



Inhibition of acid corrosion of oil tanks steel using triton surfactants

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Abstract

A series of tested surfactant compounds, namely, polyethylene glycol tertiary octyl phenyl ether, Merck; triton X- 114, triton X- 100, and triton X- 405 were investigated as inhibitors for corrosion of oil tanks steel in HCl. It was found that the three used surfactants act as good inhibitors for acid corrosion of the tested C-steel. The inhibition efficiency increases with increased surfactant concentration as well as the number of ethylene oxide units per molecule. Moreover, the inhibition efficiency decreases as the temperature was increased. The adsorption of surfactants on steel surface is a spontaneous process and follows Langmuir adsorption isotherm.

1. Introduction

Oil industry is one of the most important industries in the world. Carbon steel is the major constituent of the pipes and tanks used in the oil industry. The main problem faces this industry, especially during refining, is the corrosion of the used pipes and tanks walls. This is due to the presence of mineral compounds in the crude oil beside the other working parameters caused the scale such as purity of water and temperature [1].

During removal of the scale with acid pickling solutions, problems may arise if the acid attacks the metal, and so inhibitors must be used to stop or to decrease the attack. Hydrochloric acid is widely used for the removal of rust and scale from the petroleum containers. The corrosion of steel and ferrous alloys in such environments and its inhibition constitute a complex process.

Different groups of organic compounds have been reported to exert inhibitive effects on the corrosion of carbon steel. Compounds containing oxygen, nitrogen and sulphur groups generally gave rise to satisfying inhibitor efficiency in the case of iron corrosion in HCl medium [2-5]. Substituted benzotriazoles and other triazole derivatives were well known as corrosion inhibitors [6-11]. In these researches, attention is paid to the mechanism of adsorption and also to the relationship between inhibitor structures and their adsorption properties. It has been observed that the adsorption depends mainly on the electronics groups, steric factors, aromaticity, electron density on donor atoms, and π - orbital character of donating electrons [12-16].

A little study on surfactants usage as inhibitor has been reported [17-20]. Corrosion inhibition by surfactant molecules is related to the surfactant ability to aggregate at interfaces and in the solution. It was shown that the inhibition efficiency of the surfactant increases with increasing the concentration of the surfactant polymer and their mean molecular weight [20], and the number of its carbon atoms in the molecule. These compounds have marked

inhibition efficiency near their critical micelle concentration (CMC) values. The inhibition adsorption mode was strictly dependent on the inhibitor structure [18, 21].

In the present work, a study will be carried out for the investigation of inhibitive effects of triton series on the corrosion of carbon steel in 1M HCl using different techniques such as gravimetric, potentiodynamic, and SEM.

2. Experimental

The specimens used in this investigation were taken from the tanks of Cairo Co. for petroleum refining. The composition of the carbon steel specimen is shown in Table 1.

Table 1: Chemical composition of the used carbon steel specimen.

Chemical Composition	C	Mn	P	S	Si	Fe
Weight %	0.27	0.85	0.035	0.035	0.15	remainder

A series of tested surfactant compounds, namely, polyethylene glycol tertiary octyl phenyl ether, Merck; triton X- 114, triton X- 100, and triton X- 405, have a chemical structure $C_{14} H_{21} (OCH_2CH_2)_x OH$, where X: 7-8, 9-10, and 40, respectively, were used without any further purification. Figure (1) shows the chemical structure of the triton series.

A prepared 1M HCl solution was diluted from concentrated acid (37% Merck) with bi-distilled water and used as a corrosive media.

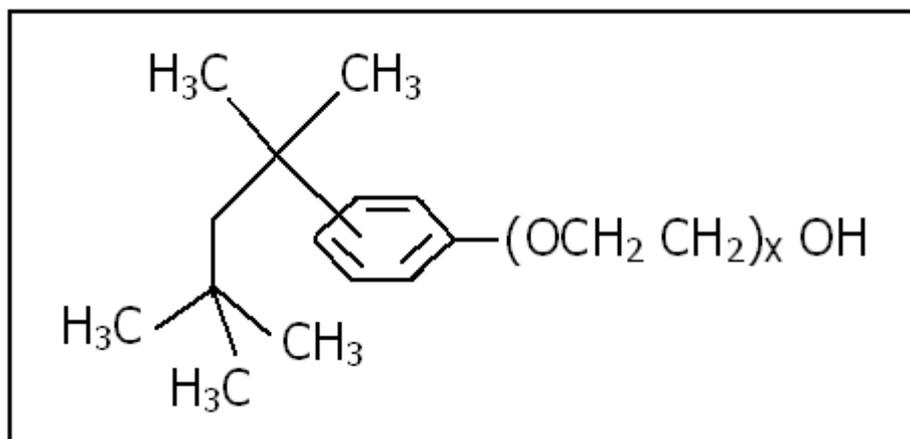


Fig 1: Chemical structure of the triton

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat cooling condenser contained in 50 cm³ of the corrosive solution. Rectangular steel specimens with the dimensions of (0.45, 0.95, 1.1 cm) were used. These sheets were abraded successively with fine emery paper (600 – 1200 grit), rinsed with bi-distilled water, degreased with acetone, dried before being weighed, and then hanged in the corrosive medium. The maximum duration of the weight loss experiment was 7 days at 298 K in naturally aerated solutions. At the end of each experiment, the specimens were carefully washed by bi-distilled water, dried between two filter papers and weighed. The corrosion rate was calculated in mpy unit using the equation:

$$Corrosion\ rate\ (mpy) = \frac{1.437\ w}{A^2 \cdot t \cdot d} \quad (1)$$

Where w is the weight loss in milligram, A is the surface area in square decimeter, t is the exposure time in days and d is the density of the corroded coupon. The inhibition efficiency, IE , was determined according to equation (2):

$$IE = [1 - (r/r^0)] \times 100 \quad (2)$$

Where r and r^0 are the corrosion rates (mpy) of steel specimen in presence and absence of the surfactant, respectively. Micrographs of the tested specimens, coated by a sputtered 50 nm gold film, was taken using scanning electron microscope, model Philips XL 30.

Electrochemical measurements were carried out using Meinsberger potentiostat/ Galvanostat with software zum ps6 remote for calculating the electrochemical parameters.

Polarization experiments were carried out in a conventional three electrode cell with a platinum counter electrode and a reference saturated calomel electrode (SCE). A cylindrical electrode of the carbon steel with a bottom surface area of 0.38 cm^2 was used as a working electrode. The electrode was abraded successively with fine emery paper (600 – 1200 grit), rinsed with bi-distilled water, degreased with acetone and water before used. At the start of each experiment, the working electrode was pre-cathodized for 10 minutes in the test solution in order to reduce the pre-immersion oxide film carried by the steel surface and attain its steady state potential. The scan rate of polarization was 10mV/ sec. The corrosion parameters were determined by extrapolation of the cathodic and anodic Tafel lines to the corrosion potential. The inhibition efficiency (IE), and the fraction of surface coverage (θ) were calculated according to following equations:

$$\text{IE \%} = [1 - (r_{\text{corr}} / r_{\text{corr}}^0)] \times 100 \quad (3)$$

$$\theta = 1 - (r_{\text{corr}} / r_{\text{corr}}^0) \quad (4)$$

where r_{corr} and r_{corr}^0 are the corrosion rates of steel specimen in presence and absence of the surfactant, respectively. All the experiments were performed in naturally aerated solutions at 298 K.

3. Results and Discussion

3.1 Gravimetric measurements

The effect of addition of different concentrations of the triton compounds on the corrosion of carbon steel in 1M HCl solution was studied using weight loss measurements at 298K after 7 days of immersion period. Figure (2) shows the relation between molar concentration and the inhibition efficiency (IE) of triton X- 114, X- 100, and X- 405. Inspection of the figure reveals that, for certain triton compound, the inhibition efficiency increases with increasing the molar concentration up to a certain limit after it a further increase of concentration leads to a slight decrease of inhibition efficiency. At low concentration of the surfactants, $4.7 \times 10^{-5} \text{ M}$, the inhibition efficiency increases in the order of, triton X- 114 < X- 100 < X-405. This behavior could be attributed to the increasing number of carbon atoms in the surfactant molecule [20], as well as increasing number of ethylene oxide group.

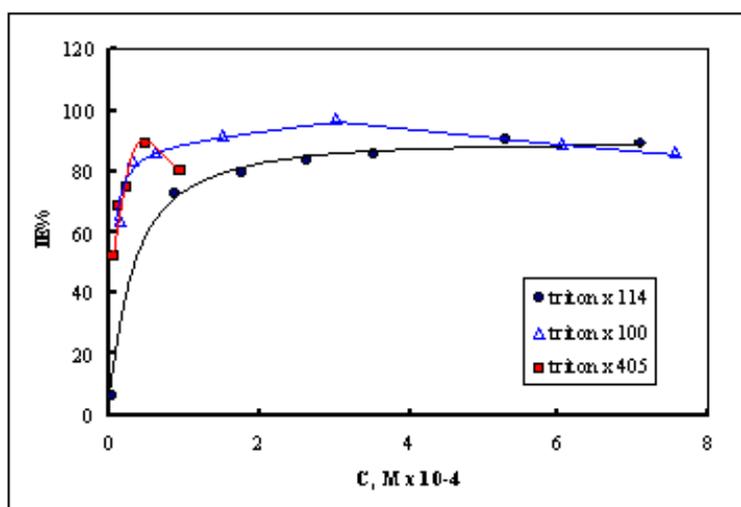


Fig 2: Effect of triton compounds concentration on their inhibition efficiencies.

When the triton compounds were used in small concentrations, their molecules were adsorbed on the metal surface making a barrier between the metal and corrosive environment. Such adsorption leads to inhibition of the corrosion reaction of the steel. On the other hand, addition of higher concentrations of these compounds gives rise to a competition between the molecules to be adsorbed on the active sites of the metal surface. The presence of such competition in addition to the steric hindrance of the large molecules results in formation of a loosely adherent adsorbed layer on the metal surface. The inhibition action resulted due to such layer is expected to be very small. Consequently, the inhibition efficiency decreases with further increasing of the inhibitor concentrations.

Scanning electron micrographs were represented in [Figures (3- a), (3- b), and (3- c)]. Figure (3- a) shows parallel features on the polished steel surface before exposure to the corrosive solution, which were associated to the polishing scratches. This polished steel surface was more corroded after immersion in the tested solution without inhibitors as shown in Figure (3- b). Figure (3-c) shows the specimen after immersion in 1M HCl solution containing 3.02×10^{-4} M triton X- 100. The surface was covered with a film of adsorbed triton molecules, which inhibits the corrosion of steel.

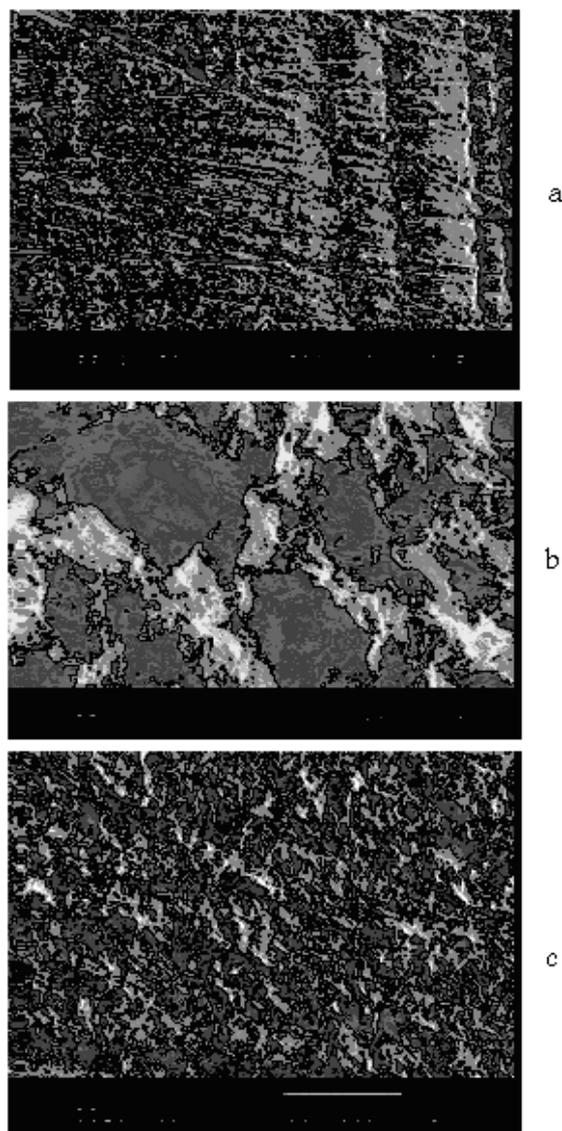


Fig 3: SEM micrograph of C-steel surface: a) polished surface b) after exposure to 1M HCl solution c) after exposure to inhibited 1M HCl solution.

3.2. Potentiostatic Polarization

Potentiostatic polarization measurements were carried out in 1M HCl devoid of and containing different concentrations of tritons. Figure 4, shows the anodic and cathodic polarization curves of carbon steel in 1M HCl, free and containing different concentrations of triton X-114. Similar figures were also obtained for the two other surfactants (not shown).

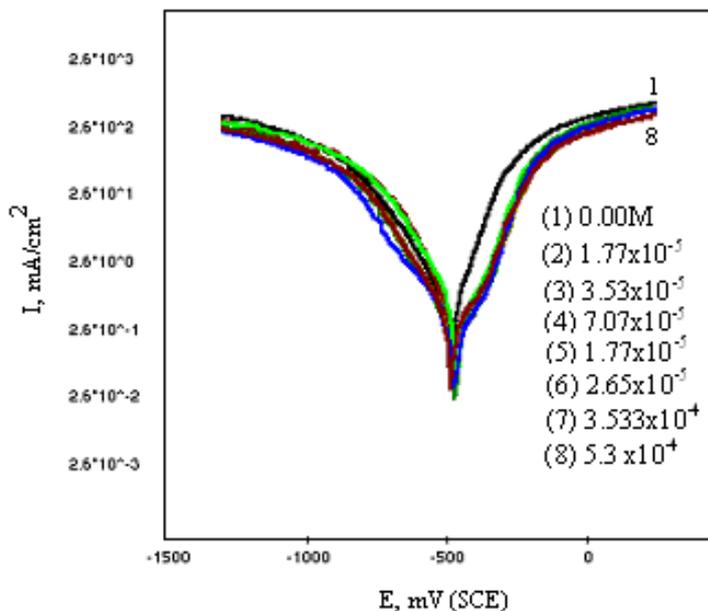


Fig 4: Anodic and cathodic polarization curves.

The corrosion parameters obtained from the polarization curves are listed in Table (2). Inspection of the data of Table (2) reveals that the corrosion current decreases markedly upon addition of the surfactants. This behaviour suggests the inhibition action of the used compounds. The inhibition efficiency increases as the concentration of triton is increased.

Table 2: The corrosion parameters obtained from the polarization curves.

Inhibitor type	Concentration M	β_a (mV/decade)	β_c (mV/decade)	E_{corr} (mV)	IE%	θ
-	0	112	-183	-447	-	-
TritonX-114	7.0×10^{-6}	95	-150	-434	30	0.30
	1.8×10^{-5}	108	-184	-425	60.3	0.603
	2.6×10^{-5}	94	-151	-440	63.24	0.6324
	3.5×10^{-4}	109	-156	-452	64.71	0.6471
	5.3×10^{-4}	109	-156	-452	66.18	0.6618
TritonX-100	1.5×10^{-5}	95	-225	-450	32.5	0.325
	3.0×10^{-5}	84	-214	-456	57.4	0.574
	6.0×10^{-5}	66	-174	-445	73.4	0.734
	1.1×10^{-4}	65	-159	-452	81.76	0.8176
	3.0×10^{-4}	63	-159	-454	83.28	0.8328
TritonX-405	2.3×10^{-6}	146	-176	-444	10.3	0.103
	4.7×10^{-6}	126	-132	-437	28.4	0.284
	9.4×10^{-6}	96	-155	-439	48	0.48
	1.9×10^{-5}	76	-151	-432	59	0.59
	4.7×10^{-5}	100	-178	-459	64.71	0.6466

On the other hand, corrosion rate values are found to be dependent on the molecular weight of triton. The corrosion potential remains almost constant upon addition of different concentrations of the surfactants. Moreover, the anodic and cathodic Tafel constants change in the same manner in presence of the surfactants. These results indicate that triton compounds act as mixed inhibitors. Further inspection of Table (2) reveals that the results of polarization technique confirm those obtained by the weight loss measurements.

3.3 Effect of Temperature

Potentiostatic polarization curves of carbon steel corrosion, in the acidic media in absence and presence of certain concentration of every surfactant, were traced in temperature range of 298 - 343 K. The chosen concentrations of different triton compounds were 5.3×10^{-4} M, 3.0×10^{-4} M and 4.7×10^{-5} M for triton X- 114, triton X- 100 and triton X- 405, respectively, were used. The corresponding results are given in Table (3). The data of Table (3) reveal that, the corrosion rate increases in the blank sample with the raising of the temperature. Moreover, the inhibition efficiency of the surfactant decreases as the temperature was increased. This result indicates that the adsorption of the inhibitor could be a physical adsorption.

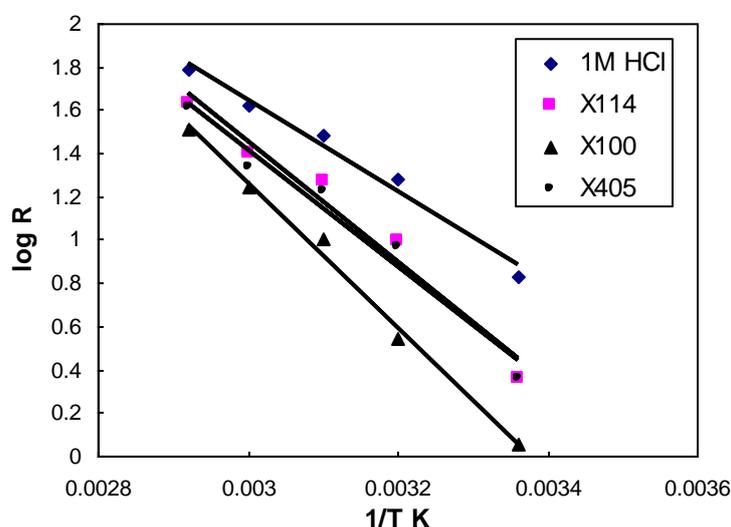


Fig 5: The Arrhenius plot of steel corrosion in free and inhibited HCl solutions.

Figure (5) represents the Arrhenius plot for the steel corrosion process in free and inhibited HCl solutions. The apparent activation energies, obtained from the slopes of the curves of Fig 5, in the absence and presence of triton compounds are 40.7, 53.2, 63.9 and 51.6 KJ.mol^{-1} for free acid, X-114, X-100 and X-405, respectively. It is obvious that the presence of triton increases the apparent activation energy. This could be done by reducing the rate of mass and charge transfer due to the presence of a film of adsorbed triton molecules. However, such types of inhibitors perform a good inhibition at ordinary temperature with considerable loss in inhibition efficiency at elevated temperatures [22].

Table 3: Effect of temperature on the corrosion of carbon steel.

T, K	r_{corr}^0	r_{corr}			IE %		
		x- 114	x- 100	x- 405	x- 114	x- 100	x- 405
298	6.8	2.3	1.14	2.4	66.18	83.24	64.71
313	18.8	10	3.5	9.3	46.81	81.383	50.532
323	30.02	18.8	10.06	17	37.38	66.49	43.371
333	37.2	24.1	17.5	21.53	35.22	52.96	42.124
343	61.5	42.36	32	40.75	31.122	47.97	33.74

3.4. Adsorption Isotherm

The mode of variation of the fraction of surface coverage (θ) with the varied concentrations of surfactants was tested graphically to find out the corresponding adsorption isotherm. It was found that the adsorption of triton molecules on steel surface in 1M HCl follows Langmuir isotherm (Fig 6). Thus, it could be concluded that there is no interaction between the molecules adsorbed on the metal surface.

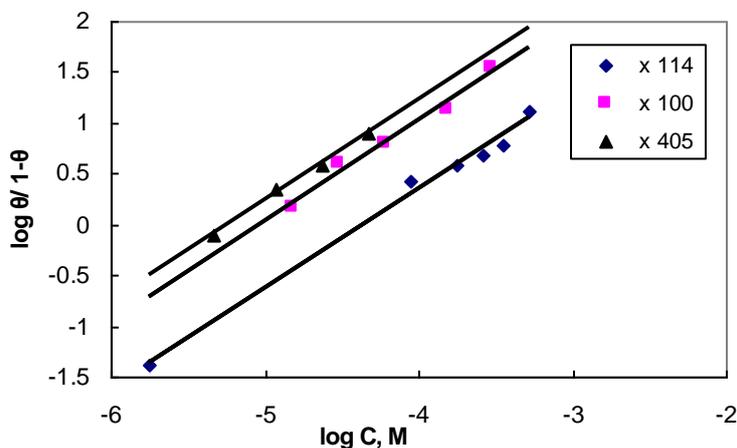


Fig 6: Langmuir adsorption isotherm plots.

The values of free energy of adsorption were calculated and presented in Table 4. The negative sign of them indicates that the adsorption of triton molecules on steel surface is a spontaneous process. It is well known that values of ΔG_{ads} in the order of -20 kJ.mol^{-1} or lower indicate a physical adsorption while those of about -40 kJ mol^{-1} or higher involve charge sharing or a transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond [23]. The obtained value of ΔG_{ads} suggests a strong physical adsorption of triton components on the steel surface in HCl solution.

Table 4: Free energy of adsorption of triton molecules on the steel surface.

Surfactant	ΔG_{ads} , kJ/mol
Triton X-114	- 34.064
Triton X-100	- 38.543
Triton X-405	- 39.427

4. Conclusions

- The three used surfactants act as good inhibitors for acid corrosion of the tested C-steel.
- The inhibition efficiency increases with increased surfactant concentration as well as the number of ethylene oxide units per molecule.
- The inhibition efficiency decreases as the temperature was increased.
- The adsorption of surfactants on steel surface is a spontaneous process and follows Langmuir adsorption isotherm.

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