for carbon steel corrosion in HCl solution in absence and presence of different concentrations of surfactants by using equation (Arrhenius (Eq. 11).

$$\text{Rate } (k_{corr}) = A\exp(-E^*_a/RT) \quad \text{(Eq. 10)}$$

Transition state equation (3.8)

$$\text{Rate } (k_{corr}) = [RT/Nh\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \quad \text{(Eq. 11)}$$

Where A is the frequency factor, h is Planck's constant and N is Avogadro's number.

A plot of (log k_{corr}) versus (1/T) was plotted which give straight lines with slope ($-E^*_a/2.303R$) and another plot between log (K_{corr}/T) versus (1/T) which gave straight line with slope of ($-\Delta H^*/2.303$), the intercepts will be A and (log $R/Nh + \Delta S^*/2.303R$) for Arrhenius and transition state equations, respectively.

Figure 12 represent log rate vs 1/T plot and figure 13 represent log (k_{corr}/T) vs 1/T curves. Also in table 9 the values of activation energy E^*_a, activation enthalpy ΔH^* and activation entropy S^* were listed. The values of activation energy increases when the surfactants are present in corrosive solution. This caused by high energy barrier occurs as a consequence of the adsorption of surfactant on surface of metal. The variation in the apparent activation energy is observed to be analogous to the pre–exponential factor (A). The results in table 9 indicated that the activation enthalpy increases with increasing of the concentration of surfactant, which confirm with the inhibition mechanism deduced from the similar variation of the activation energy values. The values of activation entropy (ΔS^*), explained that in the rate determining step of the adsorption process in the activated complex suggests an association take places rather than dissociation.

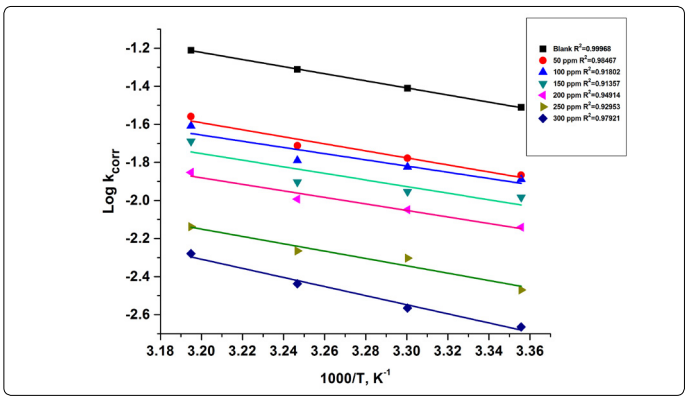


Figure 12. Arrhenius plots for corrosion rates (k_{corr}) of carbon steel in 1 M HCl in the absence and presence of different concentrations of Benzalkonium Chloride.

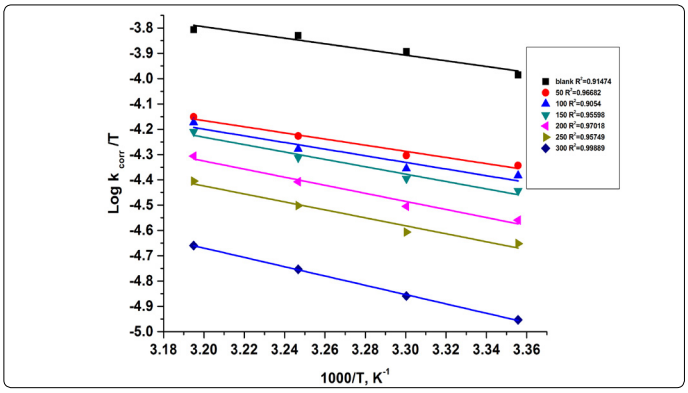


Figure 13. Plots of log (k_{corr}/T) versus (1000/T) of carbon steel in 1 M HCl in the absence and presence of different concentrations of Benzalkonium Chloride.

Table 9. Activation parameters for carbon steel in the absence and presence of different concentrations of Benzalkonium Chloride.

Conc $_{[inh],}$ ppm	Activation parameters			
	A Mg cm^{-2} min^{-1}	E^*_a kJ mol^{-1}	ΔH^* kJ mol^{-1}	$-\Delta S^*$ J mol^{-1} K^{-1}
Blank	3.3	23.8	24.8	191.7
50 ppm	3.3	35.7	24.0	202.8
100 ppm	3.7	31.2	25.1	197.5
150 ppm	5.1	33.2	27.9	189.1
200 ppm	5.4	32.8	33.2	162.5
250 ppm	5.2	36.9	30.1	185.7
300 ppm	5.4	45.7	35.2	174.2

Quantum calculation

The chemical structure of the molecule which used in quantum calculation and the optimized molecular structures, HOMO and LUMO of Benzalkonuim Chloride molecules using $Dmol^3$/GGA/BOP are shown in figures 14 and 15 respectively, also all the calculted quantum chemical parameters for the investigated surfactant are listed in table 10 which confirms with all results of experimental methods used.

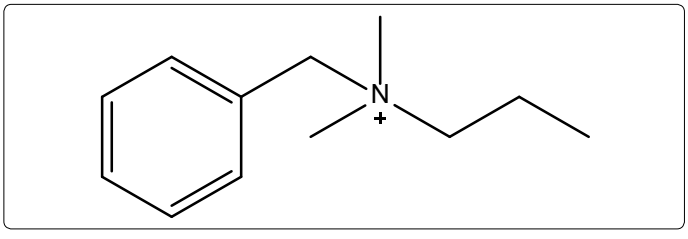


Figure 14. Chemical Structure of Benzalkonium Chloride which were used in the quantum calculation.

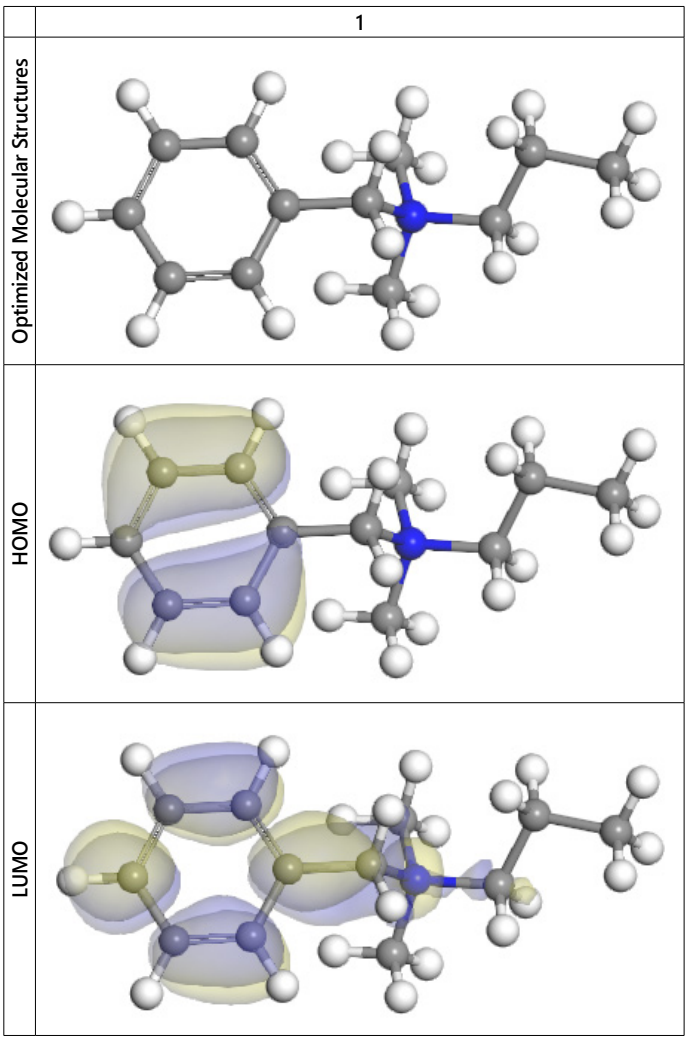


Figure 15. The optimized molecular structures, HOMO and LUMO of the inhibitors molecules using $Dmol^3$/ GGA/BOP.

Table 10. The calculated quantum chemical parameters for Benzalkonium Chloride compound.

Parameter		1
$Dmol^3$/ GGA / BOP	E_{HOMO} (eV)	-5.940 eV
	E_{LUMO} (eV)	-1.164eV
	ΔE (eV)=E_{LUMO}-E_{HOMO}	4.776
	μ (debyes)	3.2844 debye
	Molecular area (Å²)	231.651602

Conclusion

So all measurments experimental [chemical method (weight loss) or electrochemical methods (potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), or electrochemical frequency modulation (EFM)) and theoritical quantum calculation proofed that the studied cationic surfactant (Benzalkonuim Chloride) act as good inhibtor for corrosion of steel in presence of strong corrosive meduim 1 M HCl.

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Conflict of Interest Statement

The authors declare that there is no conflict of interest.

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