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Ethoxylated Fatty Amide as Corrosion Inhibitors for Carbon Steel in Hydrochloric Acid Solution

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The corrosion behavior of carbon steel in 1MHCl solution in the absence and presence of three compounds of ethoxylated fatty amide was studied using weight loss and galvanostatic polarization techniques. The percentage inhibition efficiency was found to increase with increasing of inhibitor concentrations, number of ethylene oxide unit and with decreasing temperature. The inhibitive action of these compounds was discussed in term of adsorption on the steel surface through ethylene oxide unit while the hydrocarbon parts protrude brush-like into the solution. The adsorption process follows Langmuir adsorption isotherm. The effect of temperature on the rate of corrosion in the absence and presence of these compounds was also studied. Some activated thermodynamic parameters were calculated.

Keywords: Ethoxylted fatty amide, Inhibitors, Carbon steel

1. INTRODUCTION

The development of inhibitors of steels in acid solutions has been the subject of great interest especially from the point of view of their efficiency and applications. Corrosion inhibitors may be divided into three broad classes, namely oxidizing, precipitation and adsorption inhibitors[1]. Compounds containing nitrogen, oxygen, sulphur and phosphorus in the conjugated system have particularly been reported as efficient corrosion inhibitors [2-10]. These compounds can adsorb on the metal surface by blocking the active sites and thereby decreasing the corrosion rate. The choice of inhibitors was based on the fact that these compounds contain π-electrons and heteroatom such as N,O and S which involve greater adsorption of the inhibitor molecules onto the surface of steel.

Surfactants compounds are widely employed in the petroleum industry to protect iron and steel equipment used in drilling, production, transport and refining of hydrocarbon [11]. The efficiency of the inhibition depends on the inhibitor concentration [12-15].

The aim of the present work is to investigate the inhibitive action of ethoxylated fatty amide with different number of ethylene oxides on the corrosion of carbon steel in HCl solutions. Weight loss and galvanostatic polarization techniques were used to evaluate the percentage inhibition efficiency of these compounds.

2. EXPERIMENTAL PART

The carbon steel sample used has the composition (wt%) 0.13C, 0.032 P, 0.014 Si, 0.025 S, 0.48 Mn and the remainder is Fe. Prior to each experiment the specimen was polished with different grade emery papers. Then the specimen was washed several times with distilled water, acetone and finally dried. A.R. grade hydrochloric acid was used for preparing the corrosive solution. Coupons of steel with dimension of 1x4x0.25 cm were used for weight loss measurements. For galvanostatic studies a cylindrical rod embedded in araldite with exposed surface area 0.56 cm^2 was used.

Weight loss measurements were carried out is described elsewhere [16]. Galvanostatic polarization studies have been performed with a EG &G model 173 potentiostat/ glavanostat equipment. Three compartment cell with a saturated calomel electrode and a platinum foil auxiliary electrode was used.

Inhibitor compounds

The following three compounds of ethoxylated fatty amide were prepared by method described earlier [17] and having the following formula R-CONH-$(CH_2CH_2O)_n$-H where R is $C_{12}H_{37}$ and n is the number of moles of ethylene oxide and equal 4,8,12 for compounds , I, II and III, respectively.

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements

Fig. 1 shows the effect of increasing concentrations of compound III on the weight loss of carbon steel vs. time curves at 30°C. Similar curves (not shown) were obtained for the other two compounds. Its obvious that the weight loss of carbon steel in presence of inhibitors varies linearly with time, and is much lower than that obtained in blank solution. The linearity obtained indicated the absence of insoluble surface film during corrosion and that the inhibitors were first adsorbed onto the metal surface and, therefore, impede the corrosion process [18]. The percentage inhibition efficiency (IE) and the parameter (θ) that represents the weight of the metal surface covered by inhibitor molecules were calculated using the following equations.

$$IE = [1 - \frac{W_{add}}{W_{free}}]100 \quad (1)$$

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

where, W_{free} and W_{add} are the weight loss in the absence and the presence of inhibitors, respectively. The calculated values of IE and θ are listed in Table (1). Inspection of Table 1 reveals that, the inhibition efficiency increase with an increase in inhibitor concentration. This behavior could be attributed to the increase of the number of adsorbed molecules at the metal surface. At one and the same inhibitors concentration the percentage of inhibition efficiency decreases in the following order:

Compound III> Compound II> Compound I

This behavior will be discussed later.

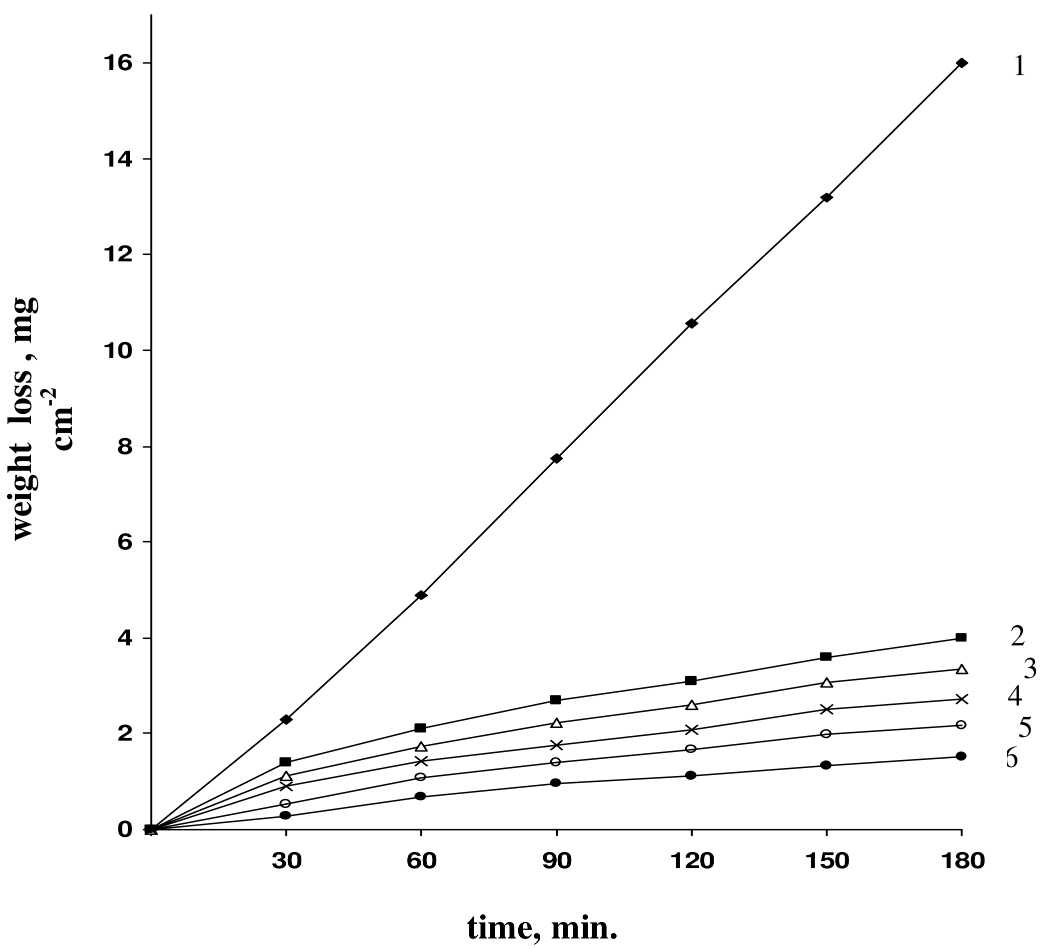

Figure 1. Weight loss-time curves for C-steel electrode in 1M HCl in presence and absence of different concentrations of compound III at 30°C. 1) 0.00ppm 2) 200 ppm 3) 400 ppm 4) 600 ppm 5) 800 ppm 6) 1000 ppm

Table 1. Effect of Ethoxylated fatty amide concentrations on the inhibition efficiency (IE) and surface coverage (θ) for corrosion of carbon steel in 1 MHCl

Concentration, M	%I.E	θ
1M HCl compound (I)	-	
200 ppm compound (I)	69.90	0.700
400 ppm compound (I)	72.07	0.721
600 ppm compound (I)	77.12	0.771
800 ppm compound (I)	84.33	0.843
1000 ppm compound (I)	87.6	0.872
1M HCl compound (II)		
200 ppm compound (II)	72.08	0.721
400 ppm compound (II)	75.88	0.759
600 ppm compound (II)	80.07	0.801
800 ppm compound (II)	87.14	0.871
1000 ppm compound (II)	90.22	0.902
1M HCl compound (III)		
200 ppm compound (III)	75.62	0.756
400 ppm compound (III)	79.37	0.794
600 ppm compound (III)	82.50	0.825
800 ppm compound (III)	88.12	0.881
1000 ppm compound (III)	93.12	0.931

3.2. Adsorption isotherm

The values of surface coverage θ for different concentrations of the studied ethyoxyalted fatty amide at 30°C have been used to explain the best isotherm to determine the adsorption process. The adsorption of organic adsorbate on the surface of steel electrode is regarded as substitution adsorption process between the organic compound in the aqueous phase (org) and the water molecules adsorbed on the steel surface $(H_2O)_{ads}$[19].

$$Org_{(sol)} + x\,(H_2O) \leftrightarrow Org_{(ads)} + x\,H_2O \tag{3}$$

where x is the size ratio, this is , the number of water molecules replaced by one organic molecules. Attempts were made to fit θ values to the Frumkin , Freundlich, Langmuir and Temkin isotherms. The best fit was obtained with Langmuir isotherm according to the following equation:

$$\frac{\theta}{\theta - 1} = KC \tag{4}$$

and rearranging it gives

$$\frac{C}{\theta} = \frac{1}{k} + C \tag{5}$$

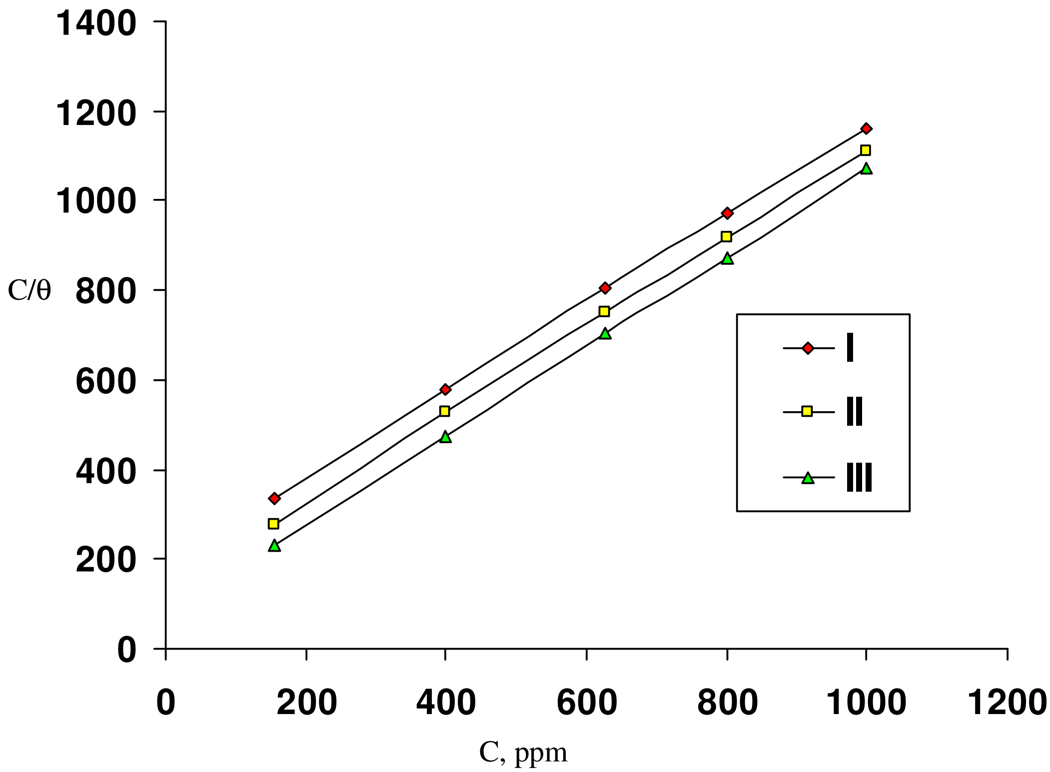

Figure 2. Langmuir adsorption isotherm relation between C and C/θ. 1) Compound I 2) Compound II 3) Compound III

The plotting $\frac{C}{\theta}$ against C gives straight line with unit slope, Fig.2. This indicates that the adsorption of ethoxylated fatty amide on the carbon steel surface in 1M HCl solution follows Langmuir's adsorption isotherm and consequently, there is no interaction between the molecules adsorbed at the metal surface.

3.3. Effect of Temperature

The effect of temperature on the rate of dissolution of carbon steel in 1M HCl containing 1000 ppm of three ethoxylated fatty amide compounds was studied by weight loss measurement over a temperature range from 30 to 60°C. Similar curves to Fig.1 were obtained (not shown) but the rate of corrosion obtained from the slope of straight line (mg cm^{-2} min^{-1}) are different. As the temperature increases, the rate of corrosion increases and hence the inhibition efficiency decreases. This is due to the adsorption in aided by increasing the temperature. This behavior proves that the adsorption of Ethoxylated fatty amide on C-steel surface occurs through physical adsorption.

The apparent activation energy E_a. the enthalpy activation for the corrosion of C- steel in 1M HCl solutions in absence and presence of different concentrations of ethoxylated fatty amide were calculated using Arrehenius equation [20].

$$K = A \exp(\frac{-E_a}{RT}) \qquad (6)$$

and transition stat equation

$$K = \frac{RT}{Nh} \exp(\frac{\Delta S^{\circ}}{R}) \exp(\frac{-\Delta H^{\circ}}{RT}) \qquad (7)$$

where K is the rate of metal dissolution, A is the frequency factor, N is Avogadro's number and R is the universal gas constant.

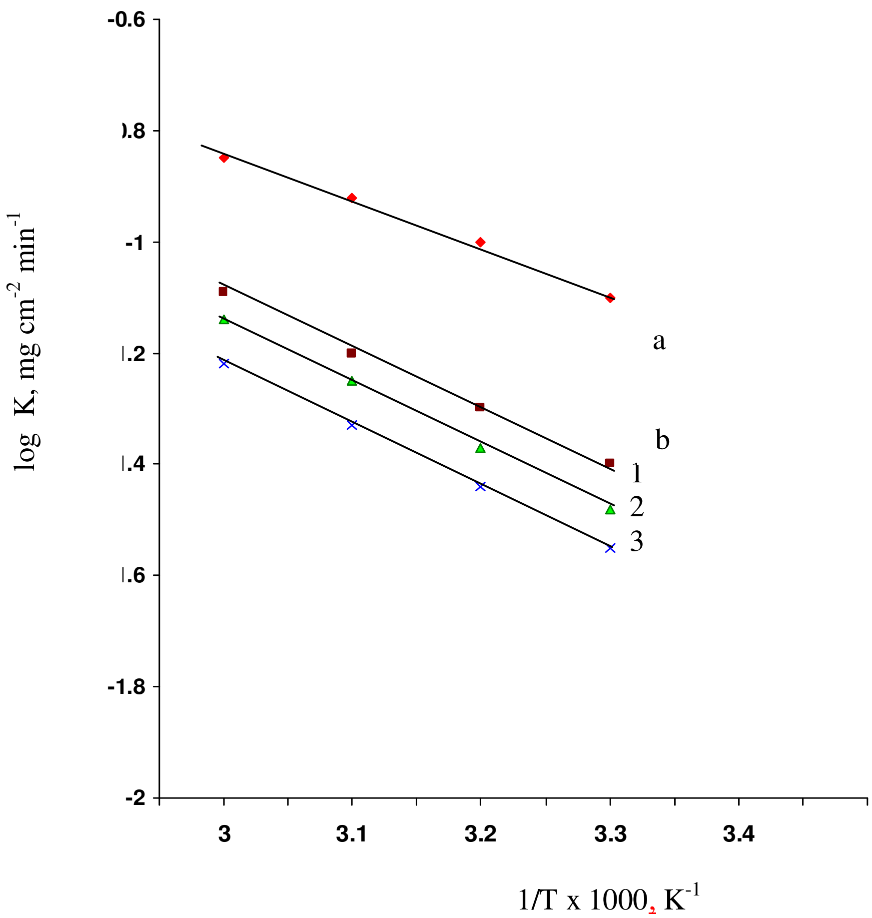

Figure 3. Relation between log rate of corrosion (K) and the reciprocal of the absolute temperature of carbon steel electrode in a) 1M HCl b) 1M HCl + 1000 ppm of studied compound 1) Compound I 2) Compound II 3) Compound III

Fig.3 represents Arrehenius plot (log K vs $\frac{1}{T}$) for uninhibited and inhibited 1M HCl containing 1000 ppm of the studied compounds. The values of E_a can be obtained from the slope of the straight lines were found to be 21.26 KJ mol^{-1} in 1M HCl and 28.67, 30.22 and 33.82 KJ mol^{-1} in presence of compound (I, II, III) respectively. The increase of the activation energies in the presence of inhibitors is attributed to appreciable decrease in the adsorption process of the inhibitors on the metal surface with increase of temperature and a corresponding increase in the reaction rate because of the greater area of the metal that is exposed to the acid [21]. On the other hand Fig.4 represents the plot log K/T against 1/T for C-steel in 1M HCl solution in absence and presence of 1000 ppm of each used compound. This relation gave straight line with slope of (-ΔH°/2.303R) and an intercept of $\log[\frac{R}{Nh}-\frac{\Delta S^{\circ}}{2.303R}]$. The value of ΔH° obtained from the slope of the straight line equal 23.92KJmol^{-1} in 1M HCl and equal 32.78, 36.93 and40.12 KJmol^{-1} in presence compounds I,II and III respectively. The values of ΔH° are different for studied compounds which mean that their structure affects the strength line. The values of ΔS° calculated from the intercept of the straight line were found to be -172.82 JKmol^{-1} in 1MHCl and -202.36, -235.14 and -256 JKmol^{-1} for compound I, II and III, respectively.

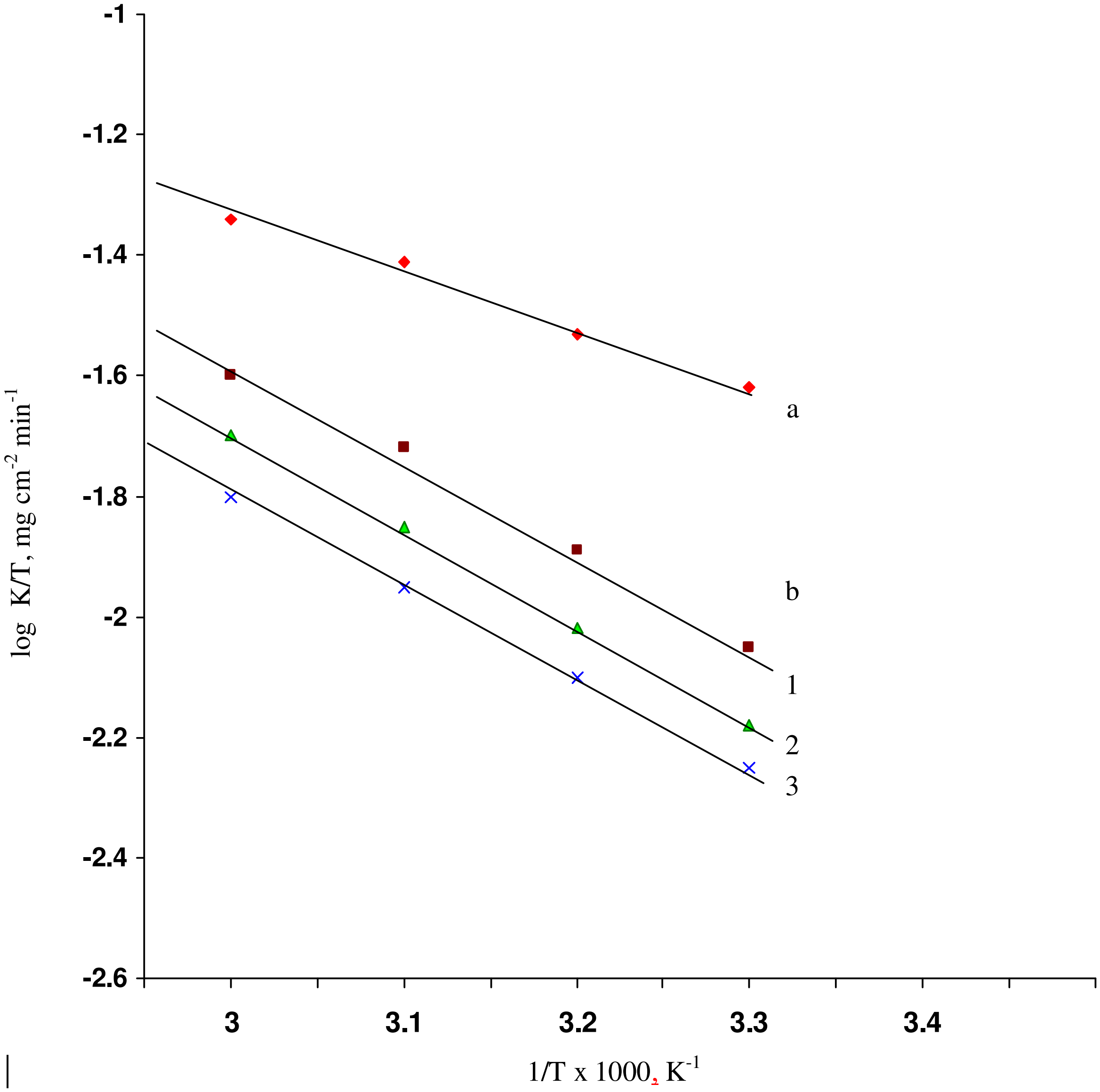

Figure 4. Relation between log K/T - 1/T curves for carbon steel dissolution in 1M HCl in presence and absence of inhibitors a) free b) 1) Compound I 2) Compound II 3) Compound III

The negative values of $\Delta S°$ in the absence and presence of the inhibitors implies that the activated complex is the rate determining step and represents association rather than dissociation. It also reveals that an increase in the order takes place in going from reactants to the activated complex.

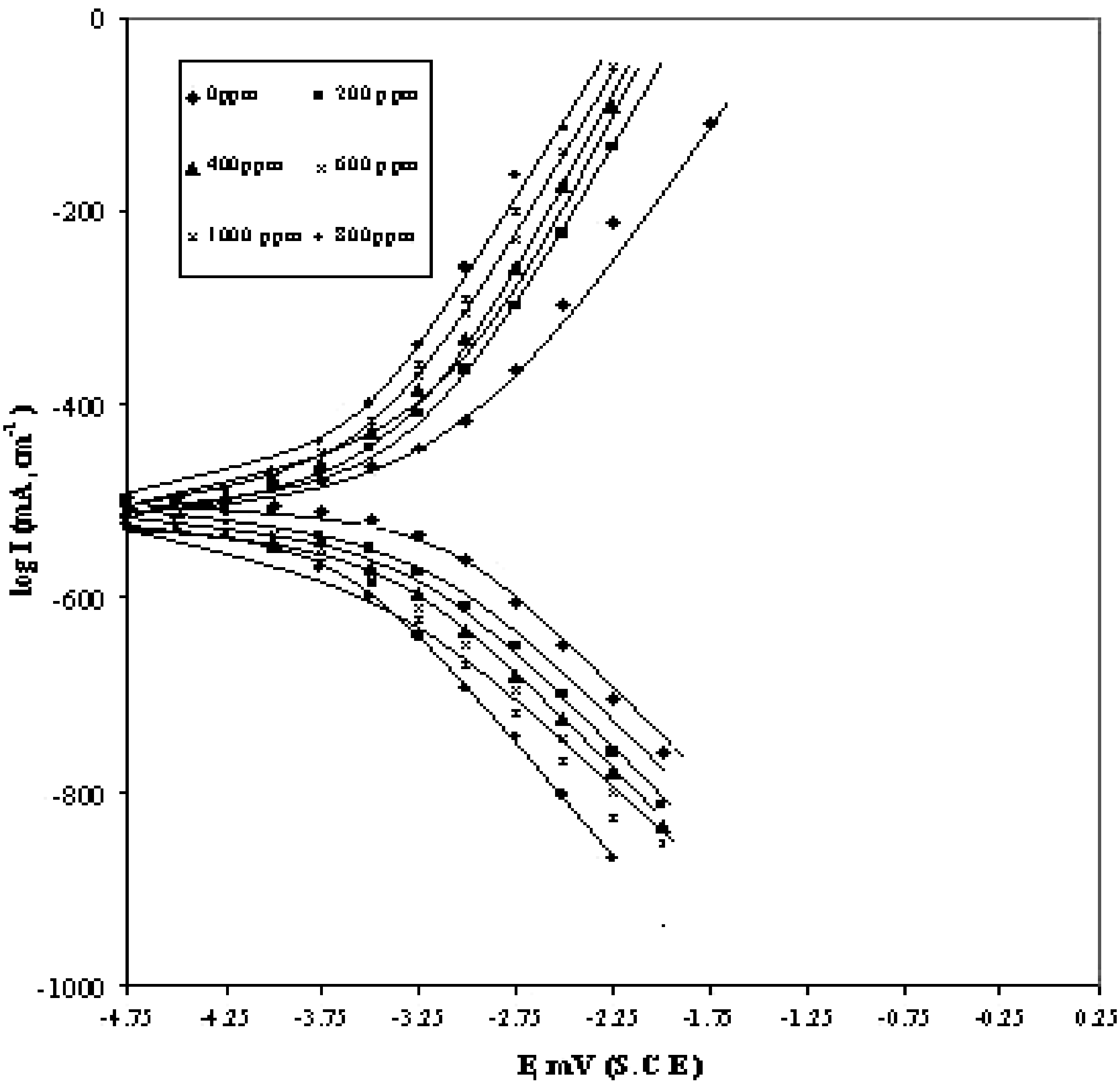

Figure 5. Galvanostatic polarization curves of C-steel electrode in 1M HCl in presence and absence of different concentrations of compound III

Galvanostatic polarization measurements

Fig. 5 shows typical galvanostatic polarization curves for mild steel in 1M HCl in absence and presence of varying concentrations of compound III. Similar curves (not shown) were obtained for the other compounds. The values of cathodic (β_c) and anodic (β_a) Tafel constants were calculated from the linear region of the polarization curves. The corrosion current density (I_{corr}) was determined from the intersection of the linear parts of the cathodic curves with the stationary corrosion potential (E_{corr}).

The percentage inhibition efficiency (IE) was calculated using the following equation:

$$IE = [1 - \frac{I_{add}}{I_{free}}]100 \qquad (8)$$

where I_{free} and I_{add} are the corrosion current densities in the absence and presence of inhibitors, respectively. Table (2) shows the effect of the inhibitor concentration on the corrosion kinetics parameters, such as β_a, β_c, E_{corr}, I_{corr} and IE.

Table 2. Corrosion parameters obtained from galvanostatic polarization of C-steel in 1MHCl containing different concentrations of ethoxylted fatty amide compounds

Conc. ,ppm	**-E corr mV(SEC)**	**I corr (μAcm^{-2})**	**β_a mV dec^{-1}**	**β_c mV dec^{-1}**	**%IE**
1M HCl compound (I)					
0.00 ppm compound (I)	502	13.75	105	165	
200 ppm compound (I)	508	3.98	105	160	71.05
400 ppm compound (I)	509	3.73	106	156	72.87
600 ppm compound (I)	510	3.31	106	160	75.93
800 ppm compound (I)	512	2.93	105	158	82.33
1000 ppm compound (I)	512	1.86	107	158	86.47
1M HCl compound (II)					
200 ppm compound (II)	512	3.95	105	164	71.05
400 ppm compound (II)	510	3.54	107	162	74.25
600 ppm compound (II)	512	2.71	108	160	80.29
800 ppm compound (II)	513	1.85	109	160	86.54
1000 ppm compound (II)	515	1.47	109	155	89.31
1M HCl compound (III)					
200 ppm compound (III)	512	3.53	108	160	74.33
400 ppm compound (III)	514	3.07	110	150	77.67
600 ppm compound (III)	515	2.63	112	162	80.87
800 ppm compound (III)	517	1.76	112	165	87.20
1000 ppm compound (III)	518	1.06	110	160	92.29

It is clear from these experimental data that ethoxylated fatty amides shifts both anodic and cathodic branches of polarization curves to lower values of current density, indicating the inhibition of both the hydrogen evolution (h.e.r) and steel dissolution reaction [22]. This may ascribed to adsorption of these compounds on the corroded surface. Inspection of Table (2) its clear that: the anodic (β_a) and cathodic (β_c) Tafel slopes are approximately constant suggesting the inhibiting action of these compounds by adsorption at the metal surface according to blocking adsorption mechanism. These compounds decrease the surface area available for anodic dissolution and cathodic hydrogen evolution reaction without affecting the reaction mechanism. Increase the concentration of these additive causes a marked shift of E_{corr} to positive values and decrease the values of I_{corr} indicating the inhibiting effect of these compounds. The inhibition efficiency (IE) from polarization and weight loss techniques increase with the increase of concentration and number of ethylene oxide units per molecule of the additives. This behavior could be explained in view of physical properties of the additives. Surfactants molecules with long hydrocarbon chains tend to be curled up in water to minimize the area of contact between the hydrophobic hydrocarbon chain and water molecules [23].

Inhibition efficiency achieved by these compounds at 1000 ppm concentration decrease in the following order:

Compound III > Compound II> Compound I

The two different techniques gave the same trend of inhibition for the tested compounds but yielded different value of IE due to the different experimental conditions.

The inhibiting effect of these compounds due to their adsorption operates via formation of a barrier film on the metal surface [24]. The adsorption of these compounds on the steel surface takes place through ethylene oxide group while the hydrocarbon parts protrude brush –like into the solution.

4. CONCLUSIONS

1- Ethoxylated fatty amide compounds act as an inhibitor for corrosion of carbon steel in 1M HCl solution.
2- The percentage inhibition efficiency increase with inhibitor concentration, number of ethylene oxide unit and with decreasing temperature.
3- The inhibition of these compounds due to its adsorption on the metal surface.
4- The adsorption of these compounds on the steel surface follows Longmuir adsorption isotherm.

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