

## Temperature Effect on Corrosion Inhibition of Carbon Steel in Formation Water by Non-ionic Inhibitor and Synergistic Influence of Halide Ions

K.Z. Mohammed, A. Hamdy\*, A. Abdel-wahab, N .A. Farid

Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt  
[amalhamdy66@hotmail.com](mailto:amalhamdy66@hotmail.com)

**Abstract:** The inhibitive effect of nonionic surfactant namely nonylphenoxy poly (ethyleneoxy) ethanol (NPPE) on carbon steel corrosion in oilfield formation water at temperature range 303-333 K was studied using electrochemical polarization technique. The inhibition efficiency increases with increasing the concentrations of NPPE but decreases with the increase in temperature. Potentiodynamic polarization studies revealed that the NPPE acts as a mixed inhibitor. Adsorption of NPPE on the carbon steel surface in oilfield formation water follows the Langmuir isotherm model. The activation energy and the thermodynamic parameters for the inhibition process were calculated and discussed. The inhibition efficiency of NPPE synergistically increased on addition of halide ions in the order  $KCl < KBr < KI$ . [K.Z. Mohammed, A. Hamdy, A. Abdel-wahab, N .A. Farid. **Temperature Effect on Corrosion Inhibition of Carbon Steel in Formation Water by Non-ionic Inhibitor and Synergistic Influence of Halide Ions**. Life Sci J 2012;9(2):424-434]. (ISSN: 1097-8135). <http://www.lifesciencesite.com>.

**Keywords:** Nonionic surfactant; oilfield formation water; corrosion; synergistic inhibition; carbon steel; thermodynamic parameters

### 1. Introduction

The main reason of corrosion problems in the oil industry is attributed to the presence of formation water (oilfield water), which accompanies the oil production. It has been shown that corrosion is related to the water content which contains a various corrosive agents including carbon dioxide, hydrogen sulphide, organic acids and salts such as chlorides and sulfates [1].

Carbon steels are the most commonly used pipeline materials in petroleum production. However, carbon steels are very prone to corrosion in environments containing acid solutions [2]. The corrosion of acid solution on the steel materials causes considerable cost. In order to reduce the corrosion of metal, several techniques have been applied, where among that utilization of organic compounds and more specifically surfactants are gaining high space as corrosion inhibitors. Surfactants are very beneficial reagents and their presence at very low quantity in any medium providing desirable properties to processes in all industries such as, petrochemical, food, paint and coating industry [3].

A fundamental property of surfactants is their ability to form micelles (colloidal sized clusters) in solution. This property is due to the presence of both hydrophobic and hydrophilic groups in each surfactant molecule. Surfactants accumulate in special order at the interfaces and modify the interfaces and thus, control, reduce, or prevent reactions between a substrate and its surroundings, when added to the medium in small quantities. Different surfactant groups have been reported to present corrosion inhibitory potential which depends on the

classification of surfactants, the substrate type, inhibitor concentration [4-12], time of immersion in inhibitor solution [13], the type of acid, pH [14], presence of salts [15-23], co-surfactant [24], temperature [25-27] and inhibitor structure [28]. Nonionic surfactants are often used because of their lower critical micelle concentration (CMC), their higher degree of surface-tension reduction, and their relatively constant properties in the presence of salt, which result in better performance and lower concentration requirements [5].

Most acid inhibitors are known for their specificity of action. However, the combination of inhibitors is more likely to provide multiple effects required for effective corrosion inhibition. Synergistic inhibition studies for corrosion inhibitors for metals have been advocated as an effective means of decreasing the amount of inhibitor usage, diversifying the application of the inhibitor and improving the inhibitive force of the inhibitor. Interestingly, addition of halide salts to acid solutions containing any organic compound had been reported to result in a synergistic effect thereby inhibiting iron corrosion [25]. Corrosion inhibition synergism results from increased surface coverage as a result of ion-pair interactions between the organic cation and the anions. Synergistic effect of halide ions on the corrosion inhibition of metals using various substances have been reported by some research groups [29-31].

The synergistic effect was found to increase in the order  $I^- > Br^- > Cl^-$ . The highest synergistic effect associated with iodide ions has been attributed to their large size and ease of polarizability hence can be chemisorbed onto metal surface [32].

## 2. Experimental

### 2.1. Materials

Tests were performed on carbon steel (CS) of the following composition (wt. %): 0.05% C, 0.28% Mn, 0.023% P, 0.019% S, 0.02% Si, and the remainder Fe. Nonylphenoxy poly (ethyleneoxy) ethanol (NPPOE) was used as inhibitor; it was obtained from commercial source.

### 2.2. Test Solutions

The test solution used was oil field formation water kindly provided by The Gulf of Suez Petroleum Company (GUPCO). A typical chemical composition is given in Table (1). The concentration range of NPPOE employed was ( $4 \times 10^{-5}$  to  $40 \times 10^{-5}$  M). Deionized water was used for the preparation of all reagents. The halides used (KCl, KBr, and KI) were all BDH laboratory supplies chemicals, England. Solutions with 0.01M concentration of KCl, KBr and KI were used for the synergistic studies. The studies were carried out at temperature range of 303–333 K.

### 2.3. Electrochemical measurements

Electrochemical experiments were carried out in the conventional three-electrode cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode. The working electrode (WE) used was in the form of a square CRS embedded in PVC holder using epoxy resin so that the flat surface is the only exposed surface in the electrode, and has an area of  $1.0 \times 1.0$  cm. Before running the experiment the electrode was abraded with emery paper (grade 320–500–800–1200) on test face, rinsed with distilled water, degreased with acetone, and dried with a cold air stream. A computer controlled EG&G PAR 273A Potentiostat/galvanostat (Princeton Applied Research) was used for the electrochemical measurements. Each experiment was repeated at least three times to check the reproducibility. Polarization curves were recorded potentiodynamically, at the scan rate of 1 mV/s, in the range of +250 mV to -250 mV versus OCP potential.

## 3. Results and Discussion

### 3.1. Polarization studies

The inhibition process of the (NPPOE) for the corrosion of carbon steel in oilfield formation water was analyzed by polarization experiments.

Some examples of both the Tafel anodic and cathodic polarization curves for carbon steel in oilfield formation water at different concentrations of the nonionic surfactant (NPPOE) and different temperatures are shown in Figure (1). It is clear that the presence of the inhibitor shifts the corrosion potential to the noble direction, i.e. decreases the

corrosion rate. This may be ascribed to adsorption of the inhibitor over the corroded surface. Corrosion parameters such as, the corrosion current density ( $I_{corr}$ ), corrosion potential ( $E_{corr}$ ), anodic and cathodic Tafel slopes ( $b_a$   $b_c$  respectively), were calculated from Figure (1) and the values are listed in Table (2). From these data, it is clear that the corrosion current decreases with the increase of the inhibitor concentration. The presence of (NPPOE) surfactant does not remarkably shift the corrosion potential while, both the anodic and cathodic Tafel slopes change with the increase of the inhibitor concentration. Therefore, the nonionic surfactant (NPPOE) can be classified as mixed-type inhibitor in oilfield formation water. These results are in good agreement with the results obtained for other organic compounds in acidic solutions [33–35].

The inhibition efficiency (IE %) and the degree of surface coverage ( $\theta$ ) were calculated according to the following equations [36]:

$$IE \% = \left( 1 - \frac{I}{I_0} \right) \times 100 \quad (1)$$

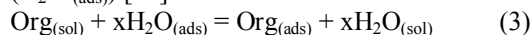
$$\theta = 1 - (I / I_0) \quad (2)$$

where  $I_0$  and  $I$  are the corrosion current density values in the absence and presence of inhibitor, respectively, determined by extrapolation of Tafel lines to the corrosion potential.

Values of the inhibition efficiency were calculated and listed in Table (2), which reveal that the inhibition efficiency ( $\eta$  %) increases with the increment of the inhibitor concentration.

### 3.2. Adsorption considerations

Basic information on the interaction between inhibitors and metal surface can be provided using the adsorption isotherms [37]. The adsorption of an organic adsorbate at metal–solution interface can occur as a result of substitutional adsorption process between organic molecules presented in the aqueous solution ( $Org_{(sol)}$ ), and the water molecules previously adsorbed on the metallic surface ( $H_2O_{(ads)}$ ) [38]:



Where  $Org_{(sol)}$  and  $Org_{(ads)}$  are the organic species in the bulk solution and adsorbed one on the metallic surface, respectively,  $H_2O_{(ads)}$  is the water molecule adsorbed on the metallic surface and  $x$  is the size ratio representing the number of water molecules replaced by one organic adsorbate. In order to obtain the adsorption isotherm, the degree of surface coverage,  $\theta$ , for different concentrations of inhibitor in oilfield formation water solutions has been evaluated by the following equation [39]:

$$\theta = I_{corr}^0 - I_{corr} / I_{corr}^0 \quad (4)$$

The  $\theta$  values are presented in Table (2). According to the Langmuir's isotherm, the surface coverage ( $\theta$ ) is related to inhibitor concentration (C) by the following equation [39]:

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

Where  $K_{\text{ads}}$  is the equilibrium constant of the inhibitor adsorption process and can be calculated from the intercept lines on the  $C_{\text{inh.}}/\theta$ -axis. As seen from Figure (2), the plot of  $C_{\text{inh.}}/\theta$  versus  $C_{\text{inh.}}$  yields a straight line with a correlation coefficient more than 0.99, showing that the adsorption of these inhibitors in oilfield formation water is fitted to Langmuir adsorption isotherm.

The data reported in Table (3) reveals that, the adsorptive equilibrium constant (K) decreases with increasing the temperature indicating that, it is easy for inhibitor to adsorb onto the carbon steel surface at relatively lower temperature, but as the temperature increases, the adsorbed inhibitor tends to desorption. These results suggest that, the inhibition of carbon steel in oilfield formation water by the NPPOE is an adsorptive process. This isotherm assumes that the adsorbed molecules occupy only one site and there are no interactions between the adsorbed species [40].

### 3.3. Thermodynamic parameters

Generally, the organic molecules inhibit corrosion by adsorption at the metal-solution interface and the adsorption process depends on the molecule's chemical composition, the temperature and the electrochemical potential at the metal-solution interface [40].

Thermodynamic parameters play an important role in understanding the inhibition mechanism. The standard adsorption heat ( $\Delta H^0$ ) could be calculated according to the Van't Hoff equation [41]:

$$\ln K = -\Delta H^0_{\text{ads}}/RT + \text{constant} \quad (6)$$

Where, R is the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), T the absolute temperature. To obtain the adsorption heat, the regression between  $\ln K$  and  $1/T$  was dealt with. Clearly, the adsorption heat can be obtained by using the slope of the regression ( $-\Delta H^0_{\text{ads}}/R$ ), and the relationship between  $\ln K$  and  $1/T$  is shown in Figure (3).

Figure (3) indicates that there is a good linear relationship between  $\ln K$  and  $1/T$  with a correlation coefficient higher than 0.99, meaning that it is safe to utilize the Van't Hoff equation to calculate the adsorption heat. Under the experimental conditions, the adsorption heat can be approximately regarded as the standard adsorption heat ( $\Delta H^0_{\text{ads}}$ ).

It is well known that the standard adsorption free energy ( $\Delta G^0_{\text{ads}}$ ) is related to the equilibrium constant of adsorption (K), and  $\Delta G^0_{\text{ads}}$  can be calculated by the following equation (42):

$$\Delta G^0_{\text{ads}} = -RT \ln (55.5 K_{\text{ads}}) \quad (7)$$

Where R is the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and T is the absolute temperature (K). The constant value of 55.5 is the concentration of water in solution expressed in M. A plot of  $\Delta G^0_{\text{ads}}$  versus T (Figure 4) gave the heat of adsorption ( $\Delta H^0_{\text{ads}}$ ) and the standard adsorption entropy ( $\Delta S^0_{\text{ads}}$ ) according to the thermodynamic basic equation:

$$\Delta G^0_{\text{ads}} = \Delta H^0_{\text{ads}} - T\Delta S^0_{\text{ads}} \quad (8)$$

Figure (4) clearly shows that the good dependence of  $\Delta G^0_{\text{ads}}$  on T, indicating the good correlation among thermodynamic parameters. The thermodynamic data obtained for NPPE in oilfield formation water using the adsorption isotherm are depicted in Table (3).

The negative sign of  $\Delta G^0_{\text{ads}}$  indicates that the inhibitors are spontaneously adsorbed on the metal surface [40, 43]. Generally, the magnitude of  $\Delta G^0_{\text{ads}}$  around  $-20 \text{ kJ mol}^{-1}$  or less negative, leads to the assumption that an electrostatic interaction exists between the inhibitor and the charged metal surface (i.e. physisorption). Standard free energy of adsorption ( $\Delta G^0_{\text{ads}}$ ) around  $-40 \text{ kJ mol}^{-1}$  or more negative indicates that a charge sharing or transferring from organic species to the metal surface occurs to form a coordinate type of bond (i.e. chemisorption) [44].

In the present study, the  $\Delta G^0_{\text{ads}}$  values obtained for the (NPPOE) in oilfield formation water solution ranges between  $-33.2$  and  $-36.8 \text{ kJ mol}^{-1}$ , which are lower than  $-40 \text{ kJ mol}^{-1}$  but higher than  $-20 \text{ kJ mol}^{-1}$ . This indicates that the adsorption is neither typical physisorption nor typical chemisorption but it is complex mixed type. That is the adsorption of inhibitor molecules on the carbon steel surface in the present study involves both physisorption and chemisorption (comprehensive adsorption) but physisorption is the predominant mode of adsorption. This assumption is supported by the data obtained from temperature dependence of inhibition process, reported in Table (2), which shows that the inhibition efficiency of the NPPOE studied decreases with increase in temperature (physisorption) [45]. Thus, we conclude that the adsorption for the inhibitor studied (NPPOE) on the carbon steel in oilfield formation water is complex in nature and predominantly physisorption. Moreover, the calculated  $\Delta G^0_{\text{ads}}$  values show that an electrostatic interaction exists between the charged molecules and the charged metal surface.

As for the value of  $\Delta S^0$  in Table 3, the sign of  $\Delta S^0$  is positive, which indicates that the adsorption process is accompanied by an increase in entropy. This could be explained as follows, The adsorption of organic inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the organic compound in the aqueous phase [ $\text{Org}_{(\text{sol})}$ ] and water molecules at the

electrode surface [ $\text{H}_2\text{O}_{(\text{ads})}$ ] [38]. In this situation, the adsorption of organic inhibitor is accompanied by the desorption of water molecules from steel surface. Thus, while the adsorption process for the inhibitor is believed to be exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent. The thermodynamic values obtained are the algebraic sum of the adsorption of organic molecules and desorption of water molecules. Therefore, the gain in entropy is attributed to the increase in solvent entropy [46].

### 3.4. Kinetic parameters

The adsorption phenomena have been explained by using thermodynamic parameters, to further elucidate the inhibition properties of the inhibitor, the kinetic model was employed. The thermodynamic functions for dissolution of carbon steel in the absence and in the presence of various concentrations of NPPOE were obtained by applying the Arrhenius equation and the transition state equation [47]:

$$I_{\text{corr.}} = A \exp(-E_a^0 / RT) \quad (9)$$

$$I_{\text{corr.}} = RT / Nh \exp(\Delta S_a^0 / R) \exp(-\Delta H_a^0 / RT) \quad (10)$$

Where  $E_a^0$  is the apparent activation energy, A the pre-exponential factor,  $\Delta H_a^0$  the apparent enthalpy of activation,  $\Delta S_a^0$  the apparent entropy of activation, h the Planck's constant and N the Avogadro number.

Arrhenius plots of  $\ln I_{\text{corr.}}$  vs.  $1/T$  for the blank and different concentrations of NPPOE are shown in Figure (5). The plots obtained are straight lines and the slope of each straight line gives its activation energy. The negative slope of ( $E_a$ ) indicates the adsorption of the inhibitor on the electrode surface. The regression between  $\ln I_{\text{corr.}}$  and  $1/T$  was calculated and the parameters were calculated and presented in Table (4), it can be seen that apparent activation energy increased with increasing concentration of NPPOE. Also, it is clear that  $E_a$  values in the presence of inhibitor are higher than that in the absence of inhibitor indicating higher activation energies for the metal dissolution reaction. Hence, the process is activation controlled. The increase in apparent activation energy with NPPOE concentration thereby indicates a more efficient inhibiting effect that can be attributed to the thickening of the electric double layer and supports the hypothesis that molecules can form micelles on the metal surface.

The increase in apparent activation energy  $E_a$  may be interpreted as physical adsorption [48]. Szauer and Brand [49] explained that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the carbon steel surface with increase in temperature and a corresponding increase in corrosion rates occurs

due to the fact that greater area of metal is exposed to the acidic solution environment.

Figure (6) shows a plot of  $\ln(I_{\text{corr.}}/T)$  vs.  $1/T$ . A straight lines were obtained with a slope equal to  $(-\Delta H_a^0 / R)$  and intercept equal to  $(\ln R/Nh + \Delta S_a^0 / R)$ , from which the values of  $\Delta H_a^0$  and  $\Delta S_a^0$  were calculated and listed in Table (4). Inspection of these data reveals that the thermodynamic parameters ( $\Delta H_a^0$  and  $\Delta S_a^0$ ) of dissolution reaction of carbon steel in oilfield formation water in the presence of NPPOE are higher than in the absence of inhibitor. The positive sign of enthalpies reflect the endothermic nature of steel dissolution process meaning that dissolution of steel is difficult [50]. On comparing the values of the entropy of activation  $\Delta S_a^0$  given in Table (4), it is clear that entropy of activation increased positively in the presence of NPPOE than in the absence of inhibitor. The increase of  $\Delta S_a^0$  reveals that an increase in disordering takes place on going from reactant to the activated complex [51].

### 3.5. Synergistic effect of halide ions

Synergistic inhibition effect of inhibitors takes place when the total action of compounds is higher than the sum of each one individually [52]. To elucidate the synergistic influence of halide ions on the corrosion inhibition of carbon steel in oilfield formation water by NPPOE, certain concentration of the inhibitor ( $10 \times 10^{-5}$ ) was studied in the absence and presence of  $1 \times 10^{-2}$  M KI, KCl and KBr to clarify this phenomenon. The synergistic inhibitive effect brought about by the inhibitor and halide ions are shown in Fig.(7). The electrochemical parameters of this study are presented in Table (5). It is clear that the addition of halide salts to the inhibitor solution enhanced inhibition and a marked change in the inhibition efficiency occurred from 61.2 to 93 %, 90 % and 87.8 % in presence of KI, KBr and KCl respectively with a noticeable increase in the surface coverage. A shift in  $E_{\text{corr.}}$  values to more anodic potentials is observed on addition of iodide salts. As  $E_{\text{corr.}}$  shifted to a more noble direction,  $I_{\text{corr.}}$  decreased considerably from 18.69 to 3.354, 4.928 and 5.998  $\mu\text{Acm}^{-2}$  for KI, KBr and KCl respectively. These values are coinciding with the polarization resistance values which increased considerably with the presence of halide salts; thus the corrosion inhibition effect of NPPOE appeared to be synergistically enhanced by the presence of the halide ions. The synergistic influence may be explained as follows: halide ions are initially chemisorbed on the metal surface and therefore, the surface becomes negatively charged. The positively charged part of the inhibitor molecule tends to become oriented towards the adsorbed anions preferentially by coulombic attraction onto the metal surface where iodide ions

already have been chemisorbed. This behavior suppresses the corrosion rate by stabilizing the adsorbed anion ( $I^-$ ) and the positively charged part of the inhibitor molecule, increasing the surface coverage of the inhibitor and this enhances the efficiency of the inhibition.

The synergistic parameter (S) was calculated using the following equation [53]:

$$S = (1 - I_{1+2}) / (1 - I_{1+2}) \quad (11)$$

Where,  $I_1$  is inhibition efficiency of halide,  $I_2$  is the inhibition efficiency of the inhibitor,  $I_{1+2} = I_1 + I_2$  and  $I_{1+2}$  is inhibition efficiency of inhibitor in combination with the anion. The value of (S) parameter was calculated for the case of each halide salt:

$$S_{KI} = 1.56, S_{KBr} = 1.67 \text{ and } S_{KCl} = 1.88$$

The (S) values in the three cases for KI, KBr and KCl respectively are more than unity, indicating clearly that, the enhanced inhibition efficiency is due to synergistic effect of halide and NPPOE (53).

#### 4. Conclusions

- NPPOE acts as a good corrosion inhibitor for carbon steel in oilfield formation water.
- The inhibition efficiency of NPPOE increases with increasing the inhibitor concentration but decreases with temperature.
- The adsorption of NPPOE obeys Langmuir adsorption isotherm. The adsorption process is a spontaneous and exothermic process accompanied by an increase of entropy.
- All the values of free energy are negative as well as less than  $-40 \text{ KJmol}^{-1}$ , indicating the spontaneous physical adsorption of the inhibitors on the metal surface.
- Addition of halide salts synergistically increased the inhibition efficiency of NPPOE in the order  $KCl < KBr < KI$ .

**Table (1): Chemical analysis of the tested oilfield formation water.**

Corrosive elements	Concentration	Test method ASTM
TDS, mg/l	122670	D-1888
Sodium as $\text{Na}^+$ , $\mu\text{g/g}$	36699	D-3561
Potassium as $\text{K}^+$ , $\mu\text{g/g}$	714	D-3561
Calcium as $\text{Ca}^{2+}$ , $\mu\text{g/g}$	3632	D-511
Magnesium as $\text{Mg}^{2+}$ , $\mu\text{g/g}$	4125	D-511
Chloride as $\text{Cl}^-$ , $\mu\text{g/g}$	59981	D-512
Sulphate as $\text{SO}_4^{2-}$ , $\mu\text{g/g}$	120	D-516

**Table (2): Electrochemical polarization parameters for the corrosion of carbon steel in oilfield formation Water containing various concentrations of (NPPOE) at different temperatures 293, 313 and 333K.**

T (K)	Conc. ( $10^{-5} \text{ M}$ )	R (mpy)	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu \text{ A cm}^{-2}$ )	$b_a$ ( $\text{mV dec}^{-1}$ )	$-b_c$ ( $\text{mV dec}^{-1}$ )	$R_p$ ( $\text{K } \Omega \text{ cm}$ )	IE (%)	$\theta$
293	Blank	15.89	-694.9	34.65	158.9	234.1	1.27	-	-
	4	9.629	-691.5	21.0	103.5	194.6	1.34	39.0	0.390
	6	8.228	-685.2	17.94	116.7	176.6	1.646	48.0	0.480
	8	6.610	-680.8	14.41	106.8	188.1	2.041	58.4	0.584
	10	5.705	-655.5	12.44	85.58	182.9	1.875	64.1	0.641
	20	3.299	546.0	7.193	81.5	155.4	2.904	79.2	0.792
	40	1.643	-512.3	3.583	71.16	111.0	3.667	89.7	0.897
313	Blank	22.49	-693.9	49.03	121.2	243.3	0.7176	-	-
	4	15.23	-668	33.20	124.2	204.7	0.9452	32.3	0.323
	6	12.85	-645.6	28.01	191.4	229.3	1.571	42.9	0.429
	8	10.61	-675.6	23.12	105.9	187.7	1.182	52.8	0.528
	10	8.572	-608	18.69	140.3	165.2	1.527	61.9	0.619
	20	6.652	-588.6	15.07	96.82	212.4	1.987	70.4	0.704
	40	3.593	-512.6	7.833	66.68	204.3	2.540	84.0	0.840
333	Blank	29.06	-707.3	63.35	134.6	484.5	0.6223	-	-
	4	20.22	-699.1	44.08	115.2	353.9	0.8110	30.4	0.304
	6	18.50	-693	40.34	120.3	241.5	0.9248	36.3	0.363
	8	15.82	-658	34.48	117.3	245.6	0.9774	45.7	0.457
	10	12.75	-699.3	27.81	122.4	214.5	1.171	56.1	0.561
	20	10.21	-679.6	22.27	112.5	204.1	1.433	64.9	0.649
	40	5.973	-634.2	13.02	98.64	195.9	1.794	79.4	0.794

**Table (3): Thermodynamic parameters for the adsorption of (NPPOE) inhibitor in oilfield formation water on the carbon steel at different temperatures.**

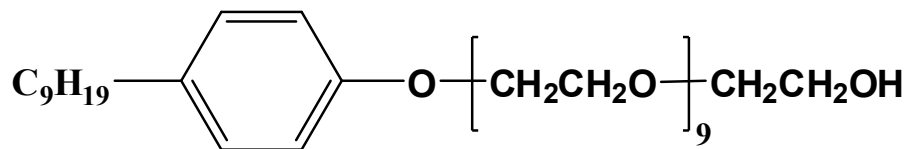
Temp. (K)	$K_{ads}$ ( $M^{-1}$ )	slope	$R^2$	$\Delta G_{ads}^{\circ}$ ( $kJ\ mol^{-1}$ )	$\Delta H_{ads}^{\circ}$ ( $kJ\ mol^{-1}$ )	$\Delta S_{ads}^{\circ}$ ( $J\ mol^{-1}K^{-1}$ )
293	15760	0.9554	0.9995	-33.2	-11.5	95
313	13020	1.002	0.9962	-35.0	-11.5	95
333	10885	1.035	0.9949	-36.8	-11.5	95

**Table (4): The values of activation parameters  $E_a$ ,  $\Delta H_a^{\circ}$  and  $\Delta S_a^{\circ}$  for carbon steel in formation water in the absence and presence of different concentrations of NPPE.**

Concentration (M) $\times 10^{-5}$	$E_a$ ( $kJ\ mol^{-1}$ )	$\Delta H_a^{\circ}$ ( $kJ\ mol^{-1}$ )	$\Delta S_a^{\circ}$ ( $J\ mol^{-1}K^{-1}$ )
Blank	12.5	10.39	-186.3
4	14.5	12.47	-182.6
6	16.6	14.55	-177.9
8	17.8	16.63	-172.7
10	16.6	14.55	-187.6
20	22.9	20.79	-164.1
40	27.0	24.94	-155.8

**Table (5): Electrochemical polarization parameters for the carbon steel in oilfield formation water containing NPPOE at concentration  $10 \times 10^{-5}$  M in the absence and presence of  $1 \times 10^{-2}$  M halide salt at  $40\ ^{\circ}C$ .**

Inh. Conc. (M)	R (Mpy)	$E_{corr.}$ (mV)	$I_{corr}$ ( $\mu Acm^{-2}$ )	$b_a$ (mVdec $^{-1}$ )	$-b_c$ (mVdec $^{-1}$ )	$R_p$ ( $K\Omega cm^{-2}$ )	IE (%)	$\theta$
Blank	22.49	-693.9	49.03	121.2	243.3	0.7176	-	-
$10 \times 10^{-5}$	8.572	-608	18.69	140.3	165.2	1.527	61.2	0.612
+ KI	1.538	-495.9	3.354	73.63	120.5	4.815	93	0.930
+ KBr	2.60	-515.9	4.928	98.54	120.9	4.107	90	0.900
+ KCl	2.751	-539.2	5.998	90.21	137.9	3.188	87.8	0.878

**Nonylphenoxy poly (ethyleneoxy) ethanol (NPPOE)****Scheme (1)**

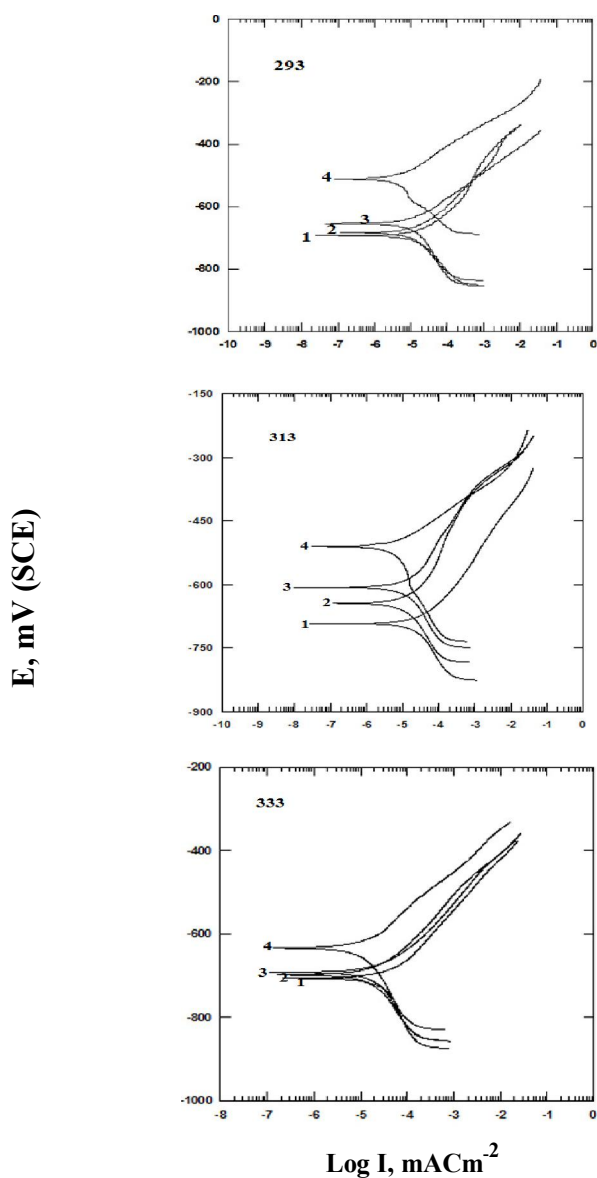


Fig. (1)- Potentiodynamic polarization curves of carbon steel in oilfield formation water with different concentrations range of NPPOE at different temperatures: (1) blank, (2)  $4 \times 10^{-5}$ , (3)  $10 \times 10^{-5}$  and (4)  $40 \times 10^{-5}$  M.

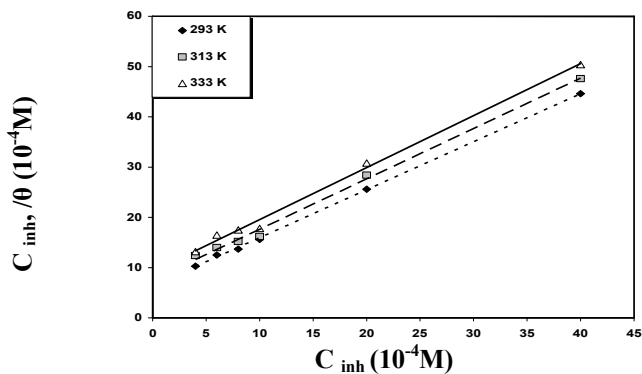


Fig. (2)- Curves fitting of the corrosion data for carbon steel in oilfield formation waters in the presence of NPPOE according to Langmuir adsorption isotherm at different temperatures.

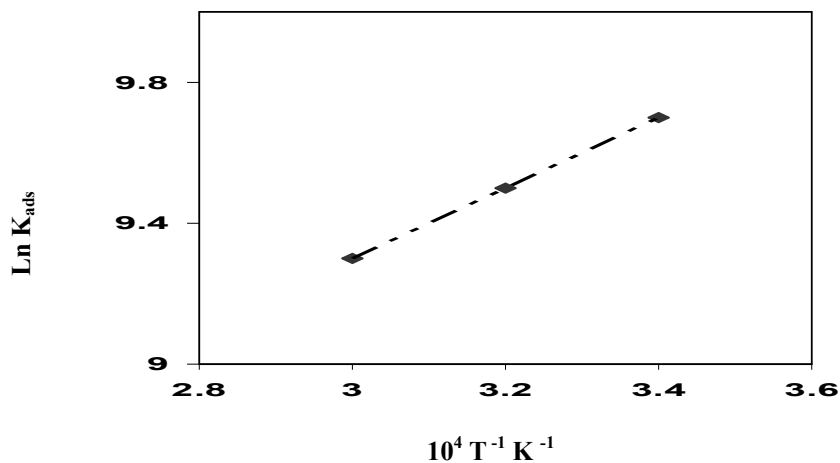
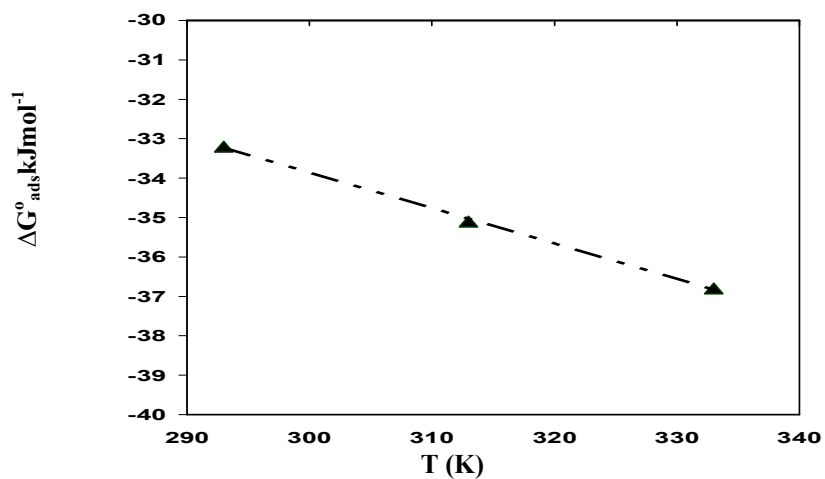


Fig. (3)-Vant'Hoff plot for the carbon steel/NPPOE/oilfield formation waters.



Fig( 4). Variation of  $\Delta G^0_{ads}$  versus T on carbon steel in oilfield formation water containing NPPOE inhibitor

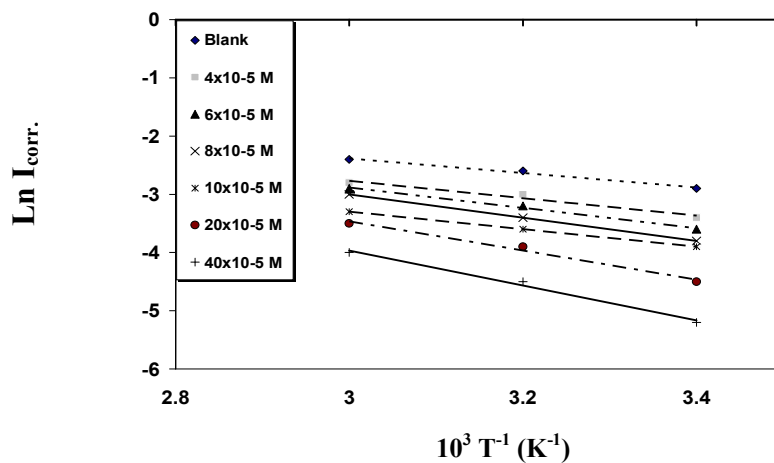


Fig. (5)-Arrhenius plots related to the corrosion rate of carbon steel in oilfield formation waters in absence and presence of different concentrations of NPPOE at various temperatures.



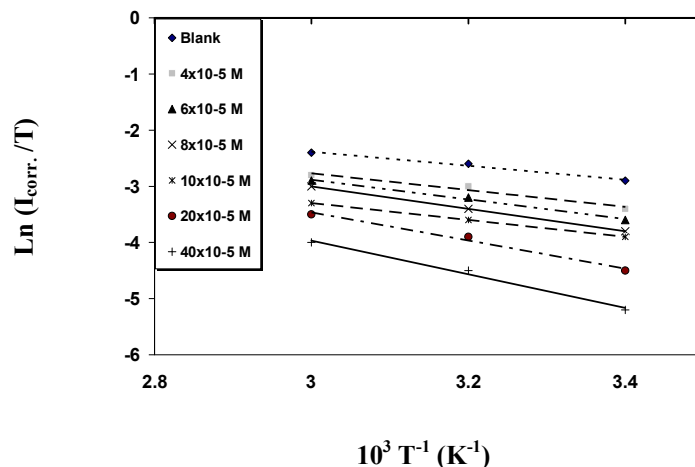


Fig. (6)-Transition state plot of  $(\ln I_{\text{corr.}}/T)$  versus  $1/T$  at different concentrations of NPPOE inhibitor in oilfield formation water.

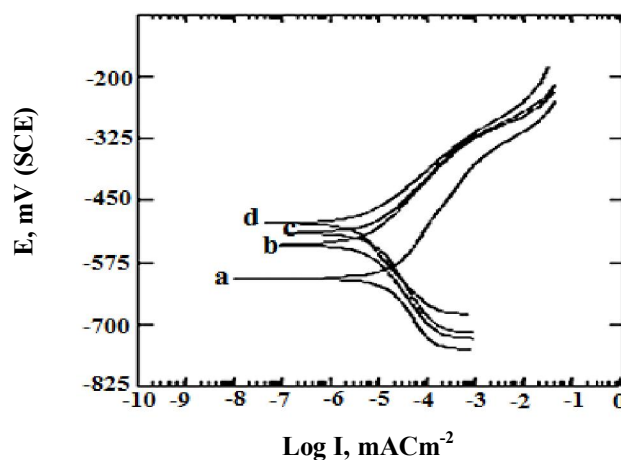


Fig.(7)-Potentiodynamic polarization curves for carbon steel in oilfield formation water inhibited with NPPOE at concentration  $10 \times 10^{-5}$  M in absence and presence of halide salts at concentration  $1 \times 10^{-4}$  M at  $40^\circ\text{C}$ , (a) blank, (b) KCl, (c) KBr and (d) KI.

#### Corresponding Author:

Amal Hamdy  
Egyptian Petroleum Research Institute (EPRI), Nasr  
City, Cairo, Egypt  
[amalhamdy66@hotmail.com](mailto:amalhamdy66@hotmail.com)

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