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Corrosion Inhibition of Mild Steel in Hydrochloric Acid Solution using Cationic Surfactant Olyel-amido Derivatives

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The effect of three compounds of cationic surfactants of olyel-amido derivatives on the corrosion of carbon steel in 1.0 M HCl solution was studied using weight loss galvanostatic, polarization measurements and potentiodynamic anodic polarization techniques. The inhibition efficiency was found to increase with increasing concentration, number of polyethelene diamine unit and with decreasing the temperature. The inhibitive effect of these compounds was explained on the basis of adsorption on the metal surface. The adsorption process follows Freundlich adsorption isotherm. Some activated thermodynamic parameters were computed and discussed. The olyel-amido derivatives provide a good protection to steel against pitting corrosion by shifting the pitting potential in the noble direction

Keywords: Mildsteel,cationic surfactants,olyel-amido derivatives corrosion inhibitors.

1. INTRODUCTION

Mild steel is widely applied as the constructional materials in many industries due to its excellent mechanical properties and low cost. Hydrochloric acid solutions are widely used in several industrial processes, some of the important fields of application being acid pickling of steel, chemical cleaning and processing, ore production and oil well acidification, Because of the general aggression of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials[1]The selection of inhibitor is controlled by its economic availability, its efficiency to inhibit the substrate material and its environmental side effects. So most of the excellent acid inhibitors for corrosion of steel in acidic medium are organic compound containing nitrogen, oxygen and/or sulphur atoms [2-12].The inhibiting action of these compounds is attributed as a first stage, to the adsorption of the additives to the metal/solution interface. The adsorption process depends upon 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.

Some cationic surfactants such as, mono and dicationic benzothiazolic quaternary ammonium bromide [13],Alkyl dimethylisopropylammonium hydroxide[14],New Schiff base cationic surfactants[15], are used as inhibitors for corrosion of steel in acidic solutions. They inhibit the corrosion by the adsorption on the steel surface

Cationic surfactants can be easily synthesized from relatively cheap raw materials, nontoxic and have surface active property. The aim of this investigation is to examine the inhibitory effect of three compounds of cationic surfactants of olyel-amido derivatives toward the corrosion of mild steel corrosion in hydrochloric acid solution. Weight loss and galvanostatic and potentiodynamic anodic polarization techniques were used in this work to evaluate the inhibition efficiency of the tested tween compounds.

2. EXPERIMENTAL METHODS

Mild steel was used for this study has the following composition (wt.%): 0.17%C, 0.46%, Mn , 0.26%Si,0.017%S and the remainder iron) Coupons steel with dimension 2cm x 2 cm x 0.3 cm were used for weight loss measurements. For galvanostatic polarization studies a cylindrical rod embedded in araldite with exposed surface area 0.68 cm^2 was used. The electrode was polished with different grades emery papers (grades300, 500and 800) degreased with acetone and rinsed with distilled water.AR grade hydrochloric acid was used for preparing the test solutions

Weight loss measurements were carried out previously [16]. The percentage inhibition efficiency (IE) and a parameter (θ) which represents the part of the metal surface covered by the inhibitor molecules were calculated using the following equation:

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

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

where, W_{free} and W_{add} are the weight loss of C-steel coupons in free and inhibited acid solutions, respectively.

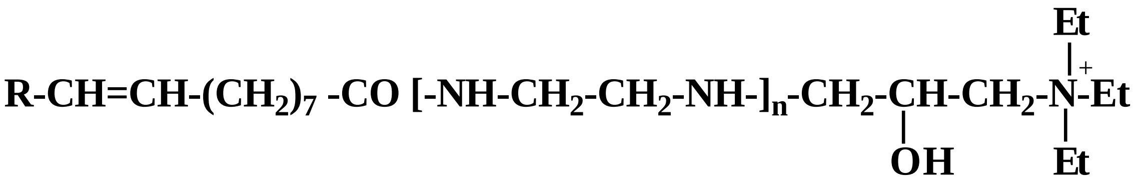
Galvanostatic polarization measurements were carried out using EG & G model 173 potentiostat/galvanostat. Three compartment cell with a saturated calomel reference electrode and platinum foil auxiliary electrode was used. The percentage inhibition efficiency (IE) was calculated from corrosion current density values using the equation.

$$\text{IE} = \left[1 - \frac{I_{add}}{I_{free}}\right] 100 \qquad (3)$$

where, I_{free} and I_{add} are the corrosion current densities in absence and presence of inhibitors.

Potentiodynamic anodic polarization technique was performed at a scanning rate of 1mV/s using a Wenking potentiostat type POS73 and the current density –potential curve were recorded on X-Y recorder type PL.3.The potentials were measured relative to a saturated calomel electode (SCE)

The three cationic surfactants of olyel-amido derivatives were prepared using a method described elsewhere [17].They has the general formula:



$$R\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CO\,[\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}]_n\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}\overset{Et}{\underset{Et}{N^+}}\text{-}Et$$

where,$R=CH_3[CH_2]_7$ and n is the number of ethylene diamine unit and equal 2,4 and 6 for compounds I,II and III, respectively.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

Fig. 1 represents the relation between time and weight losses of mild steel coupons in solution of 1.0 M HCl solution with and without addition of compound III as an example.

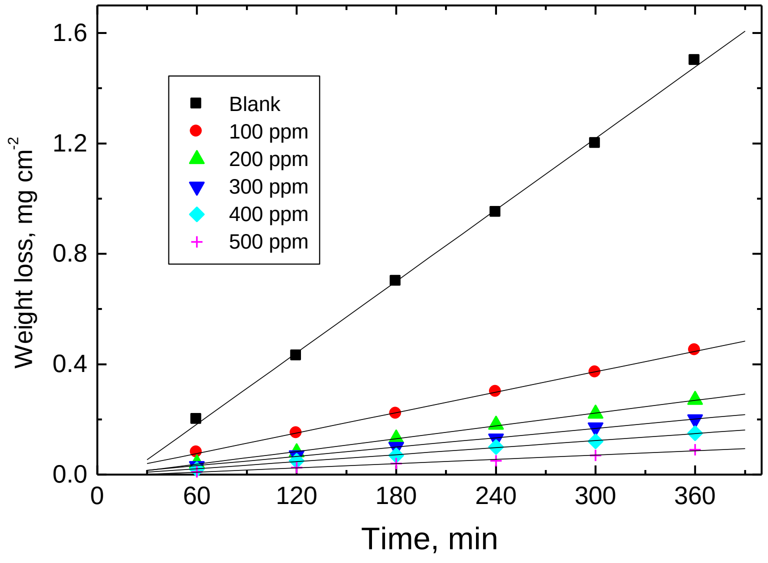


Figure 1. Weight-loss as a function of time of mild steel in 1.0 M HCl solution without and with compound III.

Similar curves were also obtained for other two compounds (not shown) .Inspection of this figure reveals that, the linear variation of weight loss with time in uninhibited and inhibited 1.0M HCl solution indicates the absence of insoluble surface films during corrosion i.e. the inhibitors are first adsorbed on the metal surface and therefore impede corrosion either by merely blocking the reaction sites anodic and cathodic or by altering the mechanism of the anodic and cathodic processes.

The percentage inhibition efficiencies obtained from weight loss are listed in Table 1. It is obvious that the IE increases with increasing the inhibitor concentration and with increasing number of ethylene diamine unit, whereas decreases in the following order:

compound I > compound II > compound III

3.2 Adsorption isotherm:

The values of the degree surface coverage θ were evaluated at different concentrations of the cationic surfactant compounds in 1.0 MHCl solution at 30 °C and given in Table (1) The values of θ have been used to explain the best isotherm to determine the adsorption process. The adsorption of organic adsorbate on the steel surface is regarded as substitutional adsorption process between the organic compound in the aqueous phase (org) and the water molecules adsorbed on the steel surface $(H_2O)_{ads}$ [18].

$$\mathrm{Org}_{(sol)} + \mathrm{X(H_2O)} \rightleftharpoons \mathrm{Org}_{(ads)} + \mathrm{XH_2O} \qquad (4)$$

Table 1. Effect of inhibitors concentration on the corrosion of mild steel in 1.0 M HCl solution determined by weight-loss measurements at 30 °C after 360 minutes immersion.

Inhibitors	Concentration (ppm)	$R_{corr.}$x 10^{-3} mg cm^{-2} min^{-1}	%I.E	Θ
Blank	0	5.12	--	--
Compound I	100	1.44	71.87	0.720
	200	1.12	78.12	0.781
	300	0.79	84.57	0.846
	400	0.48	90.62	0.906
	500	0.32	93.75	0.937
Compound II	100	1.36	73.63	0.736
	200	1.02	80.07	0.801
	300	0.62	87.89	0.879
	400	0.38	92.57	0.926
	500	0.26	94.92	0.949
Compound III	100	1.16	77.34	0.773
	200	0.83	83.78	0.838
	300	0.51	90.23	0.902
	400	0.33	93.55	0.935
	500	0.17	96.67	0.967

where, X is the size ratio, this is, the number of water molecules replaced by one organic molecule. Attempts were made to fit θ values to various isotherms including Frumkin, Temkin, Freundlich and Langmuir adsorption isotherms. By far the results were best fitted by Freundlich adsorption isotherm and can be represented using the following equation:

$\theta = KC^n$ (5)

or in the logarithmic form

$\log \theta = \log K + n \log C$ (6)

where ,K and C represent the equilibrium constant of adsorption process and additive concentrations ,respectively.

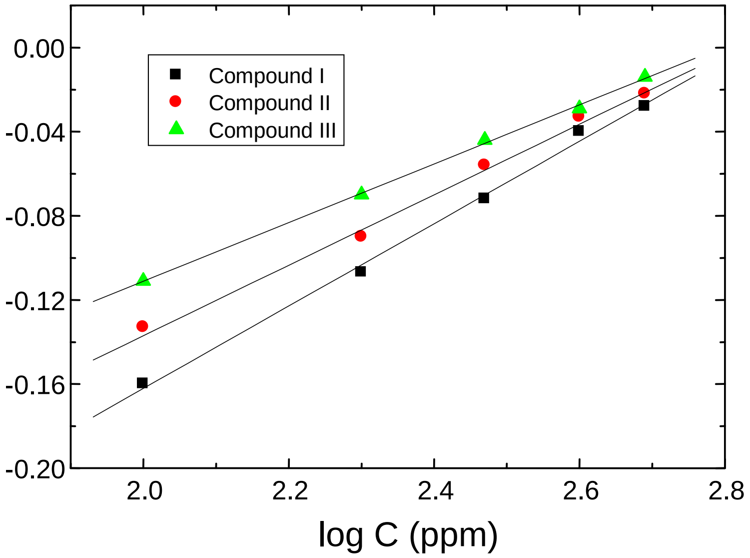


Figure 2. Freundlish adsorption isotherm (log θ – log C plot) for mild steel in 1.0 M HCl in presence of inhibitors.

Fig (2) represents the relationship between log θ and log C. Straight lines were obtained with intercept of log K suggesting that the adsorption of cationic surfactants on the mild steel surface follow Freundlich adsorption isotherm. The calculated values for the equilibrium constant of adsorption was found to be 0.77, 0.71 and 0.66 for compounds I,II and III, respectively.

The equilibrium constant of adsorption K is related to the standard free energy of adsorption ΔG^o_{ads}

$K= (1/55.5) \exp [-\Delta G^o_{ads} / RT]$ (7)

where,55.5 is the concentration of water in the solution in mol/l,R is the gas constant and T is the absolute temperature. The values of ΔG^o_{ads} for compounds I,II and III are equal to -38.369,-47.884,-58.094 kJ mol^{-1} ,respectively. The negative values of ΔG^o_{ads} indicate the spontaneous adsorption of the inhibitors and are usually characteristic of strong interaction of inhibitors with the metal surface.

3.3 Effect of temperature

The effect of rising temperature on the corrosion rate of mild steel in 1M HCl containing 500 ppm of three cationic surfactant compounds was studied in temperature range from 30 to 60°C by weight loss measurements .Similar curves to Fig.1 were obtained (not shown) but the rates of corrosion obtained from the slope of the straight line (mg cm^{-2} min^{-1}) are different.

As the temperature increases, the rate of corrosion increases and hence the inhibition efficiency of the additives decreases as showed in Table (2). This due to the adsorption is aided by increasing the temperature. This behavior proves that the adsorption of cationic surfactant compounds on C-steel surface occurs through physical adsorption [19].

Table 2. Effect of temperature on the corrosion rate and inhibition efficiency for the corrosion of mild steel in 1.0 M HCl solution in absence and presence of 500 ppm of inhibitors from weight-loss measurements.

Inhibitors	Temperature °C	$R_{corr.}$ mV. (SCE)	%I.E
Blank	30	5.12	--
	40	5.22	--
	50	5.36	--
	60	5.48	--
Compound I	30	0.32	93.75
	40	0.48	90.80
	50	0.61	80.61
	60	0.72	86.86
Compound II	30	0.26	94.92
	40	0.41	91.99
	50	0.56	89.55
	60	0.69	87.40
Compound III	30	0.17	96.67
	40	0.29	94.41
	50	0.41	92.36
	60	0.56	89.06

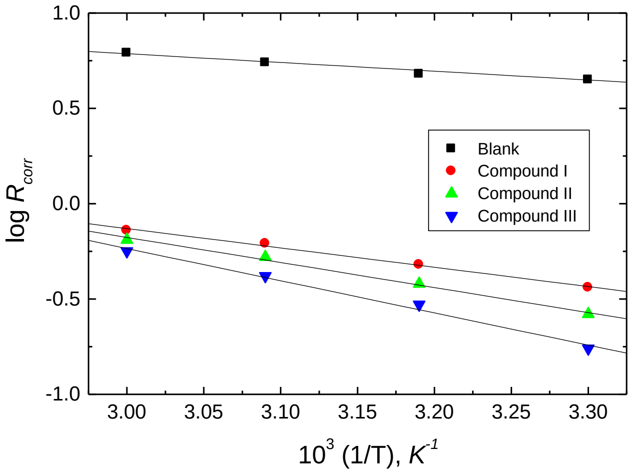


Figure 3. log corrosion rate-1/T curves for mild steel in 1.0 M HCl in absence and presence of 500 ppm of inhibitors.

The activation energy E_a, the enthalpy of activation ΔH* and the entropy activation ΔH* for corrosion of mild steel in 1.0M HCl solutions in absence and presence of different concentrations of three cationic surfactant compounds were calculated from Arrhenius-type equation [20]

$$R_{corr} = A\exp\left(\frac{-E_a}{RT}\right) \qquad (8)$$

and transition state equation

$$R_{corr} = \frac{RT}{Nh}\exp\left(\frac{\Delta s^*}{R}\right)\exp\left(\frac{-\Delta H^*}{RT}\right) \qquad (9)$$

where, R_{corr} is the rate of corrosion from weight loss, A is the frequency factor, N is Avogadro's number and R is the universal gas constant.

Fig.3 represents Areehenins plot (log R_{corr} vs.$\frac{1}{T}$) for uninhibited and inhibited 1M HCl solution containing 500 ppm of the inhibitors used. The values of E_a can be obtained from the slope of the straight lines were found to be 16.603 kJ mol^{-1} is 1.0M HCl and equal to 23.206,29.007 and 34.809 kJ mol^{-1} in presence of compounds I,II and III, respectively. The increase of E_a in the presence of inhibitors indicated that, the presence of cationic surfactants induces an energy barrier for corrosion reaction and this barrier increases with increasing the concentration of these compounds.

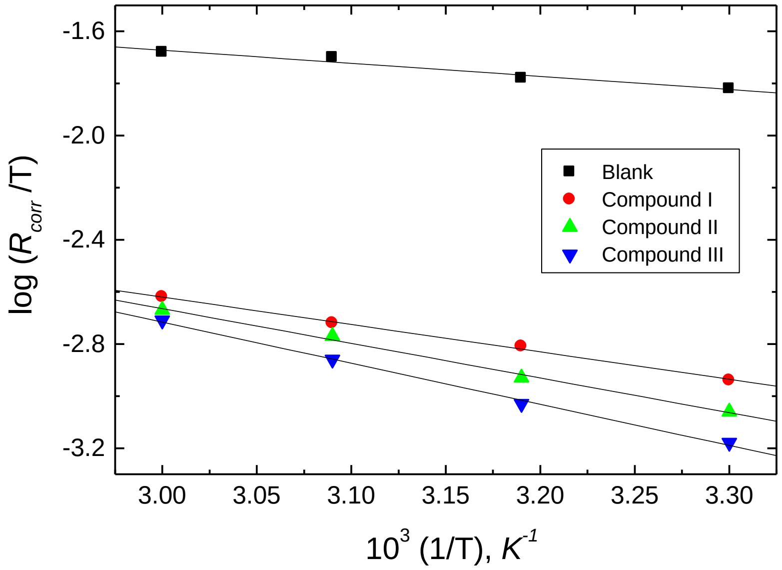


Figure 4. log corrosion rate / T vs. 1/T plots for mild steel in 1.0 M HCl in absence and presence of 500 ppm of inhibitors.

On the other hand, Fig.4 represents the plot of log $R_{corr.}$/T against 1/T for C-steel in 1M HCl solution in absence and presence of 500 ppm of each used compound. This relation gave straight line with slope of (-ΔH*/2.303R) and an intercept of $\log\left[\frac{R}{Nh} - \frac{\Delta S^*}{2.303R}\right]$.

The values of ΔH* obtained from the slope of the straight line equal 19.147kJ mol^{-1} in 1M HCl and equal 28.726,34.464 and 38.294 kJ mol^{-1} in presence of compounds I,II and III, respectively. The positive values of ΔH* reflect that the process of adsorption of the inhibitors on the steel surface is endothermic process. The values of ΔS* calculated from the intercept of the straight lines were found to be – 245.9JK^{-1} mol^{-1} in 1M HCl and 275.3,286.7 and 293.4 JK^{-1} mol^{-1} in presence of compounds I,II and III, respectively. The negative values of ΔS* in 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 [21].

3.4. Galvanostatic polarization measurements:

The effect of addition of cationic surfactants of olyel-amido derivatives on the anodic and cathodic polarization curves for mild steel in 1.0 M HCl solution at 303K was studied. The effect of increased concentration of compound III is shown in Figure (5) as an example of the studied inhibitors. Similar curves were obtained for the other two inhibitors (not shown). 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 anodic and cathodic curves with the stationary corrosion potential ($E_{corr.}$).

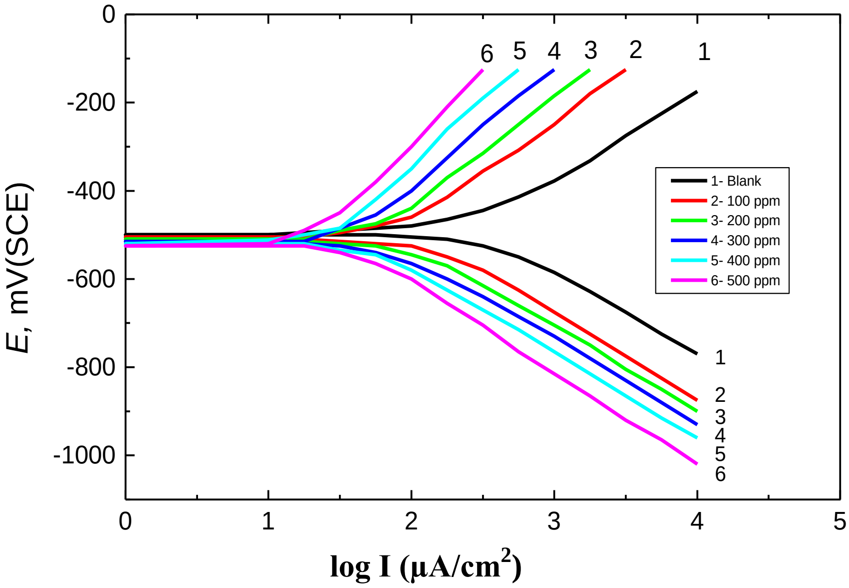


Figure 5. Galvanostatic polarization curves of carbon steel in 1.0 M HCl containing different concentrations of compound III.

Table 3 shows the effect the inhibitor concentrations on the corrosion kinetics parameters, such as βa, βc, $E_{corr.}$, I_{corr}. and %IE.

From the results given in Table 3, it is clear that, as the concentration of the inhibitor increase, the following observation could be drawn.

a) The anodic (β_a) and cathodic (β_c) Tafel slopes are increases slightly suggesting that, these compounds decrease the surface area available for anodic dissolution and cathodic hydrogen evolution reaction, i.e. mixed inhibitors.

b) The values of $E_{corr.}$change slowly to negative values and the value of I_{corr}. decreases and hence the values of IE's increases indicating the inhibiting effect of these compounds.

c) The values of IE's of the three tested compounds decrease in the following order:

compound I > compound II > compound III

Table 3. Corrosion parameters obtained from galvanostatic polarization technique for mild steel in 1.0 M HCl solution in absence and presence of different concentrations of inhibitors.

Inhibitors	Concentration (ppm)	ß$_a$ m V dec^{-1}	ß$_c$ m V dec^{-1}	-E$_{corr}$ mV. (SCE)	I$_{corr.}$, mAcm^{-2}	%I.E
Blank	0	150	140	-504	316	--
Compound I	100	302	205	-509	108	65.82
	200	314	222	-512	81	74.36
	300	322	236	-513	51	83.86
	400	360	240	-512	36	88.92
	500	380	265	-515	24	92.40
Compound II	100	322	260	-508	92	70.88
	200	360	275	-510	66	79.11
	300	375	281	-513	45	85.75
	400	380	294	-518	30	90.50
	500	388	306	-520	18	94.30
Compound III	100	350	244	-510	86	72.78
	200	360	261	-514	56	82.27
	300	382	284	-517	31	90.18
	400	390	288	-520	22	93.03
	500	395	301	-525	15	95.25

3.6. Inhibition of Pitting Corrosion

The effect of increasing concentration of cationic surfactants of olyel-amido derivatives on the potentiodynamic anodic polarization curves for mild steel in 1.0 M HCl +0.5MNaCl solution at a scan rate of 1mVs^{-1}was studied. The effect of increased concentration of compound III is illustrated in Figure (6) as an example. Similar curves were obtained for the other two inhibitors (not shown). The pitting potential (E_{pitt}.) was taken as the potential at which the current flowing along the passive film increases suddenly to higher values detonating the destruction of passive film and initiation of visible pits[23].The effect increasing concentration of olyel-amido derivatives on the values of E_{pitt}. is given in Fig (7) .This figure represents the relationship between the logarithmic of the concentration of inhibitors and E_{pitt}. It is clear from this figure that, as the concentration of the inhibitors increases, the pitting potential is shifted to more positive (noble) direction according to the following equation:

$E_{pitt.} = a + b \log C_{inh.}$ (11)

where, a and b are constants which depend on both the type of additives and the nature of the electrode. The noble shift of E_{pitt} indicates the increased resistance of steel to pitting attack.

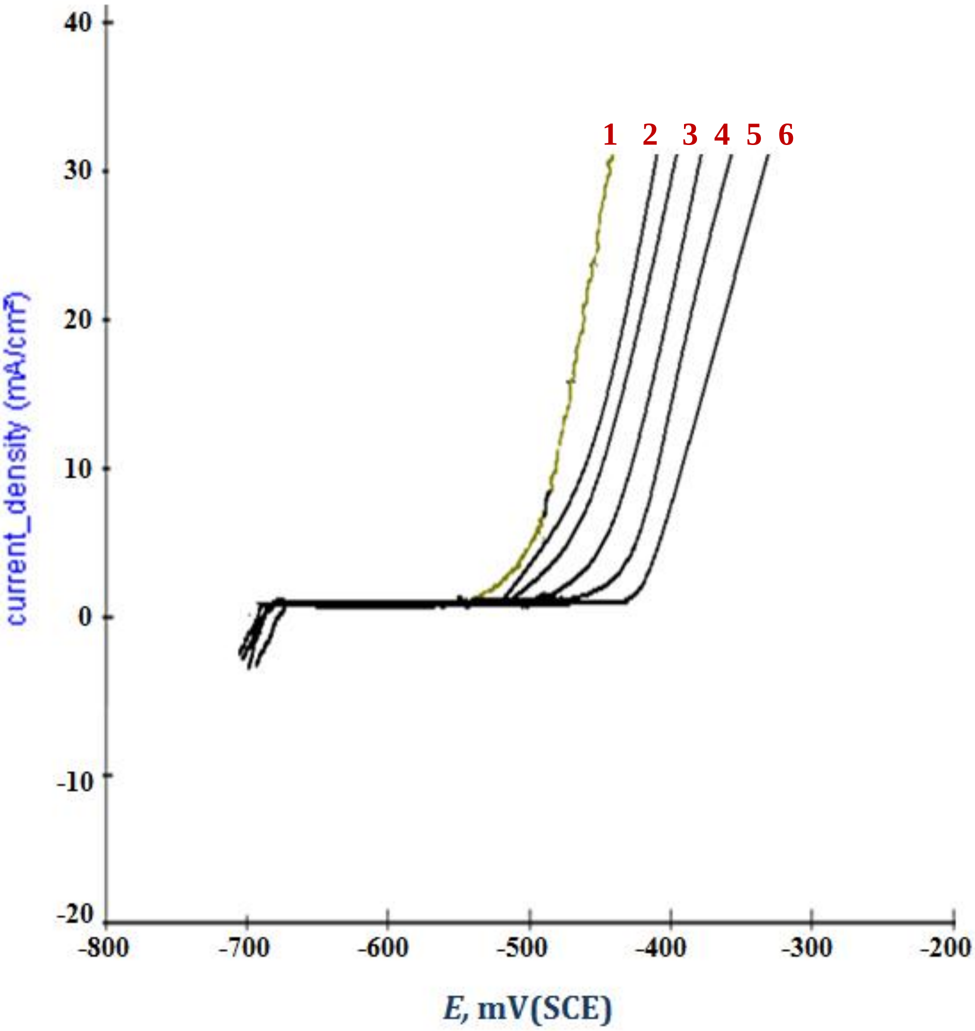


Figure 6. Potetiodynamic anodic polarization curves of mild steel in 1.0M HCl + 0.5M NaCl containing different concentrations of compound III.(1) 0.00 (2) 100 (3) 200 (4) 300 (5) 400 (6) 500 ppm at a scan rate 1 mVsec^{-1}.

The order of IE's obtained from weight loss,galvanostatic polarization and potentiodynamic anodic polarization measurements

gave the same order of inhibition efficiency but yielded different absolute values, probably due to the different experimental conditions.

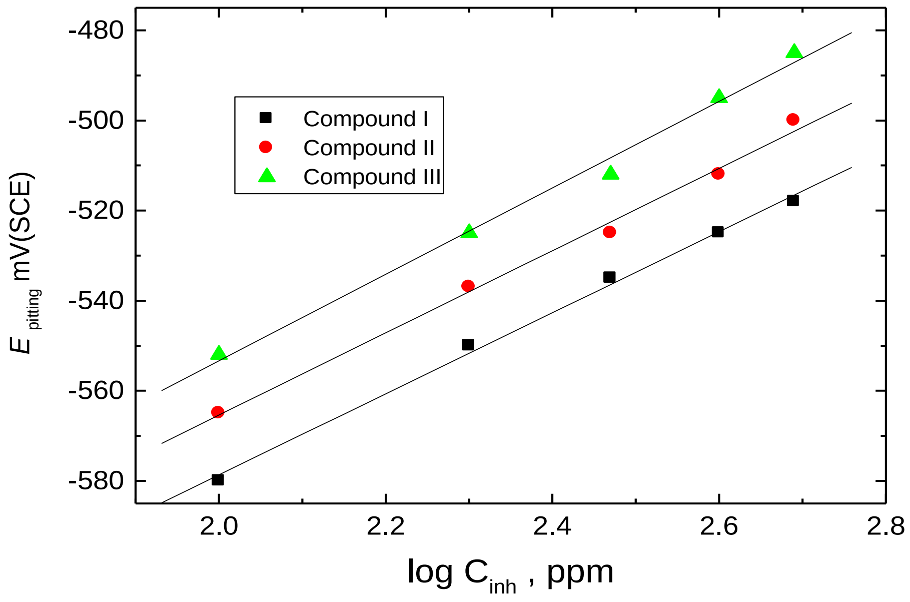


Figure 7. The relation between E_{pitt} and the logarithm of the concentration of inhibitor

3.7. Inhibition mechanism:

The inhibitive action of cationic surfactants of olyel-amido derivatives toward the corrosion of mild steel in 1.0M HCl solution could be attributed to the adsorption of their compounds on the steel surface forming a barrier between the bar metal and the corrosive environment. The surfactants molecule consists of polar hydrophilic group and non-polar hydrophobic group. The polar end of the surfactant is oriented towards the metal surface, while the non-hydrocarbon tails forms a hydrophobic barrier to the aggressive ions in the environments [24]. The increase in concentration of the inhibitors led to lowering of the interfacial tension at the metal surface. This lowering in interfacial tension is thought to cause a decrease of the bulk concentration of the inhibitor and an increase in its concentration at the metal surface.

The strength of adsorbed layer formed on the metal surface due to the electrostatic interaction occurs between the negative centers on the metal surface and the positively charged head groups of the cationic surfactants molecule (N^+) [25]. The increasing of the hydrophobic chain length increases the overlapping between the chains and also increases the thickness of adsorbed protective layer formed on the steel surface

At one and the same inhibition concentration, the values of IE's using different techniques decrease in the following order

compound I > compound II > compound III

The order of IE's increases with increasing the number of ethylene diamine unit in the chemical structure of the inhibitor.

4. CONCLUSIONS

1- The cationic surfactants of olyel-amido derivatives are considered as good inhibitors for mild steel corrosion in 1M HCl.

2- The inhibition efficiency was found to increase by increasing the inhibitor concentrations, number of ethylene diamine and with decreasing temperature.

3- The inhibitive action of cationic surfactants compounds is due to the adsorption on the steel surface.

4- The adsorption of cationic surfactants compounds on the steel surface follows Freundlich adsorption isotherm.

5- Cationic surfactants provide protection against pitting corrosion of mild steel in presence of chloride ions by shifting the pitting potential into noble direction.

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