

Evaluation of some Nonionic Surfactants Derived from Hydroquinol Compounds as Corrosion Inhibitors for Carbon Steel in Hydrochloric Acid

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The corrosion behavior of carbon steel in 1.0M HCl solution in the absence and presence of some nonionic surfactant derived from hydroquinol compounds was investigated using galvanostatic polarization, electrochemical impedance spectroscopy and potentiodynamic anodic polarization techniques. The results of these techniques indicated that the percentage inhibition efficiency, increased with increasing the concentration of inhibitors and number of ethylene oxide unit. Polarization curves revealed that the studied inhibitors act as mixed type inhibitors. Inhibition was interpreted by the horizontal adsorption of inhibitors on the steel surface due to the presence of more than one active center for adsorption. The adsorption process obeys Langmuir isotherms. All impedance spectra in the EIS technique exhibit one capacitive loop indicating a charge transfer process, mainly controlling the corrosion of carbon steel. Double layer capacitances decrease with respect to the blank solution when these inhibitors added due to the adsorption of these inhibitors on the steel surface. It is also found that these compounds inhibit the pitting corrosion of carbon steel in chloride containing solutions by shifting the pitting potential into more noble direction.

Keywords: Carbon steel, nonionic surfactant, adsorption, pitting potential

1. INTRODUCTION

Corrosion inhibition of carbon steel in acidic solutions have been widely used in many industries to reduce the corrosion rate of steel in contact with aggressive solutions. Acid solutions are widely used for removal of undesirable scale and rust in many industrial cleaning, oil well acidification and in the petrochemical processes [1]. Several methods were used to protect the steel from corrosion

in acidic solution One of these methods is to use corrosion inhibitors. The use of synthetic organic compounds containing hetero- atoms to inhibit the dissolution of steel in acidic solutions was studied [2-15]. The inhibiting action of these compounds is attributed to the adsorption of these compounds to the metal/solution interface. The adsorption process depends upon many factors such as the nature and surface charge of the metal, the type of aggressive media, the structure of the inhibitor and the nature of its interaction with the metal surface. However, these compounds, despite their inhibition efficiency are toxic and carcinogenic. However, only a few nontoxic and eco-friendly compounds have been studied as corrosion inhibitors. The use of some nonionic surfactants as corrosion inhibitors have many advantages such as high protection efficiency, low toxicity, low price and easy production [16-20]

In the previous work three compounds of nonionic surfactants derived from phenol compounds were used to inhibit the corrosion of carbon steel corrosion in acidic solution [21]. The target of this study is to complete the previous study and examine the effect of three compounds of nonionic surfactants derived from hydroquinol compounds as an inhibitor for carbon steel corrosion in hydrochloric acid solution. Galvanostatic, potentiodynamic anodic polarization and electrochemical impedance techniques were used in this work to evaluate the inhibition efficiency of the tested compounds.

2. EXPERIMENTAL TECHNIQUES

Carbon steel of type G-1018 used in this study has the following chemical composition (weight %) C 0.14 %, Mn 0.6%, P 0.04 %, S 0.05 % and the remainder is iron. For galvanostatic, potentiodynamic anodic polarization and electrochemical impedance techniques, a cylindrical rod embedded in Araldite with an exposed surface of 0.42 cm² was used. The electrode was polished with different grades of emery paper, degreased with acetone and rinsed with distilled water. The experiments were carried out at the 25±1 °C using air thermostat.

For galvanostatic experiments, the electrode was put under open circuit potential until stable potential was attained (about 30 min) and for potentiodynamic anodic polarization experiments, the electrode was held at hydrogen evolution potential for 10 min in order to get rid of any pre-immersion oxide film.

The galvanostatic and potentiodynamic anodic polarization experiments were carried out using a PS remote potentiostat with PS6 software for calculation of some corrosion parameters, e.g. corrosion current density (I_{corr}), corrosion potential (E_{corr}) and anodic and cathodic Tafel constants (b_a and b_c). The corrosion parameters were calculated from the intercept of the anodic and cathodic Tafel lines.

The percentage inhibition efficiency (% I.E) and a parameter (θ) which represents the part of the metal surface covered by the inhibitor molecules were calculated according to the following relations.

$$\% \text{ IE} = \left[1 - \frac{I_{add}}{I_{free}} \right] * 100 \quad (1)$$

$$\theta = \left[1 - \frac{I_{add}}{I_{free}} \right] \quad (2)$$

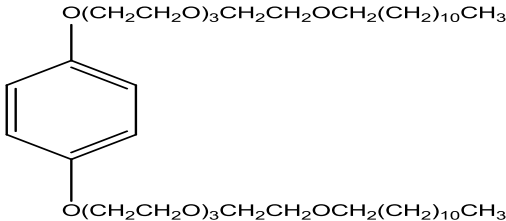
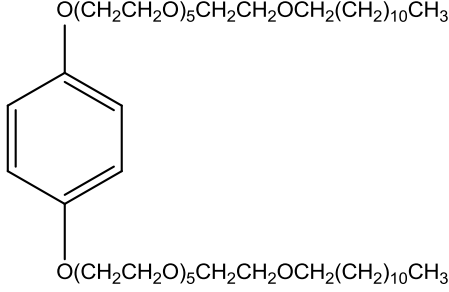
where, I_{free} and I_{add} are the corrosion current densities in free and inhibited solution, respectively.

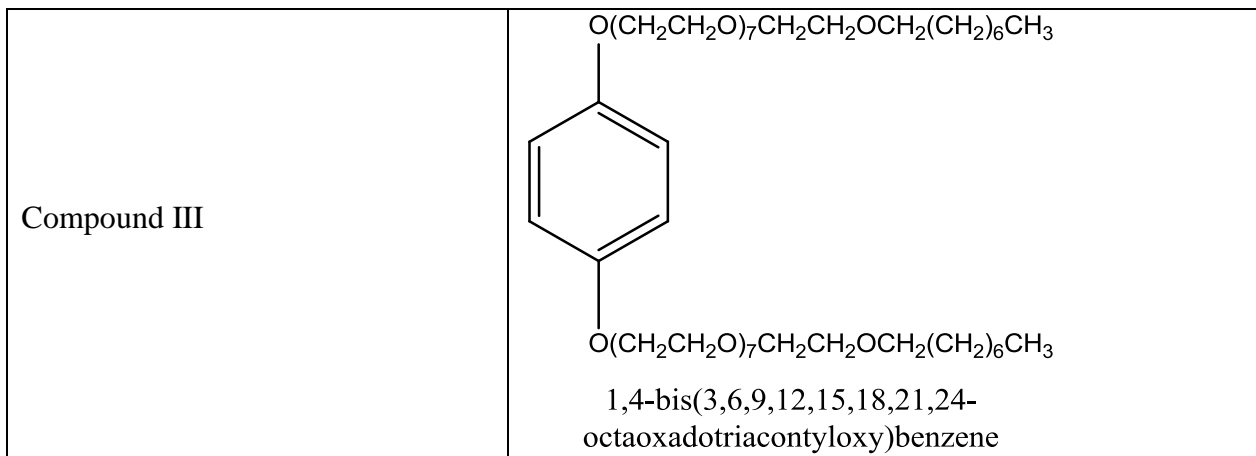
The potentiodynamic anodic polarization curves were carried out at a scan rate of 1 mVs^{-1} . A three compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used

The electrochemical impedance spectroscopy measurements were carried out at open circuit potential (E_{ocp}) in the frequency range from 10 kHz to 100 mHz with signal amplitude perturbation of 5 mV by using a computer-controlled potentiostat (Auto Lab 30, Metrohm).

Three nonionic surfactants derived from hydroquinol compounds were prepared using a method described elsewhere [22] are given in Table 1.

Table 1. The chemical structure of nonionic surfactants derived from hydroquinol compounds

Compounds	Structure
Compound I	 <p>O(CH₂CH₂O)₃CH₂CH₂OCH₂(CH₂)₁₀CH₃</p> <p>O(CH₂CH₂O)₃CH₂CH₂OCH₂(CH₂)₁₀CH₃</p> <p>1,4-bis(3,6,9,12-tetraoxatetracosyloxy)benzene</p>
Compound II	 <p>O(CH₂CH₂O)₅CH₂CH₂OCH₂(CH₂)₁₀CH₃</p> <p>O(CH₂CH₂O)₅CH₂CH₂OCH₂(CH₂)₁₀CH₃</p> <p>1,4-bis(3,6,9,12,15,18-hexaoxatriacontyloxy)benzene</p>



3. RESULTS AND DISCUSSION

3.1. Galvanostatic polarization

Fig.1 shows the cathodic and anodic polarization curves of carbon steel type G-1018 in 1.0M HCl solution devoid of and containing varying concentrations of compound III as an example of the investigated nonionic surfactant compounds. However, similar curves were obtained for the other two compounds (not shown).

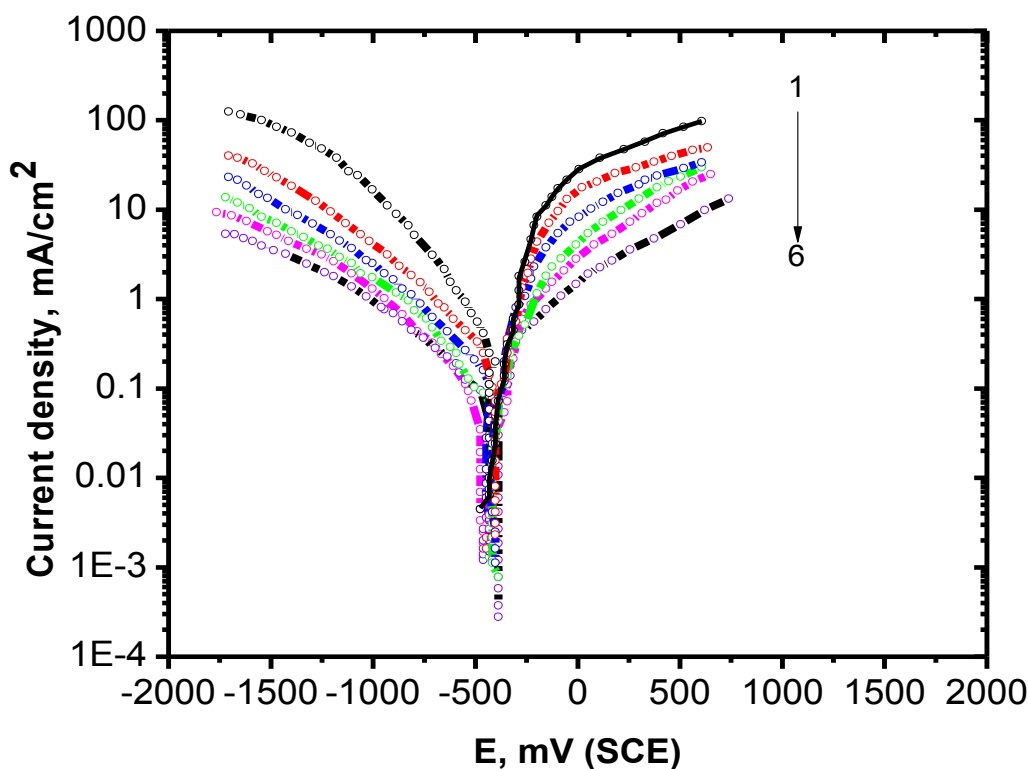


Figure 1. Galvanostatic polarization curves of carbon steel in 1.0M HCl solution containing different concentrations of compound III (1) 0.00 (2) 100 (3) 200 (4) 300 (5) 400 (6) 500 ppm.

The electrochemical corrosion parameters such as, corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c), and percentage inhibition efficiency (I.E.) were calculated and given in Table 2. Inspection of the data given in this table reveals that, the values of β_a and β_c increases with the increase of inhibitor concentration. This indicates that the addition of inhibitors retards both the anodic dissolution of steel and the cathodic hydrogen evolution reactions and hence acting as a mixed type inhibitor [23]. The values of E_{corr} were shifted to more negative potentials, whereas, the values of I_{corr} decreases and the those of %IE increases indicating the inhibiting action of these compounds. The inhibition efficiencies of these compounds decrease in the following order: Compound III > compound II > compound I and this trend will be discussed later.

Table 2. Corrosion parameter obtained from galvanostatic polarization measurements of carbon steel in 1.0M HCl solution containing different concentrations of inhibitors at 30 °C

Comp.	Conc., ppm	$-E_{\text{corr}}$ Mv (SCE)	I_{corr} Ma cm ⁻²	β_a mVdec ⁻¹	$-\beta_c$ mVdec ⁻¹	% IE	θ
Blank	-	485	1.22	65	309	-----	-----
I	100	510	0.46	80	368	62.29	0.623
	200	520	0.41	95	316	66.39	0.664
	300	528	0.35	113	407	71.31	0.713
	400	532	0.28	155	422	77.04	0.770
	500	535	0.18	190	466	85.24	0.852
II	100	505	0.39	86	354	68.03	0.680
	200	508	0.37	111	387	69.67	0.697
	300	511	0.31	140	408	74.59	0.746
	400	513	0.22	165	450	81.96	0.820
	500	515	0.14	198	460	88.52	0.885
III	100	503	0.34	65	302	72.13	0.721
	200	509	0.32	78	352	73.77	0.738
	300	515	0.26	98	388	78.68	0.787
	400	520	0.18	124	442	85.24	0.852
	500	525	0.11	182	486	90.98	0.910

3.2. Electrochemical impedance spectroscopy (EIS)

Figs.2 represents the Nyquist plots curves of carbon steel electrode type G-1018 in 1.0M HCl solution in the absence and presence of varying concentrations of compound III as an example of the studied surfactant compounds. However, similar curves were obtained for the other two compounds (not shown). The Nyquist plots contain depressed semi-circles with their center located under the real axis, and their size increases with inhibitor concentration, indicating a charge transfer process, mainly

controlling the corrosion of carbon steel [24,25]. Deviations from perfect circular shape are often referred to the frequency dispersion of interfacial impedance which arises due to surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, and formation of porous layers and in homogenates of the electrode surface [26]. Fig.3 represents The electrical equivalent circuit model used to analyze and interpret the obtained impedance data. This circuit consists of R_s (the resistance of solution between the carbon steel electrode surface and the counter electrode), the double-layer capacitance (C_{dl}) in parallel to the charge-transfer resistance (R_{ct}). The main parameters deduced from the analysis of Nyquist diagram are the resistance of charge transfer R_{ct} (diameter of the high frequency loop) and the capacity of double layer C_{dl} which is defined as:

$$C_{dl} = 1 / (2 \pi f_{max} R_{ct}) \tag{3}$$

where, f_{max} is the maximum frequency

The percentage inhibition efficiency from the impedance measurements were calculated using the following relation:

$$IE \% = [1 - (R_{ct}^o / R_{ct})] \times 100 \tag{4}$$

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

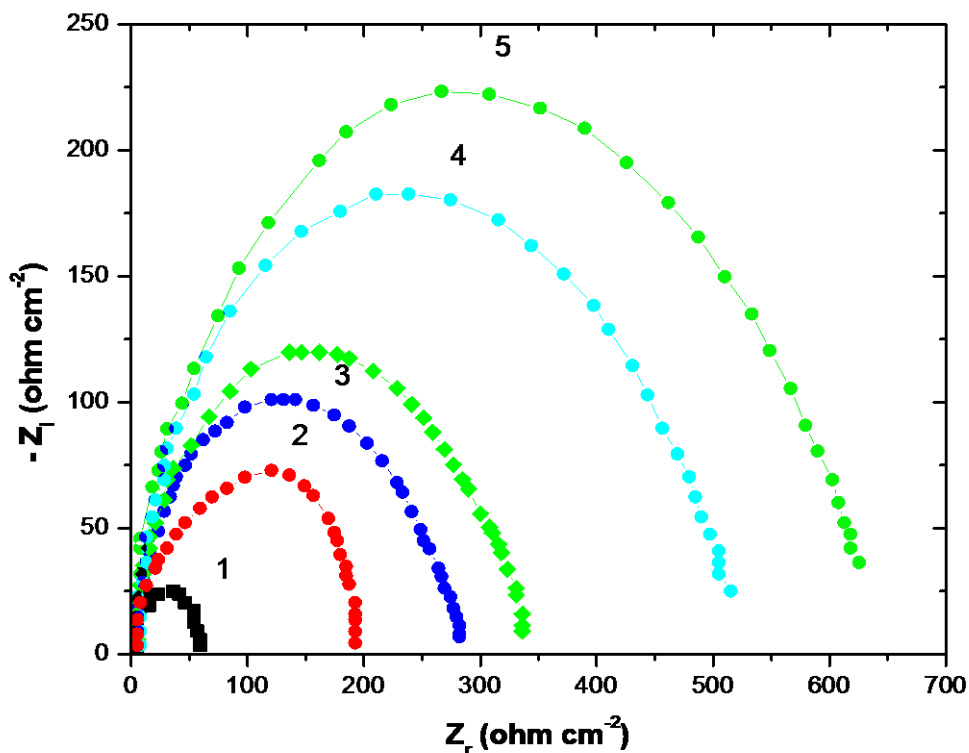


Figure 2. The Nyquist plots for carbon steel in 1.0 M HCl solution in the absence and presence of different concentrations of compound (III) at 30 °C.

Table 3 represents the EIS parameters (R_s , R_{ct} and C_{dl} and % IE). As can be seen from Table 3 the R_{ct} values of the investigated compounds increase with increasing inhibitor concentration. At the same time the C_{dl} has the opposite trend in the whole concentration range. This was explained due to

the gradual replacement of water molecules by the adsorption of the inhibitor molecules at the metal/solution interface, decreasing the extent of dissolution reaction. The higher values of (R_{ct}), are generally associated with the slower corroding system [27].

The order of inhibition efficiency obtained from EIS measurements decreases in the following sequence is : compound III > compound II > compound I

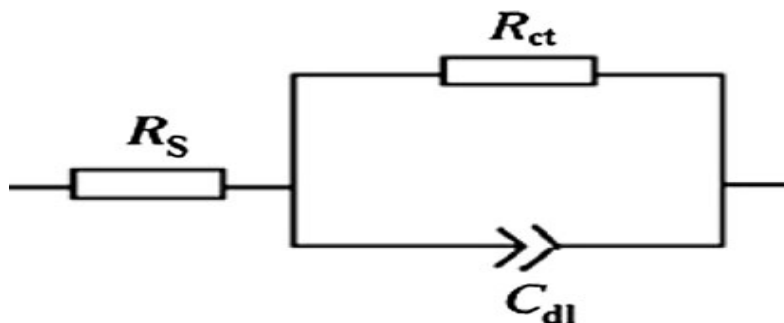


Figure 3. Electrical equivalent circuit (R_s = uncompensated solution resistance, R_{ct} = charge transfer resistance, and C_{dl} = double layer capacitance)

Table 3. Electrochemical parameters obtained from by EIS technique for carbon steel electrode in 1.0 M HCl solution in absence and presence of various concentrations of nonionic surfactants derived from hydroquinol compounds

	Conc., ppm	$C_{dl}, \mu Fcm^{-2}$	$R_s(\Omega cm^2)$	$R_{ct}, \Omega cm^2$	IE%
HCl	1M	97	1.48	70	-
Compound I	100 ppm	82	1.42	190	63.15
	200 ppm	73	1.38	245	71.42
	300 ppm	65	1.32	270	74.07
	400 ppm	50	1.28	326	78.52
	500ppm	44	1.24	462	84.84
Compound II	100 ppm	76	1.38	220	68.18
	200 ppm	70	1.30	236	70.33
	300 ppm	58	1.26	268	73.88
	400 ppm	52	1.22	332	78.91
	500ppm	46	1.18	528	86.74
Compound III	100 ppm	73	1.30	200	65.00
	200 ppm	68	1.26	290	75.86
	300 ppm	45	1.22	350	80.00
	400 ppm	38	1.18	545	87.15
	500ppm	32	1.12	650	89.23

3.3. Potentiodynamic anodic polarization curves

3.3.1. Effect of chloride ions

Fig.4 shows the potentiodynamic anodic polarization curves of the C-steel electrode in 1.0 M HCl solution with a varying concentrations of NaCl as pitting corrosion agent at a scanning rate of 1 mVs^{-1} . As inspection of the curves of Fig. (4) reveals that, the addition of Cl^- ions don't change the shape of the polarization curves recorded in the chloride free solution. There is a sudden and marked increase of current at a certain definite potential denoting the destruction of the passivating film and initiation of visible pits [28]. The potential at which the sudden rise takes place is defined as the pitting potential. The higher concentration of Cl^- ions, the higher is the shift of the pitting potential in an active (negative) direction.

The breakdown of passivity could be referred to the adsorption of chloride ions on the passive film formed on the steel surface which create an electrostatic film across a film / solution interface [29]. Thus, when the electrostatic field reaches a certain value, the adsorbed anions start to penetrate into the passive film and the pitting corrosion is initiated.

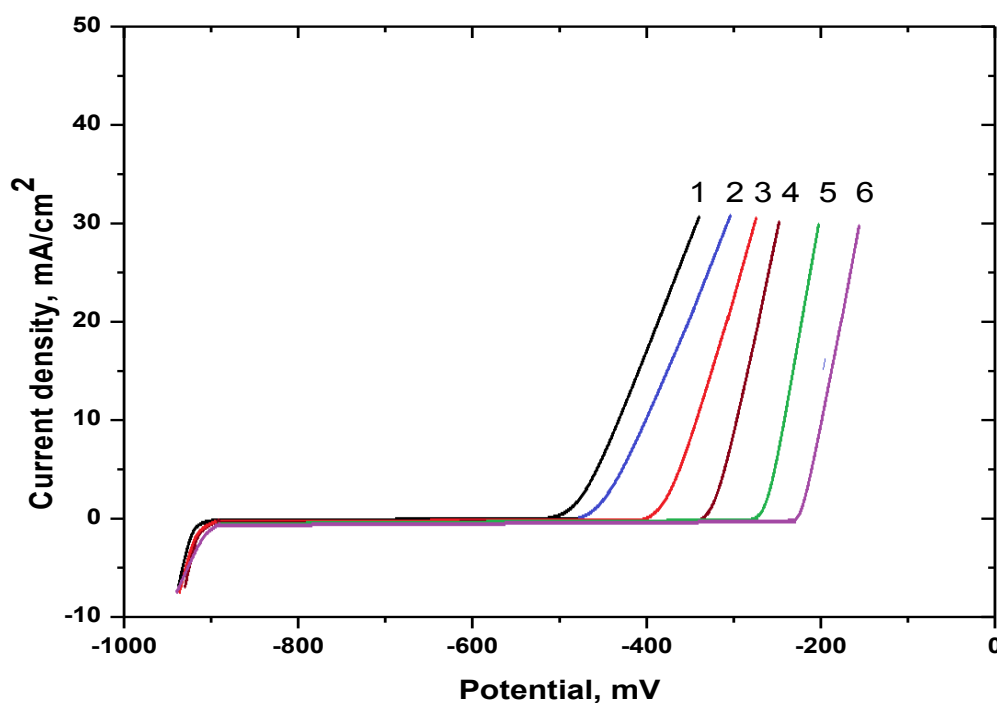


Figure 4. Potentiodynamic anodic polarization curves of carbon steel in 1.0 M HCl solution containing different concentrations of NaCl solutions at a scan rate 1 mV sec^{-1} . (1) 0.00 (2) 0.001 (3) 0.005 (4) 0.01 (5) 0.05 (6) 0.1M.

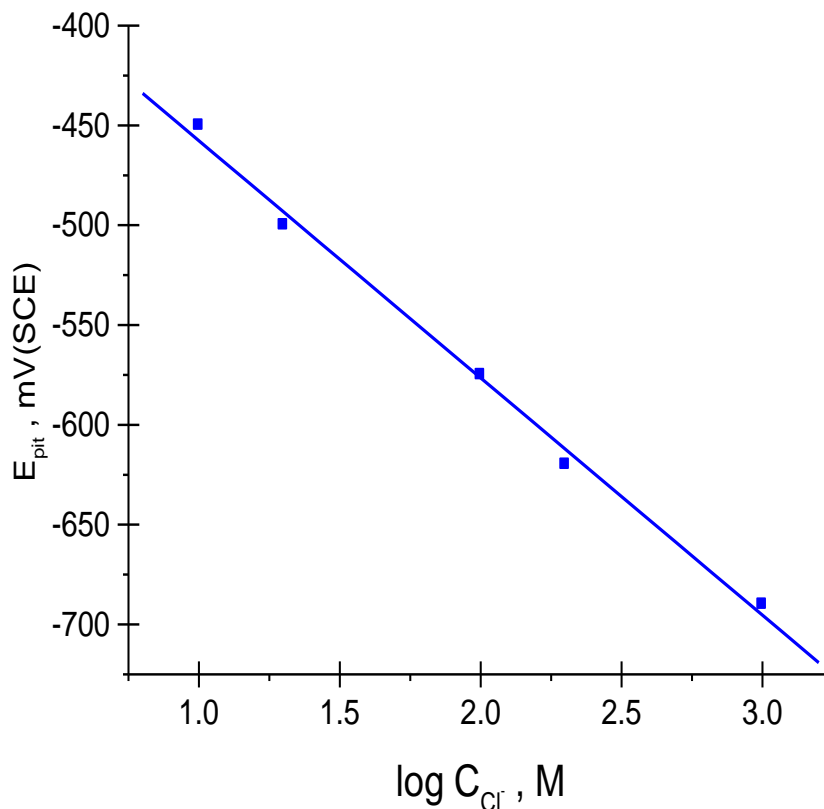


Figure 5. Relationship between pitting potential of C-steel and logarithm the concentrations of chloride ion in presence 1.0M HCl solution.

The dependence of the pitting potential E_{pitt} on the Cl^- ion concentration is illustrated in the Fig.5. A straight line relationship is obtained that obeys the equation [30,31]:

$$E_{pitt.} = a_1 - b_1 \log C_{Cl^-} \quad (5)$$

where a_1 and b_1 are constants which depend on both the nature, type of the electrode and type of the aggressive anion and the.

3.3.2. Inhibition of pitting corrosion

The effect of increasing concentration of three compounds of nonionic surfactants derived from hydroquinol compounds on the potentiodynamic anodic polarization curves of C- steel electrode in 1.0 M HCl + 0.1 M NaCl solution at a scan rate of 1 mVs^{-1} was studied. Similar curves to Fig.4 were obtained (not shown).

The characteristic features of these curves are the shift of the pitting potential in the noble (positive) direction as the additive concentration is increased indicating an increased resistance to pitting attack. Fig.6 represents the relationship between the pitting potential of the carbon steel

electrode and the logarithm of the molar concentrations of inhibitors. From the curves of this figure, the following conclusions could be drawn.

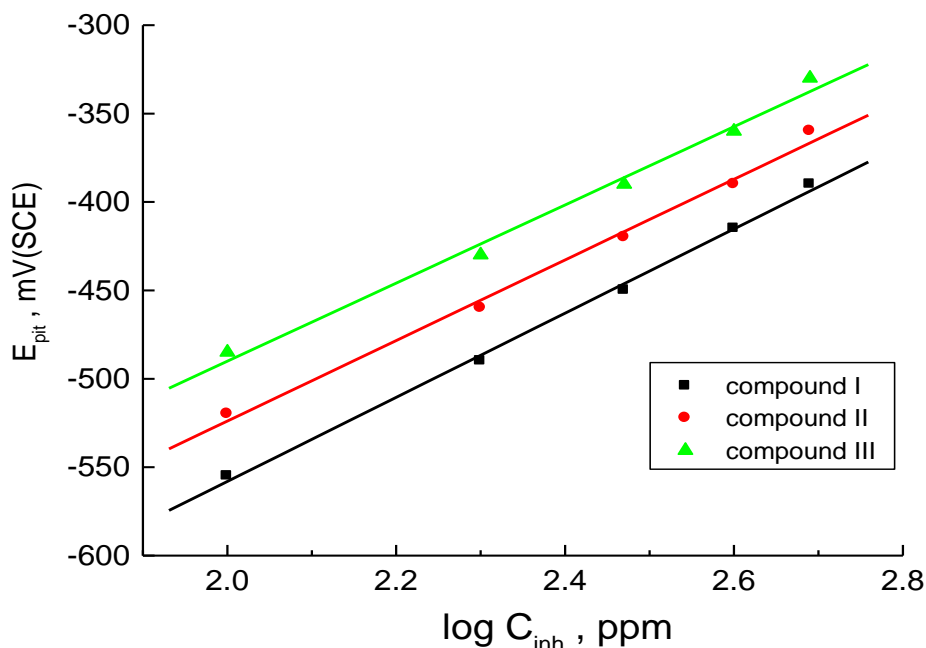


Figure 6. The relation between the pitting potential of C-steel and logarithm the concentration of nonionic surfactant compounds 1) Compound I 2) compound II 3) compound III

7) An increase of inhibitor concentrations led to a positive shift of E_{pitt} . In accordance with the following equation [32,33]:

$$E_{pitt} = a_2 + b_2 \log C_{inh} \tag{6}$$

Where, a_2 and b_2 are constants which depend on both the type of additive and the nature of the electrode.

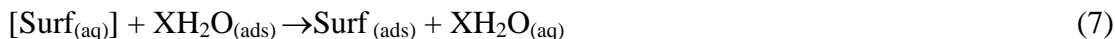
ii) Inhibition afforded by these compounds (i.e. more positive shift of E_{pitt} .) decreases in the following order:

Compound III > compound II > compound I

The order of % IE obtained from galvanstatic and EIS measurements is in a good agreement with that obtained from potentiodynamic anodic polarization measurement

3.4. Adsorption Isotherm and Inhibition mechanism

Nonionic surfactants derived from hydroquinol compounds inhibit the corrosion process by the horizontal adsorption on steel surface due to the presence to the presence of more than one active center for adsorption. The presence of two series of ethylene oxide unit in the chemical structure of inhibitors facilitates the adsorption process. Theoretically, the adsorption process can be regarded as a single substitution process in which a surfactant molecule, in the aqueous phase [Surf. (aq)] substitutes an "x" number of water molecules adsorbed on the metal surface.



Where x is known as the size ratio and simply equals the number of adsorbed water molecules replaced by a single inhibitor molecule.

The adsorption depends on the structure of the inhibitor, the type of the metal, the nature of its surface, the nature of the corrosion medium and its pH value, the temperature, the electrochemical potential of the metal-solution interface. Adsorption isotherm equations are generally of the form [34]:

$$f(\theta, x) \exp(-a\theta) = KC \tag{8}$$

where, if (θ, x) is the configurationally factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm and a is a molecular interaction parameter depending upon molecular interactions in the adsorption layer and the degree of heterogeneity of the surface.

A number of mathematical relationships for the adsorption isotherms have been suggested to fit the experimental data of the present work. Attempts were made to fit θ values to various isotherms includes Freundlich, Temkin, Frumkin, Bockris-Swinkels, Flory-Huggins and Langmuir isotherms. However, the best agreement was obtained using the Langmuir adsorption isotherm. According to this isotherm θ is related to inhibitor concentration by the following equation:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \tag{9}$$

where C is the inhibitor concentration, and K_{ads} the adsorptive equilibrium constant,

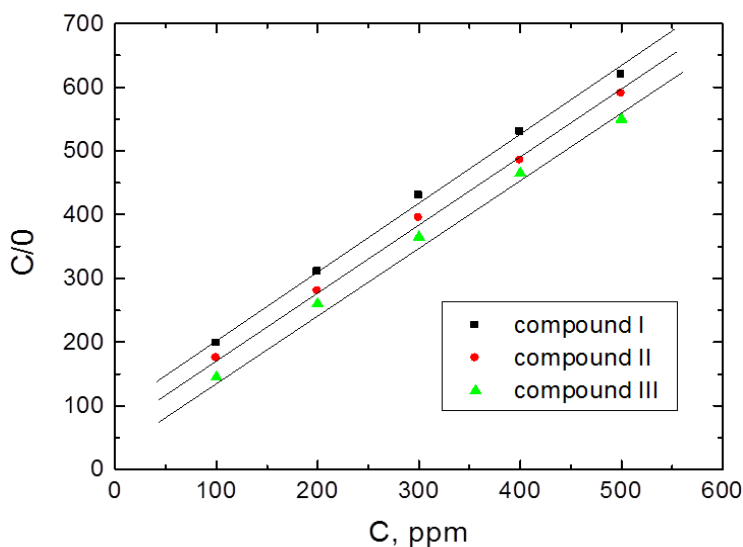


Figure 7. Langmuir adsorption isotherm

Fig.7 represents the plot of C/θ vs. C . A straight lines with slope equal unity were obtained indicating that the adsorption of nonionic surfactants derived from hydroquinol compounds on the

carbon steel surface in 1M HCl solution follows Langmuir's adsorption isotherm. Langmuir isotherm postulates monolayer adsorption hence no interaction between the adsorbate species on the steel surface.

The equilibrium constant of the adsorption process, K , is related to the standard free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$) by the following equation:

$$K = 1/55.5 \exp(-\Delta G^{\circ}_{\text{ads}}/RT) \quad (10)$$

where, R is the universal gas constant, T is the absolute temperature and the value 55.5 is the concentration of water in mol / l.

The calculated values of $\Delta G^{\circ}_{\text{ads}}$ for nonionic surfactants derived from hydroquinol compounds on the carbon steel surface is -22.75, -26.25 and -34.37 kJ mole⁻¹ for compounds I, II and III, respectively.

The negative sign values of $\Delta G^{\circ}_{\text{ads}}$ indicate that the adsorption of these compounds on the carbon steel surface is proceeding spontaneously and is accompanied by a highly efficient adsorption.

From the above results the order of the inhibition efficiencies of these compounds decrease in the following order:

Compound III > compound II > compound I

It is obvious that, the values of % IE increased with an increase in the number of ethylene oxide unit. The values of % IE increases than that obtained in previous work [21] and this is due to increase of number ethylene oxide units in this work. These findings could be explained on the bases of the fact that, an increase in concentration of the inhibitor would result in a lowering of the interfacial tension at the metal surface. This lowering in the interfacial tension is thought to a decrease of the bulk concentration of the inhibitor and an increase in its concentration at the metal surface

4. CONCLUSION

1- Nonionic surfactant derived from hydroquinol compounds have been used for inhibiting the corrosion of C-steel in 1.0M HCl

2-The percentage inhibition efficiency increases by concentration of inhibitors and number of ethylene oxide units per molecule.

3-The adsorption process obeys Langmuir isotherms.

4- Polarization curves revealed that the studied inhibitors act as mixed type inhibitors

5-The investigated compounds are efficient pitting corrosion inhibitors.

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