

Novel cationic surfactant based on triazole as a corrosion inhibitor for carbon steel in phosphoric acid produced by dihydrated wet process

M.A. Hegazy*

Egyptian Petroleum Research Institute (EPRI), Nasr City 11727, Cairo, Egypt

Abstract

The corrosion inhibition effect of novel cationic surfactant based on triazole derivatives on carbon steel in 7 M H₃PO₄ solution has been evaluated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The inhibition efficiency increases with increasing inhibitor concentration, but it decreases with increasing the temperature. The adsorption of inhibitor is mixed physical and chemical adsorption and found to obey the Langmuir adsorption isotherm. Data obtained from EIS studies were analyzed to model inhibition process through appropriate equivalent circuit model. Potentiodynamic polarization studies have shown that inhibitor acts as a mixed type of inhibitor.

Keywords: Carbon steel; Cationic surfactant; EIS; Tafel; Weight loss; Adsorption.

* Corresponding author. Tel.: +20 1002653529; fax: +20 222747433.

E-mail address: mohamed_hgazy@yahoo.com (M.A. Hegazy).

1. Introduction

The use of corrosion inhibitors is an important method to protect metallic materials against corrosion in acidic medium. Phosphoric acid (H₃PO₄) is widely used in the production of fertilizers and surface treatment of steel such as chemical and electrolytic polishing or etching, chemical coloring, removal of oxide film, phosphating, passivating, and surface cleaning. Most of the acid is produced from phosphate rocks by the so-called dihydrate wet process, equivalent to 7.0 M H₃PO₄ (about 35% H₃PO₄) [1]. There is a great need to protect steel materials used in the phosphoric acid industry produced by dihydrate wet method process. However, little work appears to have been done on the corrosion inhibition of steel in 7.0 M H₃PO₄ (35% H₃PO₄). Organic compounds containing N, O and S atoms are considered to be effective corrosion inhibitors. The effectiveness of organic inhibitors depends on the nature and the condition of the metallic surface, the chemical composition and structure of the inhibitor. The inhibitors which have N and S simultaneously provide a better inhibition performance [2]. The inhibitory action of the hetero compounds is usually attributed to their adsorptive interaction with the metal surface [3-5]. A bond may be formed between electron lone pairs and/or electron cloud of the donor atoms of the inhibitor and the metal surface, thereby reducing the corrosive attack in an acid medium [6]. The stability of the adsorbed inhibitor film on the metal surface depends on some physicochemical properties of the molecule related to their functional groups, aromaticity, the possible steric effects, electronic density of donor atoms, type of corrosive environment and the nature of the interaction between the p orbital of the inhibitors and the d orbitals of iron [7]. It has been proposed that n-alkyl-quaternary ammonium salts act inhibition by adsorption on the metal surface, and the adsorption takes place through electrostatic attraction between positively charged N⁺ ion and the induced negative charges on the metal surface. Study of the inhibition actions of n-alkyl-quaternary ammonium compounds on the corrosion of steel is of

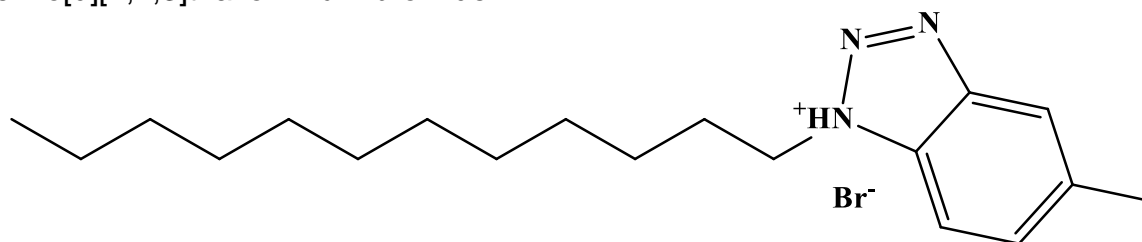
considerable interest due to its academic and industrial importance. 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide is a new class of n-alkyl-quaternary ammonium salt. However, to the best of our knowledge, 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide has not been used as a corrosion inhibitor in 7 M H_3PO_4 . However, no substantial information is available on the corrosion inhibition of quaternary ammonium salts in H_3PO_4 solution.

In the present work, we are development of n-alkyl-quaternary ammonium salt based on triazole derivatives as corrosion inhibitors in 7.0 M H_3PO_4 produced by dihydrated wet process. The inhibition effect of novel cationic surfactant, namely, 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide, on the corrosion of carbon steel in 7 M H_3PO_4 was studied using weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) methods. Also, the effect of inhibitor concentration and temperature on the corrosion inhibition was discussed. Adsorption thermodynamic parameters are calculated and discussed in detail.

2. Materials and experimental techniques

2.1. Inhibitor

A novel cationic surfactant used in this study was synthesized from reaction of one mol 5-methyl-1H-benzo[d][1,2,3]triazole with one mol 1-bromododecane in ethanol at 70 °C for 24 h [8]. The mixture was allowed to cool-down. The obtained pale brown precipitate product was further purified by diethyl ether then recrystallized from ethanol to form white precipitate is called 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide.



1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide

Fig. 1. Chemical structure of the synthesized 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide.

Chemical structure of the synthesized inhibitor (Fig. 1) was confirmed by FTIR and 1H NMR spectroscopy. FTIR analysis was carried out using ATI Mattson infinity series TM, Bench top 961 controlled by Win First TM V2.01 software. 1H NMR analysis was measured in $DMSO-d_6$ using Jeol ECA 500 MHZ NMR spectrometer.

2.2. Steel specimen

Tests were performed on a carbon steel of the following chemical composition (wt. %): 0.28% C, 0.06% Ti, 1.40% Mn, 0.03% P, 0.03% S and the remainder is Fe.

2.3. Electrochemical measurements

The electrochemical experiments were carried out in a conventional three-electrode cell with a platinum counter electrode (CE) and a silver/silver chloride (RE) as a reference electrode. The working electrode (WE) was a rod of carbon steel embedded in PVC holder using epoxy resin so that the flat surface was the only exposed surface in the electrode. The area of the working exposure surface was 0.42 cm^2 . This area was abraded with emery paper (grade 320-400-600-800-1000-1200) on the test face, rinsed with distilled water, degreased with acetone and dried. Before measurement, the electrode was immersed in a test solution at open circuit potential (OCP) for 30 min. until a steady state was reached. All Electrochemical

measurements were carried out using a VoltaLab 40 (PGZ301 & VoltaMaster 4) - (Radiometer Analytical- FRANCE) at 20 °C.

EIS measurements were carried out as described elsewhere [9,10]. A small alternating voltage perturbation (5 mV) was imposed on the cell over the frequency range from 100 kHz to 30 mHz at open circuit potential at 20 °C. Simulation of Nyquist diagrams with the suggested model was done by ZSimWin program.

The potentiodynamic polarization measurements were obtained by changing the electrode potential automatically from -800 to -300 mV vs. Ag/AgCl with scan rate 2 mV s⁻¹ at 20 °C.

2.4. Weight loss measurements

The carbon steel pipeline sheets of 6 cm x 3 cm x 0.4 cm were abraded with a series of emery paper (grade 320-400-600-800-1000-1200) and then cleaned successively with distilled water, ethanol and acetone, and finally dried in dry air. A&D analytical balance, (Model: HR 200, readability: 0.1 mg and standard deviation: ± 0.2 mg), was used for the gravimetric analysis. After accurately weighting, the samples were immersed in 100 ml of 1 M HCl solution with and without the addition of different concentrations of cationic surfactant at various temperatures. The temperature for weight loss measurements was controlled by water bath provided with thermostat control ±0.5 °C. The carbon steel specimens were taken out after 24 h and then rinsed with distilled water twice and degreased with acetone. Then specimens were immersed in 1 M HCl solution for 10s, (chemical method for cleaning rust products), rinsed twice with distilled water, ethanol, and acetone and finally dried in dry air and accurately weighted. The experiments were carried out in triplicates in order to give a good reproducibility and the average weight loss of three parallel carbon steel pipeline sheets was obtained. All tests in this paper were done under aerated conditions.

3. Results and discussion

3.1. Structure confirmation of the synthesized inhibitor

FTIR spectroscopy

FTIR spectrum of the synthesized cationic surfactant showed the following absorption bands at 716.86 cm⁻¹ ((CH₂)_n rocking), 1249.31 cm⁻¹ (CH₃ symmetric bending), 1461.31 cm⁻¹ (CH₂ asymmetric bending), 2851.50 cm⁻¹ (CH symmetric stretching), 2919.50 cm⁻¹ (CH asymmetric stretching) and 1035.63 cm⁻¹ (R₄N⁺), 1506.34 and 1610.04 cm⁻¹ (CH stretching of aromatic ring), 1361.40 cm⁻¹ (CH₃ rocking of benzene) and 3418.19 cm⁻¹ (NH stretching). The data of FTIR spectrum confirmed the expected functional groups in the synthesized cationic surfactant.

¹H NMR spectroscopy

¹H NMR (DMSO-d₆) spectrum of the synthesized cationic surfactant (Fig. 2) showed different bands at δ=0.8448 ppm (t, 3H, (CH₃(CH₂)₉CH₂CH₂N⁺); δ=1.2160 ppm (m, 18H, CH₃(CH₂)₉CH₂CH₂N⁺); δ=1.6351 ppm (m, 2H, CH₃(CH₂)₉CH₂CH₂N⁺); δ=2.0090 ppm (t, 2H, CH₃(CH₂)₉CH₂CH₂N⁺); δ=3.3528 ppm (s, 3H, CH₃-toluidene nucleus); δ=7.8638 ppm (d, 1H, 4-benzene nucleus); δ=8.3404 ppm (s, 1H, 6-benzene nucleus); δ=8.3626 ppm (d, 1H, 3-benzene nucleus). The data of ¹H NMR spectrum confirmed the expected hydrogen proton distribution in the synthesized cationic surfactant.

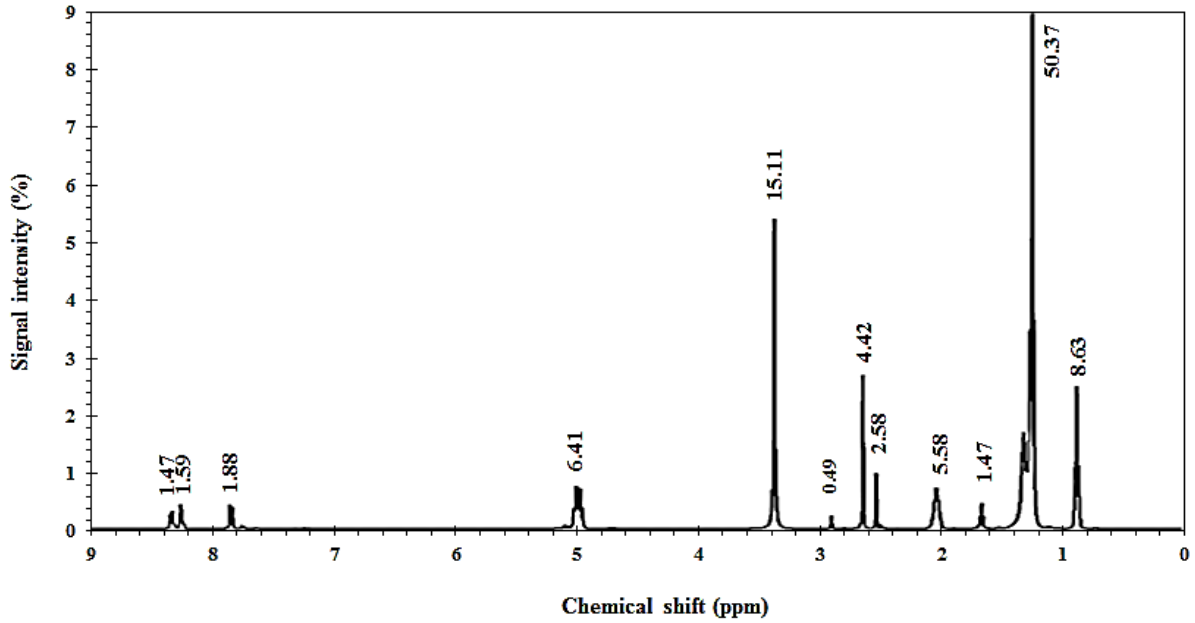


Fig. 2. ^1H NMR spectrum of 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide.

3.2. Electrochemical impedance spectroscopy

Fig. 3 shows Nyquist plot for carbon steel in 7 M H_3PO_4 solution in the absence and presence of different concentrations of the synthesized inhibitor. Nyquist plot shows the depressed capacitive loop in the high frequency range, indicating that the corrosion of carbon steel is controlled mainly by charge transfer process. The high frequency capacitive loops are not perfect semicircles, such behavior are characteristic for solid electrodes and often referred to frequency dispersion effect which could be attributed to non-homogeneity and roughness of solid electrodes [11]. All the impedance parameters were calculated with the application of the equivalent circuit model given in **Fig. 4**. The circuit consists of R_s (the resistance of solution between working electrode and counter electrode), and R_{ct} . The double layer usually behaves as a constant phase element (CPE) rather than pure capacitor. From data in **Table 1**, we find that the charge transfer resistance value, R_{ct} , increases in inhibited system than uninhibited system. A large R_{ct} is associated with a slower corroding system, due to decrease in the active surface necessary for the corrosion reaction.

The CPE is substituted for the capacitor to fit the semicircle more accurately. The impedance, Z_{CPE} , is calculated from the following equation [12,13]:

$$Z_{\text{CPE}} = \frac{1}{Y_0(j\omega)^n} \quad (1)$$

where the exponent n is the phase shift, gives information about the degree of heterogeneity or roughness of the carbon steel surface capacitive behavior, and Y_0 is a proportional factor, $J^2 = -1$, $\omega = 2\pi f$ and n is the phase shift. For $n = 0$, Z_{CPE} represents a resistance with $R = Y_0^{-1}$, for $n = 1$ a capacitance with $C = Y_0$, for $n = 0.5$ a Warburg impedance with $W = Y_0$ and for $n = -1$ an inductive with $L = Y_0^{-1}$. The values of phase shift, n (ranges from 0.78 to 0.90) were not changes significantly and its ongoing stability showed the charge transfer controlled dissolution mechanism of carbon steel in 7 M H_3PO_4 with and without inhibitor.

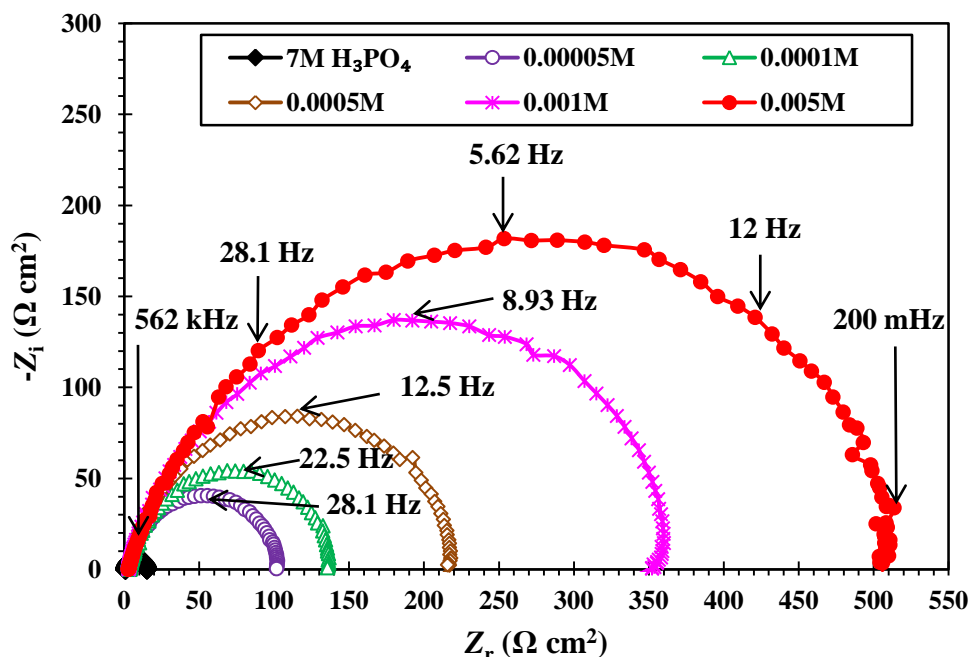


Fig. 3. Nyquist plots for carbon steel in 7 M H_3PO_4 in absence and presence of different concentrations of 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide.

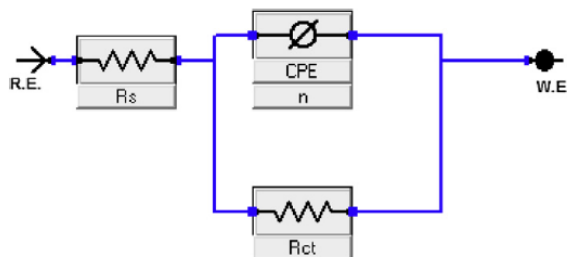


Fig. 4. Suggested equivalent circuit model for the studied systems.

Table 1: Electrochemical impedance spectroscopy results for carbon steel in 7 M H_3PO_4 in the absence and presence of different concentrations of the synthesized cationic inhibitor at 20 °C

Conc. of inhibitor M	R_s $\Omega \text{ cm}^2$	Q_{dl} $\text{m}\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	n	Error of n	R_{ct} $\Omega \text{ cm}^2$	C_{dl} $\mu\text{F cm}^{-2}$	η_l %
0.00	1.02	0.0004505	0.90	0.74	14.22	248.4	-
5×10^{-5}	2.63	0.0000666	0.89	0.99	98.16	48.0	85.51
1×10^{-4}	3.68	0.0000483	0.86	0.85	131.8	29.7	89.21
5×10^{-4}	2.79	0.0000299	0.85	0.82	214.8	21.3	93.38
1×10^{-3}	2.87	0.0000175	0.83	0.80	357.4	15.9	96.02
5×10^{-3}	2.79	0.0000123	0.78	0.47	516.1	14.7	97.24

The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The double layer capacitance, C_{dl} , for a circuit including a CPE was calculated from the following equation [14,15]:

$$C_{dl} = Y_o(\omega_{max})^{n-1} \quad (2)$$

where $\omega_{max} = 2\pi f_{max}$ and f_{max} is the frequency at which the imaginary component of the impedance is maximal.

The calculated C_{dl} values are listed in Table 1. It was clear that the double layer capacitance value decreases by increasing the inhibitor concentration. This behaviour is may be due to the adsorption of inhibitor on the carbon steel surface

decreases its electrical capacity by displacing water molecules and other ions which are adsorbed on its surface. The capacity decrease in inhibited system may be attributed to the formation of a protective layer on the electrode surface. The decreased C_{dl} values can result from the increase of thickness of electrical double layer or decrease of the local dielectric constant which suggest the substitution of H_2O molecules (with higher dielectric constant) with inhibitor molecules (with lower dielectric constant) leading to a protective film on electrode surface [16,17].

The Bode and phase angle plots recorded for carbon steel electrode immersed in 7 M H_3PO_4 in the absence and presence of optimum concentration of inhibitors are given in Fig. 5. It is observed that in the intermediate frequency region, a linear relationship between $\log|Z|$ vs. $\log f$ with a slope near -1 and the phase angle approaching -70° has been observed. This indicates the capacitive behavior at intermediate frequencies. An ideal capacitive behavior would be the result if a slope value attained -1 and a phase angle value attained -90° [18]. The slope values of Bode impedance magnitude plots at intermediate frequencies, S , and the maximum phase angles, α° , showed deviation from the values of -1 and 90° , respectively. These deviations were considered to be the deviation from the ideal capacitive behavior at intermediate frequencies. The gradual approach of $-S$ and α° to the ideal capacitive values in the beginning of the immersion may be related to slowing of the rate of dissolution with time. For the same reason, the faster attainment of steady state of $-S$ and α° and their higher values in inhibited solutions than in uninhibited solution reflect the inhibitive action of the inhibitors in the carbon steel dissolution process [19]. The Phase angle plots (Fig. 4) show single maximum (one time constant) at intermediate frequencies, broadening of this maximum in presence of inhibitors accounts for the formation of a protective layer on the electrode surface.

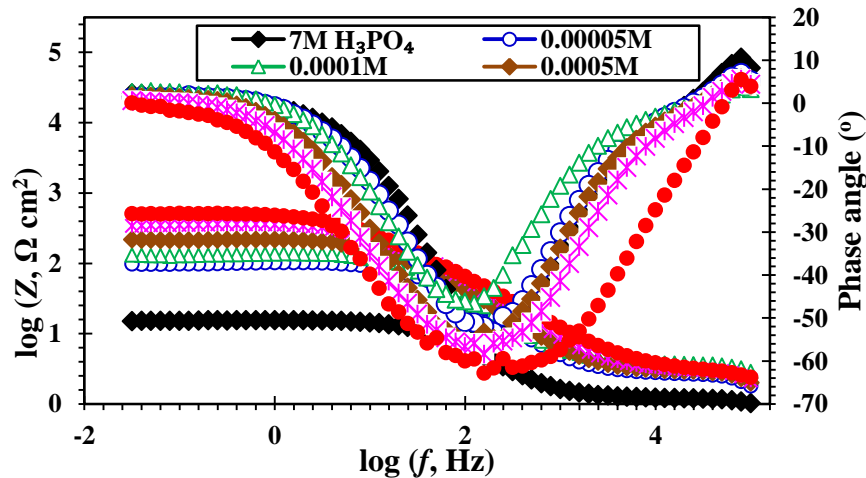


Fig. 5. Bode and Phase angle plots for carbon steel in 7 M H_3PO_4 in the absence and presence of different concentrations of 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide.

The corrosion inhibition efficiency (η_i) was calculated using the following equation [20]:

$$\eta_i = \left(\frac{R_{ct}^o - R_{ct}}{R_{ct}^o} \right) \times 100 \quad (3)$$

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

As it is seen from Table 1, The inhibition efficiency increases with increasing the inhibitor concentration suggests that this compound acts by adsorption on the carbon steel surface. The maximum inhibition efficiency of 1-dodecyl-5-methyl-1H-

benzo[d][1,2,3]triazol-1-ium bromide reaches of 97.24 % with respect to the concentration of the inhibitor (5×10^{-3} M).

3.3. Polarization curves measurements

Anodic and cathodic polarization plots recorded on carbon steel electrode in 7 M H_3PO_4 in the absence and presence of different concentrations of cationic surfactant at 20 °C are presented in Fig. 6. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), corrosion inhibition efficiency (η_p), anodic Tafel slope (β_a) and cathodic Tafel slope (β_c) and the results are presented in Table 2. It can be seen from Fig. 5 that the existence of inhibitor molecule in the corrosive medium decreases corrosion current (i_{corr}). These changes increase with increasing inhibitor concentration. This behavior supports the adsorption of inhibitor onto metal surface and causes a barrier effect for mass and charge transfer for anodic and cathodic reactions. As can be seen from Table 2, E_{corr} values are slightly changed (only the displacement was <10 mV) in the presence of cationic surfactant inspect to blank suggesting the cationic surfactant is acted as mixed-type inhibitor. But it can also be observed that both anodic Tafel slope (β_a) and cathodic Tafel slope (β_c) values does not change much in the presence of cationic surfactant inspect to blank [21]. This behavior indicating that the inhibitor merely blocks the corrosion reaction sites of the carbon steel and without changes the mechanism of metal dissolution (anodic) and/or hydrogen evolution (cathodic) reaction.

The corrosion inhibition efficiency (η_p) was calculated following this equation [22,23]:

$$\eta_p = \left(\frac{i_{corr} - i_{corr}^0}{i_{corr}} \right) \times 100 \quad (4)$$

where i_{corr}^0 and i_{corr} are the corrosion current density values with and without inhibitor, respectively.

Table 2: Potentiodynamic polarization results for carbon steel in 7 M H_3PO_4 in the absence and presence of different concentrations of the synthesized cationic inhibitor at 20 °C

Conc. of inhibitor M	E_{corr} mV	i_{corr} mA cm ⁻²	β_a mV dec ⁻¹	β_c mV dec ⁻¹	η_p %
0.00	-474.4	3.0638	74.6	-146.8	-
5×10^{-5}	-477.7	0.4118	94.1	-176.1	86.56
1×10^{-4}	-482.2	0.3266	94.6	-179.5	89.34
5×10^{-4}	-478.9	0.2150	94.4	-183.2	92.98
1×10^{-3}	-483.7	0.1215	91.5	-183.1	96.03
5×10^{-3}	-481.9	0.0902	94.2	-178.3	97.06

As it can be seen from Table 2, when the concentration of inhibitor increases the inhibition efficiencies increase while corrosion current densities decrease. This may be due to the increase in cationic surfactant concentration leads to increasing the surface coverage of the inhibitor and hence increase the adsorption on the steel surface. The maximum inhibition efficiency was observed around 96.06 % at 5×10^{-3} M of the synthesized cationic surfactant. These results are in good agreement with the results obtained from electrochemical impedance spectroscopy measurements.

3.4. Weight loss measurements

The effect of addition of the cationic surfactant based on triazole on the corrosion of carbon steel in 7 M H_3PO_4 solution was studied by weight loss measurements at 20, 40, 60 and 80 °C after a 24 h immersion period. The value of corrosion rate (k) was calculated from the following equation [24]:

$$k = \frac{\Delta W}{St} \quad (5)$$

where ΔW is the average weight loss of three parallel carbon steel sheets, S is the total area of the specimen, and t is the immersion time.

The surface coverage, θ , and the corrosion inhibition efficiency, (η_w), on carbon steel were calculated using the following equations [25, 26]:

$$\theta = \left(\frac{W - W_0}{W} \right) \quad (6)$$

$$\eta_w = \left(\frac{W - W_0}{W} \right) \times 100 \quad (7)$$

where W and W_0 are the values of the weight loss without and with addition of the inhibitor, respectively.

The calculated corrosion rate, surface coverage and corrosion inhibition efficiency are listed in Table 3. It can be seen from Table 3 that the corrosion rate significantly decreased after the addition of the synthesized cationic surfactant at all temperatures, while the inhibition efficiency increased by increasing the inhibitor concentration suggests that the inhibitor molecules act by adsorption on the metal surface. From data in Table 3, it was observed that the corrosion inhibition efficiency decreases with increasing the temperature. This behaviour is due to desorption of inhibitor molecules through N^+ atom Br^- ion. The maximum inhibition efficiency was to be around 97.23 % at 5×10^{-3} M of the synthesized cationic surfactant. The high inhibition efficiency can be explained by the adsorption of the synthesized cationic surfactant on the carbon steel surface.

Table 3: Weight loss data for carbon steel 7 M H_3PO_4 in the absence and presence of different concentrations of the synthesized cationic surfactant at various temperatures

Inhibitor conc. M	20 °C			40 °C			60 °C			80 °C		
	k mg cm ⁻² h ⁻¹	θ	η_w %	k mg cm ⁻² h ⁻¹	θ	η_w %	k mg cm ⁻² h ⁻¹	θ	η_w %	k mg cm ⁻² h ⁻¹	θ	η_w %
0.00	2.9703	-	-	4.3089	-	-	7.9007	-	-	12.3111	-	-
5×10^{-5}	0.3938	0.87	86.74	0.8344	0.81	80.64	0.8344	0.81	80.64	3.8955	0.68	68.36
1×10^{-4}	0.3109	0.90	89.53	0.6571	0.85	84.75	0.6571	0.85	84.75	3.2945	0.73	73.24
5×10^{-4}	0.2039	0.93	93.13	0.4023	0.91	90.66	0.4023	0.91	90.66	2.5453	0.79	79.32
1×10^{-3}	0.1166	0.96	96.08	0.2871	0.93	93.34	0.2871	0.93	93.34	1.9340	0.84	84.29
5×10^{-3}	0.0824	0.97	97.23	0.2513	0.94	94.17	0.2513	0.94	94.17	1.4971	0.88	87.84

The results obtained from the weight loss measurements are in accordance with the previously obtained results from the electrochemical measurements.

3.5. Adsorption isotherm

The adsorption of organic molecules at the metal/solution interface consists of the replacement of water molecules by organic molecules according to following process [27]:



where $Org_{(sol)}$ and $Org_{(ads)}$ are organic molecules in the solution and adsorbed on the metal surface, respectively, and x is the number of water molecules replaced by the organic molecules.

The inhibition efficiencies of the organic molecules mainly depend on their adsorption ability on the metal surface. Therefore, the determination of relation between adsorption and corrosion inhibition is of great importance. In order to clarify the nature and the strength of adsorption, the experimental results were fitted to a series of adsorption isotherms, and the best fit was obtained with the use of the Langmuir

adsorption isotherm, which is presented graphically in Fig. 7. The correlation coefficients and the slopes are close to 1 which confirms this assumption. Therefore, it is concluded that, a monolayer inhibitor film forms on the carbon steel surface, and there are no interactions between the adsorbed inhibitor molecules [28]. Langmuir adsorption isotherm can be expressed by the following equation [29]:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (9)$$

where θ is the surface coverage, which can be calculated from the weight loss experimental results, C is the molar concentration of the inhibitor and K_{ads} is the standard adsorption equilibrium constant.

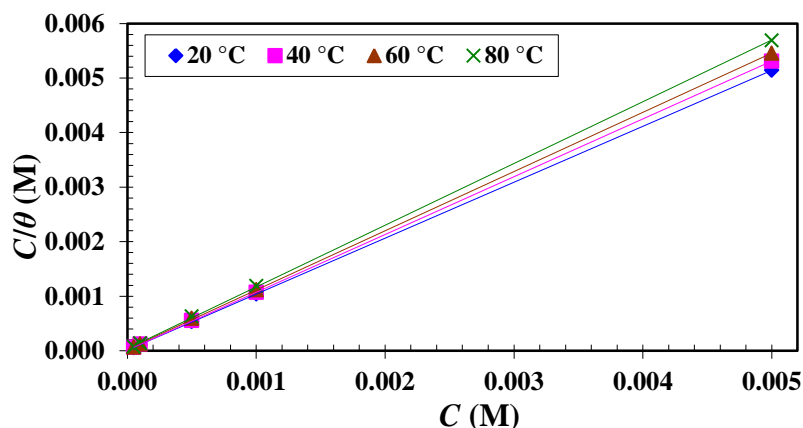


Fig. 7. Langmuir's adsorption plots for carbon steel in 1 M HCl solution containing different concentrations of 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide at 20 °C.

The values of K_{ads} were 75905.4, 73206.3, 37140.5 and 26049.0 M^{-1} , at 20, 40, 60 and 80 °C, respectively, which reflects strong interactions between the inhibitor molecules and the metal surface [30–33]. The value of K_{ads} increases with the temperature increasing indicates that the adsorption ability of 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide on the carbon steel surface decreases with the temperature increasing.

The standard free energy of adsorption, $\Delta G_{\text{ads}}^{\circ}$, on the mild steel surface is related to the K_{ads} with the following equation [34]:

$$\Delta G_{\text{ads}}^{\circ} = -RT \ln(55.5K_{\text{ads}}) \quad (10)$$

where the value 55.5 is the concentration of water in solution expressed in M.

It is well identified that the values of -20 kJ mol^{-1} or lower show a physisorption; those around -40 kJ mol^{-1} or higher include charge sharing or transfer between inhibitor molecules and metal to form a co-ordinate covalent bond [35]. However, the adsorption of organic molecules on metal surfaces cannot be considered as a purely physical or chemical phenomenon. In addition to the chemical adsorption, inhibitor molecules can also be adsorbed on the metal surface via physical interactions. $\Delta G_{\text{ads}}^{\circ}$ values were -37.16 , -39.60 , -40.25 and $-41.63 \text{ kJ mol}^{-1}$, at 20, 40, 60 and 80 °C, respectively, indicated that, the adsorption of 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide molecules on the carbon steel surface is a mixed type of chemical and physical adsorption [36–38].

Another parameter that has been used to determine whether a process may be associated to a physical or a chemical interaction is the adsorption enthalpy. If the absolute value is lower than $41.86 \text{ kJ mol}^{-1}$ a physisorption mechanism or mixture of physisorption and chemisorption mechanism operates, while for values close to 100 kJ mol^{-1} a chemisorption mechanism acts [39]. The enthalpy of adsorption ($\Delta H_{\text{ads}}^{\circ}$) is obtained from the Van't Hoff's equation [40]:

$$\ln K_{\text{ads}} = -\left(\frac{\Delta H_{\text{ads}}^{\circ}}{RT}\right) + \text{constant} \quad (11)$$

When $\ln K_{\text{ads}}$ vs. $(1/T)$ is plotted, the value of $\Delta H_{\text{ads}}^{\circ}$ is obtained from the slope. The value of $\Delta H_{\text{ads}}^{\circ}$ is $-16.50 \text{ kJ mol}^{-1}$ indicates that the adsorption of the studied inhibitor on the carbon steel surface in $7 \text{ M H}_3\text{PO}_4$ is exothermic process, which illustrated that the corrosion inhibition efficiency decreased with the temperature increasing. In the present work, enthalpy is lower than 41.8 kJ mol^{-1} which indicates that the adsorption of 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide molecules on the carbon steel surface are mixture of physisorption and chemisorption. The standard adsorption entropy, $\Delta S_{\text{ads}}^{\circ}$, was calculated from the following equation [40]:

$$\Delta G_{\text{ads}}^{\circ} = \Delta H_{\text{ads}}^{\circ} - T\Delta S_{\text{ads}}^{\circ} \quad (12)$$

$\Delta S_{\text{ads}}^{\circ}$ values were $70.52, 73.82, 71.34$ and $71.20 \text{ J mol}^{-1} \text{ K}^{-1}$, at $20, 40, 60$ and $80 \text{ }^{\circ}\text{C}$, respectively. The positive values of entropy suggest that adsorption is coupled with a increase in the system disorder due to the adsorption of inhibitor on the steel surface.

3.6. Inhibition mechanism

In Fig. 1, the inhibition mechanism derived from the interaction of 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide on carbon steel in aqueous $7 \text{ M H}_3\text{PO}_4$ is proposed. The steel surface in acidic medium contains anodic and cathodic sites on which the simultaneous electrochemical reactions of iron oxidation and hydrogen evolution take place, respectively.

The studied inhibitor can be dissociated into the surfactant part being the cation and the counter ion (Br^-) being the anion. The surfactant cations have many adsorption centers which are the N atoms of triazole ring in addition benzene ring.

In view of the above, the inhibition of the synthesized cationic surfactant may be carried out by the participation of three mode of adsorption: (a) Electrostatic interaction (physical adsorption) between the positively charged of cationic head of surfactant and the negatively charged carbon steel surface (cathodic sites, i.e. cathodic inhibition). And electrostatic interaction between the negatively charged Br^- ion and the positively charged carbon steel surface (anodic sites, i.e. anodic inhibition), (b) Chemical interaction (chemisorptions) between the N^+ atoms of triazole ring in addition double bonds of benzene ring (de-localized electrons) and the vacant, low energy d-orbitals of iron surface atoms (anodic sites, i.e. anodic inhibition) and (c) Aliphatic chain contributed to inhibition by rejecting water molecule from metallic surface through orientation of these aliphatic chains to corrosive solution.

According to the suggested dipole adsorption model, the studied inhibitor must be of mixed-type inhibitor which is in agreement with that obtained from potentiodynamic polarization measurements.

4. Conclusions

1. 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide is a mixed corrosion inhibitor for carbon steel in $7 \text{ M H}_3\text{PO}_4$ solution that acts both over the cathodic process of hydrogen evolution and the anodic process of metal dissolution.
2. Inhibition efficiency was determined by three different methods: weight loss, potentiodynamic polarization and electrochemical impedance, all giving comparable results.
3. Inhibition efficiency increases with increasing the inhibitor concentration and the maximum value was 97% for $5 \times 10^{-3} \text{ M}$.

4. The adsorption of 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide on carbon steel surface obeys Langmuir isotherm, and the values of Gibbs free energy reveal the physical and chemical adsorption of the inhibitor on carbon steel surface are occur.
5. The double layer capacitance obtained from EIS measurements decreases with the increasing of inhibitor concentration, arguing an adsorption process of the synthesized cationic surfactant on the carbon steel surface.
6. The good inhibition efficiencies of 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide in 7 M H₃PO₄ solution makes it a suitable alternative as corrosion inhibitor in deicing solution in which phosphoric acid produced by dihydrated wet process sodium acetate is a main component.

References

- [1] Jianguo, Y.; Lin, W.; Otieno-Alego, V.; Schweinsberg, D.P. Polyvinylpyrrolidone and polyethylenimine as inhibitors for the corrosion of a low carbon steel in phosphoric acid. *Corros. Sci.* **1995**, *37*, 975–985.
- [2] Li, X.H.; Deng, S.D.; Fu, H. Allyl thiourea as a corrosion inhibitor for cold rolled steel in H₃PO₄ solution. *Corros. Sci.* **1995**, *55*, 280–288.
- [3] Quraishi, M.A.; Ansari, F.A.; Jamal, D. Thiourea derivatives as corrosion inhibitors for mild steel in formic acid. *Mater. Chem. Phys.* **2002**, *77*, 687–690.
- [4] Hegazy, M.A.; Abdallah, M.; Awad, M.K.; Rezk, M. Three novel di-quaternary ammonium salts as corrosion inhibitors for API X65 steel pipeline in acidic solution. Part I: Experimental results. *Corros. Sci.* **2014**, *81*, 54–64.
- [5] Agrawal, R.; Namboodhiri, T.K.G. The inhibition of sulphuric acid corrosion of 410 stainless steel by thioureas. *Corros. Sci.* **1990**, *30*, 37–52.
- [6] Torres, V.V.; Amado, R.S.; de Sá, C.F.; Fernandez, T.L.; Riehl, C.A.S.; Torres, A.G.; D'Elia, E. Inhibitory action of aqueous coffee ground extracts on the corrosion of carbon steel in HCl solution. *Corros. Sci.* **2011**, *53*, 2385–2392.
- [7] Hegazy, M.A.; Badawi, A.M.; Abd El Rehim, S.S.; Kamel, W.M. Corrosion inhibition of carbon steel using novel N-(2-(2-mercaptoacetoxy)ethyl)-N,N-dimethyl dodecan-1-aminium bromide during acid pickling. *Corros. Sci.* **2013**, *69*, 110–122.
- [8] Badawi, A.M.; Hegazy, M.A.; El-Sawy, A.A.; Ahmed, H.M., Kamel, W.M. Novel quaternary ammonium hydroxide cationic surfactants as corrosion inhibitors for carbon steel and as biocides for sulfate reducing bacteria (SRB). *Mater. Chem. and Phys* **2010**, *124*, 458–465.
- [9] Hegazy, M.A.; El-Tabei A.S.; Bedair A.H.; Sadeq M.A. An investigation of three novel nonionic surfactants as corrosion inhibitor for carbon steel in 0.5 M H₂SO₄. *Corros. Sci.* **2012**, *54*, 219–230.
- [10] Babić-Samardžija, K.; Lupu, C.; Hackerman, N.; Barron, A.R.; Luttge, A. Inhibitive properties and surface morphology of a group of heterocyclic diazoles as inhibitors for acidic iron corrosion. *Langmuir* **2005**, *21*, 12187–12196.
- [11] Lebrini, M.; Lagrenée, M.; Vezin, H.; Traisnel, M.; Bentiss, F. Experimental and theoretical study for corrosion inhibition of mild steel in normal hydrochloric acid solution by some new macrocyclic polyether compounds. *Corros. Sci.* **2007**, *49*, 2254–2269.
- [12] Tang, Y.; Zhang, F.; Hu, S.; Cao, Z.; Wu, Z.; Jing, W. Novel benzimidazole derivatives as corrosion inhibitors of mild steel in the acidic media. Part I: Gravimetric, electrochemical, SEM and XPS studies. *Corros. Sci.* **2013**, *74*, 271–282.

- [13] Stoynov, Z.B., Grafov, B.M.; Savova-Stoynova, B., Elkin, V.V.; Electrochemical Impedance, Nauka, Moscow, **1991**.
- [14] Qian, B.; Wang, J.; Zheng, M.; Hou, B. Synergistic effect of polyaspartic acid and iodide ion on corrosion inhibition of mild steel in H₂SO₄. *Corros. Sci.* **2013**, *75*, 184–192.
- [15] Fuchs-Godec, R.; M.G. Pavlovic, M.G. Synergistic effect between non-ionic surfactant and halide ions in the forms of inorganic or organic salts for the corrosion inhibition of stainless-steel X4Cr13 in sulphuric acid *Corros. Sci.* **2012**, *58*, 192–201.
- [16] Finšgar, M.; Merl, D.K. 2-Mercaptobenzoxazole as a copper corrosion inhibitor in chloride solution: Electrochemistry, 3D-profilometry, and XPS surface analysis. *Corros. Sci.* **2014**, *80*, 82–95
- [17] Yıldız, R.; Döner, A.; Doğan, T.; Dehri, İ. Experimental studies of 2-pyridinecarbonitrile as corrosion inhibitor for mild steel in hydrochloric acid solution. *Corros. Sci.* **2014**, *82*, 125–132.
- [18] Solmaz, R. Investigation of adsorption and corrosion inhibition of mild steel in hydrochloric acid solution by 5-(4-Dimethylaminobenzylidene)rhodanine. *Corros. Sci.* **2014**, *79*, 169–176.
- [19] Xu, B.; Yang, W.; Liu, Y.; Yin, X.; Gong, W.; Chen, Y. Experimental and theoretical evaluation of two pyridinecarboxaldehyde thiosemicarbazone compounds as corrosion inhibitors for mild steel in hydrochloric acid solution. *Corros. Sci.* **2014**, *78*, 260–268.
- [20] Ostapenko, G.I.; Gloukhov, P.A.; Bunev, A.S. Investigation of 2-cyclohexenylcyclohexanone as steel corrosion inhibitor and surfactant in hydrochloric acid. *Corros. Sci.* **2014**, *82*, 265–270.
- [21] Hegazy, M.A.; Hasan, A.M.; Emara, M.M.; Bakr, Mostafa F.; Youssef, Ahmed H. Evaluating four synthesized Schiff bases as corrosion inhibitors on the carbon steel in 1 M hydrochloric acid. *Corros. Sci.* **2012**, *65*, 67–76.
- [22] Cao, P.G.; Yao, J.L.; Zheng, J.W.; Gu, R.A.; Tian, Z.Q. comparative study of inhibition effects of benzotriazole for metals in neutral solutions as observed with surface-enhanced raman spectroscopy. *Langmuir*, **2002**, *18*, 100–104.
- [23] Farag, Ahmed A.; Hegazy, M.A. Synergistic inhibition effect of potassium iodide and novel Schiff bases on X65 steel corrosion in 0.5 M H₂SO₄. *Corros. Sci.* **2013**, *74*, 168–177.
- [24] Abd El Aal, E.E.; Abd El Wanees, S.; Farouk, A.; Abd El Haleem, S.M. Factors affecting the corrosion behaviour of aluminium in acid solutions. II. Inorganic additives as corrosion inhibitors for Al in HCl solutions. *Corros. Sci.* **2013**, *68*, 14–24.
- [25] Abdallah, M. Rhodanine azosulpha drugs as corrosion inhibitors for corrosion of 304 stainless steel in hydrochloric acid solution. *Corros. Sci.* **2002**, *44*, 717–728.
- [26] Hegazy, M.A.; El-Tabei, A.S. Synthesis, surface properties, synergism parameter and inhibitive performance of novel cationic gemini surfactant on carbon steel corrosion in 1 M HCl solution. *J. Surf. Deter.* **2013**, *16*, 221–232.
- [27] Bockris, J.O'M.; Reddy, A. K.N. *Modern Electrochemistry*, vol. 2, Published by Plenum Publishing Corporation, 227 West 17th, Street, New York, **1976**.
- [28] Keles, H.; Keles, M.; Dehri, I.; Serindag, O. The inhibitive effect of 6-amino-m-cresol and its Schiff base on the corrosion of mild steel in 0.5 M HCl medium. *Mater. Chem. Phys.* **2008**, *112*, 173–179.

- [29] El-Tabei, A.S.; Hegazy, M.A.; Bedair, A.H.; Sadeq, M.A. Synthesis and inhibition effect of a novel Tri-cationic surfactant on carbon steel corrosion in 0.5 M H₂SO₄ solution. *J. Surf. Deter.* **2014**, *17*, 341-352.
- [30] Bayol, E.; Gurten, A.A.; Dursun, M.; Kayakırılmaz, K. *Acta Phys.-Chim. Sin.* **2008**, *24*, 2236–2242.
- [31] Avci, G. Inhibitor effect of N,N'-methylenediacrylamide on corrosion behavior of mild steel in 0.5 M HCl. *Mater. Chem. Phys.* **2008**, *112*, 234–238.
- [32] Lebrini, M.; Robert, F.; Vezin, H.; Roos, C. Electrochemical and quantum chemical studies of some indole derivatives as corrosion inhibitors for C38 steel in molar hydrochloric acid. *Corros. Sci.* **2010**, *52*, 3367–3376.
- [33] Bahrami, M.J.; Hosseini, S.M.A.; Pilvar, P. Experimental and theoretical investigation of organic compounds as inhibitors for mild steel corrosion in sulfuric acid medium. *Corros. Sci.* **2010**, *52*, 2793–2803.
- [34] Migahed, M.A.; Hegazy, M.A.; Al-Sabagh, A.M. Synergistic inhibition effect between Cu²⁺ and cationic gemini surfactant on the corrosion of downhole tubing steel during secondary oil recovery of old wells. *Corros. Sci.* **2012**, *61*, 10–18.
- [35] Abiola, O.K.; Oforka, N.C. Adsorption of (4-amino-2-methyl-5-pyrimidinyl methylthio) acetic acid on mild steel from hydrochloric acid solution (HCl)—Part 1. *Mater. Chem. Phys.* **2004**, *83*, 315–322.
- [36] Li, X.; Deng, S.; Fu, H. Triazolyl blue tetrazolium bromide as a novel corrosion inhibitor for steel in HCl and H₂SO₄ solutions. *Corros. Sci.* **2011**, *53*, 302–309.
- [37] Deng, S.; Li, X.; Fu, H. Two pyrazine derivatives as inhibitors of the cold rolled steel corrosion in hydrochloric acid solution. *Corros. Sci.* **2011**, *53*, 822–828.
- [38] Ahamad, I.; Prasad, R.; Quraishi, M.A. Inhibition of mild steel corrosion in acid solution by Pheniramine drug: Experimental and theoretical study. *Corros. Sci.* **2010**, *52*, 3033–3041.
- [39] Ali, S.A.; Al-Muallem, H.A.; Rahman, S.U.; Saeed, M.T. Bis-isoxazolidines: A new class of corrosion inhibitors of mild steel in acidic media. *Corros. Sci.* **2008**, *50*, 3070-3077.
- [40] Hegazy, M.A.; El-Tabei, A.S.; Ahmed, H.M. Synthesis of nonionic surfactants and their inhibitive action on carbon steel in hydrochloric acid. *Corros. Sci.* **2012**, *64*, 115–125.