Faculty of Science
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Effect of some inhibitors on electrochemical behavior of steels in different aqueous solutions

Thesis

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

“قَالُوا سُبْحَانَكَ لاَ عِلْمَ لَنَا إِلاَّ مَا عَلَّمْتَنَا إِنَّكَ أَنْتَ العَلِيمُ الحَكِيمُ”

صدق الله العظيم

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Influence of Nonoxynol-9 on the Corrosion Inhibition of Carbon Steel in 1.0 M Hydrochloric Acid Solution

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Abstract: The inhibitory performance of nonoxynol-9 (N9) as a corrosion inhibitor for carbon steel was evaluated in 1.0 M HCl solution at different temperatures. Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and quantum chemical calculation methods were used in this study. The results indicated that the corrosion rate decreased with increasing concentration of N9 up 150 ppm and decreased with the increase in temperature of the medium. The comparison between the results obtained by polarization and EIS methods showed a good agreement. The corrosion inhibition effect of N9 could be related to the adsorption of N9 molecules on the metal surface. Polarization curves indicated that N9 behaves as a mixed type inhibitor. EIS exhibited one capacitive loop which indicates that the corrosion reaction is controlled by charge transfer process. The inhibition mechanism of N9 involves physical interaction between the inhibitor and metal surface. The adsorption of N9 on carbon steel affords physisorption process and obeyed the Langmuir adsorption isotherm.

Keywords: Carbon Steel, Corrosion, Inhibitor, Nonoxynol-9, Electrochemistry.

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1 Introduction

Carbon steel is the most commonly used material in the fabrication and manufacturing of oil field and cooling systems because of its availability, low cost, ease of fabrication and high strength [1, 2].

Carbon steel is subjected to several industrial processes such as acid pickling, acid cleaning and oil well acidizing. However the main problem of applying carbon steel is its dissolution in acidic solutions [3, 4]. Therefore, it must be protected against corrosion in especially aggressive media.

The study of carbon steel corrosion in acidic media is a matter of tremendous theoretical and practical concern and as such has received a considerable amount of interest [5, 6].

The use of corrosion inhibitors is essential for corrosion control of carbon steel in acid media [7, 8].

The corrosion inhibition is achieved regarding the interaction between inhibitor molecules and the metal surface; resulting in formation of an inhibitive surface film [9].

Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms. Among them, the surfactant inhibitor has many advantages such as high inhibition efficiency, low price, low toxicity and easy production [10–12].

Surfactant exerts its inhibition action through adsorption on the metal surface such that the polar or ionic group (hydrophilic part) attaches to the metal surface while its tail (hydrophobic part) extends to solution [13].

In this work, the inhibitory influences of nonionic surfactant (nonoxynol-9. abbreviated as N9) on carbon steel corrosion in 1.0 M HCl solution at temperature range of 298–328 K were studied using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques beside quantum chemical calculation method.

The choice of this compound was based on molecular structure considerations, i.e. this is an organic compound with adsorption centres (Figure 1). On other hand, the data regarding the use of nonoxynol-9 as potent corrosion inhibitor for carbon steel in acidic media appears to be very poor.

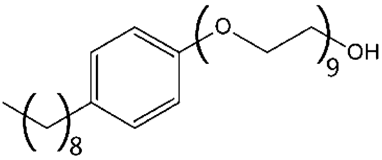

Figure 1: The molecular structure of nonoxynol-9.

2 Experimental work

Carbon steel specimens were used as the working electrodes throughout the study. The composition (wt.%) of carbon steel was: 0.06 C; 0.06 Si; 0.7 Mn; 0.005 P; 0.001 S; 0.012 Ni; 0.015 Cr; 0.004 Mo; 0.002 V; 0.02 Cu and remainder Fe.

The metal disc was coated with polyester except its bottom surface with surface area of 0.45 cm^2. Prior to each run, the surface of working electrode was mechanically abraded using different grades of sand papers (400–1200 grade). The disc was cleaned by washing with distilled water and ethanol solution, respectively. For each test, a freshly abraded electrode was used.

Measurements were carried out in naturally aerated non-stirred 1.0 M HCl solution at temperature range of 298–328 K in the absence and presence of various concentrations (50–150 ppm by weight) of nonoxynol-9 (N9). Solutions were freshly prepared from analytical grade chemical reagents using distilled water.

For the electrochemical measurements the arrangement used was a conventional three-electrode cell with a platinum foil as counter-electrode, a saturated calomel electrode (SCE) provided as reference electrode and carbon steel was the working electrode.

The potentiodynamic polarization measurements were carried in a potential range of $\pm$ 50 mV vs. open circuit potential with the scan rate of 1.0 mV s^{-1}.

Electrochemical impedance spectroscopy (EIS) measurements were performed at open circuit potential with voltage amplitude 32 mV in the frequency range of 1.0 Hz to 10 000 Hz.

The potentiodynamic polarization and EIS measurements were carried out using ACM instruments Potentiostat/Galvanostat (Gill AC Serial no. 947).

Quantum chemical calculations were performed using density function theory (DFT) program for molecular modeling from Scientific Computing & Modeling Company. Theoretical calculations were carried out at the level of B3LYP/6-31G (d,p) basis set for all atoms with Gaussian 03W program.

3 Results and discussion

3.1 Potentiodynamic polarization measurements

3.1.1 Effect of N9 concentration

Figure 2 represents the potentiodynamic polarization curves of carbon steel in 1.0 M HCl in the absence and presence of various concentrations of N9 at 298 K.

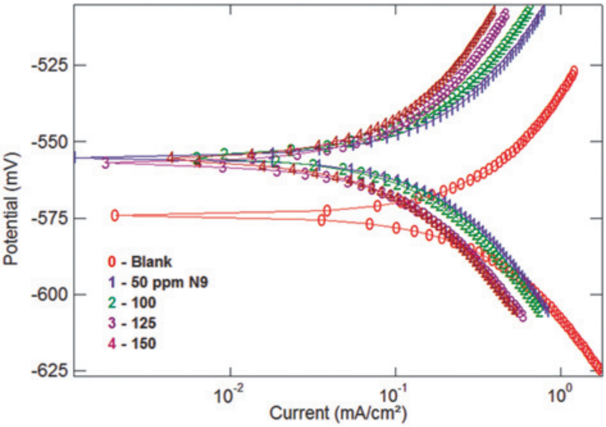

Figure 2: Potentiodynamic polarisation curves for carbon steel in 1.0 M HCl solution containing various concentrations of N9 at 298 K.

Table 1: Electrochemical parameters and the corresponding corrosion inhibition efficiency for carbon steel in 1.0 M HCl in the absence and presence of N9 at 298 K.

Inhibitor conc. (ppm)	I_{corr} (mA cm^{-2})	E_{corr} (mV vs. SCE)	P_{pol} %
Blank	0.72	−575	–
50	0.38	−555	47.2
100	0.32	−555	55.5
125	0.24	−557	66.6
150	0.21	−556	70.8

Table 1 gives the electrochemical parameters, i.e. corrosion potential (E_{corr}), corrosion current density (I_{corr}) and percentage inhibition efficiency (P_{pol} %). The P_{pol} % was calculated from polarization measurements according to following equation [14]:

$$P_{pol}\,\% = [(I_{corr(0)} - I_{corr})/I_{corr(0)}] \times 100 \tag{1}$$

where $I_{corr(0)}$ and I_{corr} are the corrosion current densities in the absence and presence of inhibitor, respectively.

From Figure 2, it is clear that both anodic metal dissolution and cathodic reactions are hindered when N9 compound was added to the corrosive solution. The values of the corrosion current density significantly decrease with increasing N9 concentration up to 150 ppm. It is evident that the presence of different concentrations of N9 has no significant effect on the values of corrosion potential E_{corr}, suggesting that the N9 is a mixed-type inhibitor [15, 16]. The results indicated that the inhibition efficiency of N9 increases with increasing the inhibitor concentration.

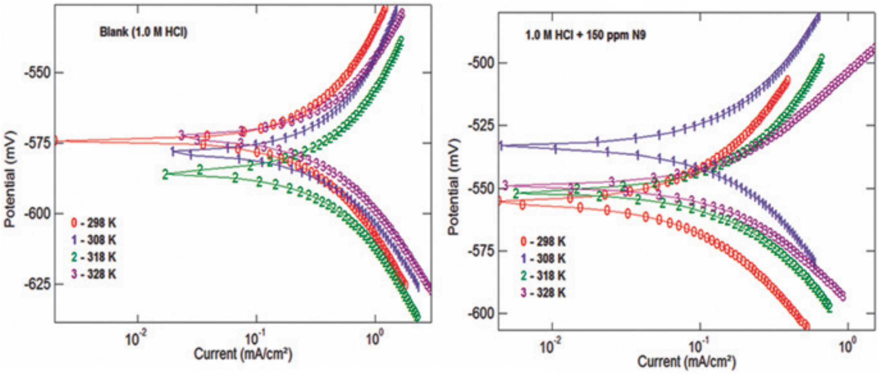

Figure 3: Potentiodynamic polarisation curves for carbon steel in 1.0 M HCl solution in the absence (blank) and presence of 150 ppm of N9 at different temperatures.

The highest inhibition efficiency of N9 was found at 150 ppm (P_{pol} % = 70.8). Further increase in N9 concentration did not cause any significant change in the value of the inhibition efficiency.

Corrosion inhibition of carbon steel in 1.0 M HCl by N9 can be explained on the basis of adsorption. Where N9 includes high number of adsorption active centers (O atoms) with high charge density [17, 18]. Owing to the adsorption of the inhibitor onto the surface of metal, a thin film is formed on the metal surface to retard the corrosion reactions [19, 20].

3.1.2 Effect of temperature

Figure 3 illustrates the effect of temperature (298–328 K) on the potentiodynamic polarization behavior of carbon steel in 1.0 M HCl in the absence (blank) and presence of 150 ppm of N9.

The influences of temperature on the electrochemical parameters and the inhibition efficiency of N9 were reported in Table 2.

The results showed that the values of I_{corr} in the absence and presence of N9 increase with raising temperature, suggesting that the corrosion process is endothermic process. However, the inhibition efficiency decreases with increase in temperature from 298 to 328 K. This is due to N9 desorption from the metal surface at high temperatures. This leads to exposure greater area of metal to the corrosive medium [21, 22]. In addition, an increase in temperature accelerates the rates of diffusion and migration of the reactant and product species [23].

Table 2: Electrochemical parameters and the corresponding corrosion inhibition efficiency for carbon steel in 1.0 M HCl in the absence (blank) and presence of 150 ppm N9 at different temperatures.

Solution	Temperature (K)	I_{corr} (mA cm^{-2})	E_{corr} (mV vs. SCE)	P_{pol} %
Blank	298	0.72	−575	–
	308	0.93	−576	–
	318	0.96	−587	–
	328	1.05	−557	–
150 ppm N9	298	0.21	−556	70.8
	308	0.30	−530	67.7
	318	0.35	−547	63.5
	328	0.47	−543	55.2

The activation parameters such as apparent activation energy (E_a), the enthalpy change of activation (ΔH_a) and the entropy change of activation (ΔS_a) were obtained from an Arrhenius-type (Equation (2)) and Eyring transition-state (Equation (3)) [24, 25]:

$$I_{corr} = A \exp(-E_a/RT) \tag{2}$$

$$I_{corr} = (RT/Nh) \exp(\Delta S_a/R) \exp(\Delta H_a/RT) \tag{3}$$

where I_{corr} is related to the corrosion rate in the absence and presence of inhibitor, R is the universal gas constant, A is the frequency factor, N is Avogadro's number and h is Planck's constant.

Plots of $\ln(I_{corr})$ against $(1/T)$ (as shown in Figure 4) and $\ln(I_{corr}/T)$ against $(1/T)$ (as shown in Figure 5) give straight lines with slopes of $(-E_a/R)$ and $(-\Delta H_a/R)$, respectively. The intercepts are A and $\ln(R/Nh) + (\Delta S_a/R)$ for Arrhenius and Eyring transition-state equations, respectively. The calculated values of E_a, ΔH_a and ΔS_a are tabulated in Table 3.

It is obvious that the addition of N9 to blank acid solution enhances the apparent activation energy. The increase in apparent activation energy E_a may be interpreted as physical adsorption [26, 27]. The increase in activation energy can be attributed to an appreciable decrease in the adsorption of N9 on the metal surface with increase in temperature and a corresponding increase in corrosion rates.

The positive values of ΔH_a both in absence and presence of N9 reflect the endothermic nature of the carbon steel dissolution process [28].

The values of entropy of activation ΔS_a are large and negative. The negative ΔS_a value in the presence of N9 signify that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning

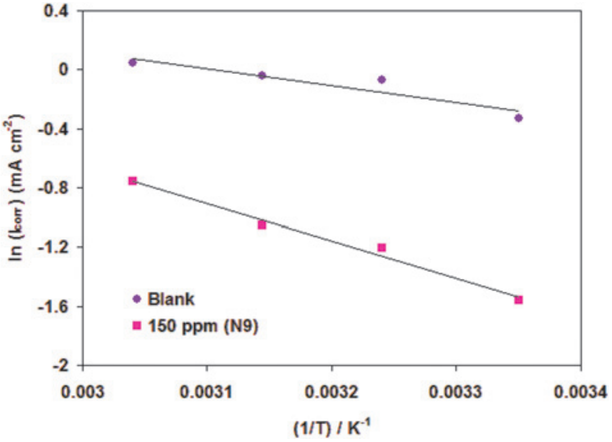

Figure 4: Arrhenius plots for carbon steel in 1.0 M HCl solution in the absence and presence of 150 ppm of N9.

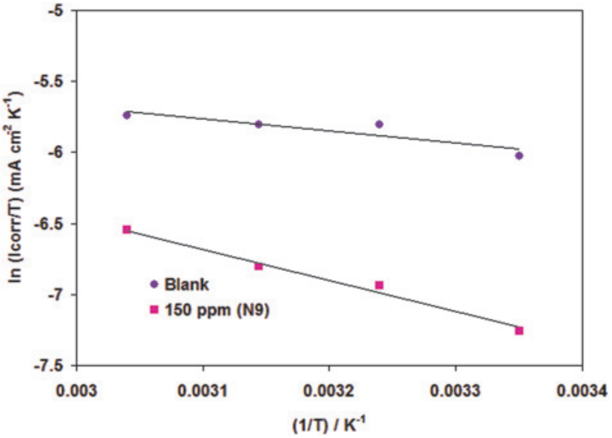

Figure 5: Eyring plot for carbon steel in 1.0 M HCl solution in the absence and presence of 150 ppm of N9.

Table 3: Activation thermodynamic parameters of the corrosion process in the absence and presence of N9.

Solution	E_a (kJ mol^{-1})	ΔH_a (kJ mol^{-1})	ΔS_a (J K^{-1} mol^{-1})
Blank	9.4	6.9	−223
150 ppm N9	20.8	18.26	−195

that a decrease in disordering takes place on going from reactants to the activated complex [29, 30].

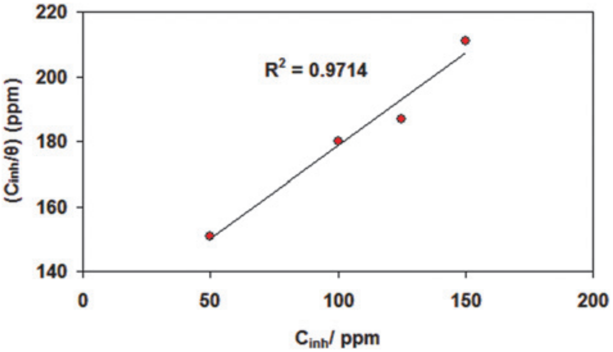

Figure 6: Curve fitting of the corrosion data of carbon steel in 1.0 M HCl solution in the presence of N9 at 298 K to Langmuir isotherm.

3.1.3 Adsorption isotherms

In this part several adsorption isotherms were tested to explain the best isotherm to determine the adsorption process. The best correlation between the experimental results and isotherm functions was obtained using Langmuir adsorption isotherm. The Langmuir isotherm is given by the equation [31]:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \tag{4}$$

where C_{inh} is the inhibitor concentration, θ is the fraction of the surface covered ($\theta = P_{\text{pol}}\,\%/100$) and K_{ads} is the equilibrium constant.

The plot of C_{inh}/θ versus C_{inh} is shown in Figure 6. The correlation coefficient (R^2) was used to choose the isotherm that best fit the experimental data. From the plot, straight line was obtained with $R^2 > 0.9$. This indicates that the experimental data fit well with the Langmuir adsorption [32]. The extracted value of K_{ads} was 8.22×10^{-3} ppm^{-1}.

The free energy of adsorption ($\Delta G^{\text{o}}_{\text{ads}}$) is related to the equilibrium constant of adsorption K_{ads} by the following equation [33]:

$$\Delta G^{\text{o}}_{\text{ads}} = -RT\ln(55.5K_{\text{ads}}) \tag{5}$$

where 55.5 is the concentration of water in the solution (M), R is the universal gas constant and T is the absolute temperature.

In present study, $\Delta G^{\text{o}}_{\text{ads}}$ value obtained for N9 adsorption on carbon steel in 1.0 M HCl solution was -31.03 kJ mol^{-1}. The negative sign of $\Delta G^{\text{o}}_{\text{ads}}$ refers to strong spontaneous adsorption of N9 on carbon steel [34].

The calculated $\Delta G^{\text{o}}_{\text{ads}}$ value was less negative than -40 kJ mol^{-1}. This indicates that the adsorption mechanism of N9 on carbon steel in 1.0 M HCl at the studied temperature was predominantly physisorption [35].

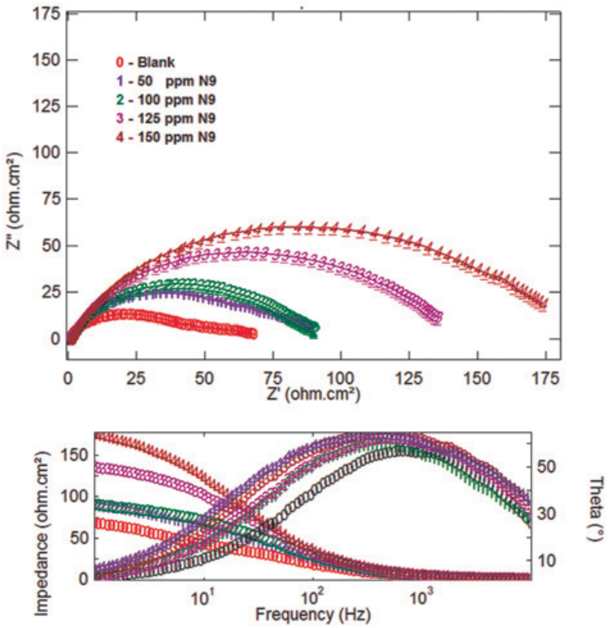

Figure 7: Nyquist/Bode plots for carbon steel in 1.0 M HCl solution in absence and presence of different concentrations of N9 at 298 K.

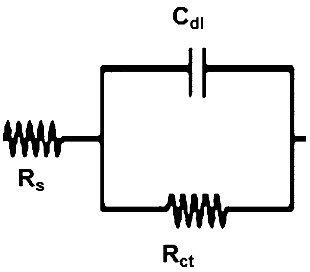

Figure 8: Equivalent circuit used for modeling the impedance results.

3.2 EIS measurements

Impedance spectra for carbon steel in 1.0 M HCl in the absence and presence of various concentrations of N9 at 298 K are shown in the form of Nyquist and Bode plots (Figure 7).

In all cases, the Nyquist plots were not perfect semicircles. This anomalous phenomenon can be attributed to the in-homogeneity and the roughness of the electrode surface [36, 37]. Based on the shape of Nyquist plots, the simplest equivalent circuit (Figure 8) was used for fitting of the impedance spectra. In this equivalent circuit, solution resistance (R_s) was in series with charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}). The charge transfer resistance values R_{ct}