Some Polysorbate Compounds as Corrosion Inhibitors for Carbon Steel in Hydrochloric Acid

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ABSTRACT

Some commercial non-ionic surfactants polysorbate, namely, polysorbate 80, polysorbate 40 and polysorbate 20, were tested as inhibitors for corrosion of C-steel in 2.0M HCl solution using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. It was found that all the three used compounds act as inhibitors for acid corrosion of C-steel. The inhibition efficiencies obtained by the three techniques were almost the same, and increase with increasing the hydrocarbon chain length and the surfactant concentration. The polarization studies show that these compounds act as mixed inhibitors. The inhibition action of these surfactants can be explained by their ability to adsorb on the metal surface making a barrier to mass and charge transfer. It was found that the adsorption of these surfactants follows Langmuir adsorption isotherm. The negative values of adsorption free energy indicating that the adsorption process is spontaneous and increases, for different surfactants, in the same direction as inhibition efficiency.

Keywords: C-steel; corrosion inhibition; polysorbate surfactants.

1. Introduction

The use of inhibitors is one of the most practical methods for metals protection against corrosion in acidic media [1]. Acidic solutions are used extensively in chemical and several industrial processes such as acid pickling, acid cleaning, acid descaling and oil wet cleaning, etc. [2]. Chemical inhibitors are often used for these processes mainly to control the metal dissolution and acid consumption. Most of well-known acid corrosion inhibitors are organic compounds containing nitrogen, sulfur or oxygen atoms [3-6]. It has been found that most of the organic inhibitors act by adsorption on the metal surface [7]. This phenomenon is influenced by the nature and surface charge of metal, the type of aggressive electrolyte and the chemical structure of inhibitors [8]. Many studies were done on the corrosion and inhibition of carbon steel in acidic media [9-13]. The efficiency of the surfactants is higher than the other organic inhibitors because of surfactant compounds exist at the interface between corrosive media and steel surface by more concentration. Accordingly, the surfactant compounds are more efficient than the same organic compounds at the same concentration. The adsorbed species protect the metal from the aggressive medium, which causes decomposition of the metal. Adsorption depends not only on the nature and charge of the metal but also on the chemical structure of the inhibitor .The objective of this study is to investigate the effect of some polysorbate compounds on the corrosion of carbon steel in hydrochloric acid solution. The inhibition efficiency of these compounds was determined by using weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) techniques.

2. Experimental methods

The carbon steel specimen used for this study has the following composition (wt. %); C = 0.26; Mn = 1.35, P = 0.04, S = 0.05, Nb = 0.005, V = 0.02, Ti = 0.03, and Fe to balance. For weight loss measurements, the test pieces were cut specimen in dimensions of 2 x 2 x0.2 cm. The coupons were successively abraded with SiC paper to a final finish using 1200 grade paper. Before immersion in the test solution (50 ml), the dimensions of each coupon were ascertained. They were then degreased in AR grade acetone, etched in HCl for 30 S, washed with double distilled water, followed by acetone, dried and weighed. Each of the C-steel specimens was immersed, for 24 hours, in 50 ml of 2.0 M HCl solutions containing different concentrations of polysorbate compounds, at 25 (± 1) ^{o}C. The average weight loss for each to identical experiments was taken and expressed in mg cm^{-2}.

For potentiodynamic polarization technique, the carbon steel electrode was of dimensions of 1cm x 1cm and was weld from one side to a copper wire used for electric connection. The sample embedded in glass tube of just larger diameter than the copper wire. Before each experiment, the exposed area was polished with different emery paper in the normal way starting from coarser to finer, followed by degreasing in acetone and finally washed with bi-distilled water, just before the insertion on the electrolytic cell. BDH grade hydrochloric acid was used for the preparation of the test solutions.

A three electrodes cell, with saturated calomel reference electrode (SCE) and platinum foil counter electrode was used in polarization experiments. Potentiodynamic polarization technique was carried out using a PS remot potentiostat with zum PS6 software for calculation of electrochemical parameters.

The impedance 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 potentiostate (Auto Lab 30, Metrohm). All experiments were performed using three-electrode system.

The used polysorbate surfactants are organic compounds which have surface active properties and commercially available with relatively low price. Three different polysorbate compounds are used in the present study, namely, polysorbate 20, 40 and 80.Polysorbate compounds are basically polyoxythelene sorbitan combined with different fatty acids. The number associated with the polysorbate name determines the predominant fatty acid contained in the polysorbate structure. Thus, for polysorbate 20, 40, and 80, the acids are, respectively, monolaurate, monopalmitate and monooleate.

3. Results and Discussion

3.1. Weight loss measurements

The losses of weight of C-steel sheets due to their immersion in solutions of 2.0 M HCl containing different concentrations of polysorbate compounds were measured. It was found that, the addition of any of the used three polysorbate compounds lowers the weight loss of the C-steel specimen than its value in the free acid solution. This result indicates that the three polysorbate compounds act as inhibitors for C-steel corrosion in hydrochloric acid solution. The inhibition efficiencies (IE %) of different concentrations of the three polysorbate compounds are given in Table (1). The inhibition efficiency was calculated using the following equation:

$$IE\% = \frac{W_o - W}{W_o} \times 100 \qquad (1)$$

where, W_o and W are weight loss of C-steel coupon in absence and presence of additives, respectively.

Table1. Dependence of IE of polysorbate compounds on their concentrations as revealed from weight loss measurements.

| Conc./ppm	IE %		
	Polysorbate 20	Polysorbate 40	Polysorbate 80
100	52.00	56.00	57.00
200	58.40	60.80	63.10
300	62.11	67.80	69.33
400	71.00	74.00	74.00
500	80.11	81.33	82.11

Inspection of Table 1 reveals that, the inhibition efficiency increases as the inhibitor concentration is increased. This behavior could be attributed to the increase of the metal surface area covered by the adsorbed inhibitor molecules with the increasing inhibitor concentration. Furthermore, data in Table 1 show that the extent of inhibition of different polysorbate compounds depends on their structures. The inhibition efficiency increases in the following order:

Polysorbate 20 < Polysorbate 40 < Polysorbate 80

This sequence will be discussed later.

3.2. Potentiodynamic polarization

Figure.1 represents the cathodic and anodic polarization curves of C-steel electrode, in 2.0 M HCl solutions containing different concentrations of polysorbate 40 compound as an example. Similar curves were also obtained for the polysorbate 20 and polysorbate 80(not shown). Inspection of Fig. 1 reveals that, both anodic and cathodic polarization curves are shifted to less current density values in the presence of polysorbate compound. This behavior suggests the inhibitive action of the polysorbate compounds. The extent of the shift in current density increases with increasing of polysorbate compounds concentration. The values of corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic Tafel constant (β_a) and cathodic Tafel constant (β_c), excluded from polarization curves are given in Table 2. Inspection of Table 2 reveals that the corrosion potential of C-steel in the acid solution is largely shifted to less negative values (noble direction) upon addition of polysorbate compounds. The magnitude of this shift increases with increasing of the associated number of polysorbates and with increasing of the additive concentration.
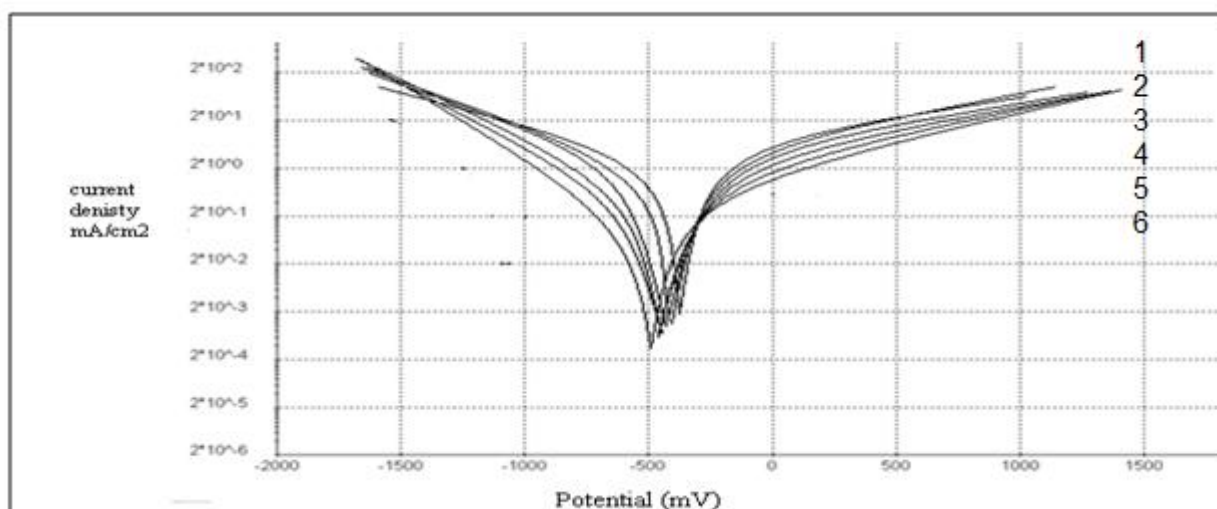
Fig.1. Potentiodynamic polarization curves of C-steel electrode in 2.0 M HCl solution with and without polysorbate 40. (1) 0.00 ppm polysorbate 40, 2) 100 ppm, 3) 200 ppm, 4) 300 ppm, 5) 400 ppm , 6) 500ppm.

On the other hand, the corrosion current density is greatly reduced upon addition of the three polysorbate compounds. These results suggest the inhibitive action of the tested compounds. The data in Table 2 reveal that the values of inhibition efficiency obtained by polarization technique are comparable to those obtained by weight loss measurements. The inhibition efficiency increases with increasing polysorbate concentration. The inhibition efficiency depends on the type of polysorbate compounds.

It could be recognized in Table 2 that the inhibition efficiency of the three polysorbate compounds increases in the following order:

Polysorbate 20 < Polysorbate40 < Polysorbate 80

It is of interest to note that this sequence is similar to that obtained by weight loss measurements. Further inspection of Table 2 reveals that the addition of increasing concentrations of polysorbate compounds increases both the anodic and cathodic Tafel constants. This result indicates that the non-ionic surfactants act as mixed inhibitor which means that the surfactant molecules are adsorbed on both the anodic and cathodic sites resulting in an inhibition of both anodic dissolution and cathodic reduction reactions.

3.3. Adsorption isotherm

The inhibiting power of polysorbate compounds is mainly dependent on its ability to get adsorbed on the metal surface, The adsorption of inhibitor molecules from an aqueous solution can be regarded as a quasi-substitution process between the surfactant compound in the aqueous phase, $Surf_{(aq)}$, and water molecules at the steel surface, $H_2O_{(sol)}$.

$$Surf_{(aq)} + x\ H_2O\ _{(ads)} = Surf\ _{(ads)} + x\ H_2O\ _{(aq)} \qquad (2)$$

where, x the size ratio, is the number of water molecules displayed by one molecule of organic inhibitor.

The degree of surface coverage (θ) which represents the fraction of the metal surface covered by adsorbed molecules is calculated using the following equation:

$$\theta = \frac{i_f - i_{inh.}}{i_f} \qquad (3)$$

where, i_f and $i_{inh.}$ are the corrosion currents in free and inhibited acid solutions, respectively. The values of θ corresponding to different concentrations of polysorbate compounds are given in Table 2.

The values of surface coverage θ were found to increase with increasing the concentration of polysorbate compounds. This indicates that the inhibitive action of these compounds toward the acid corrosion of carbon steel could be attributed to the adsorption of its compound on the steel surface .Attempts were made to fit θ values to the several adsorption isotherms like Frumkin, Freundlich,Temkin and Langmuir.The best fit was obtained with Langmuir isotherm according to the following equation (Zhang and Hua, 2009):

$$\log \frac{\theta}{1-\theta} = \log C + \log k \qquad (4)$$

where, C is the concentration of polysorbate compounds and k is the equilibrium constant of adsorption .

The standard free energy of adsorption, (ΔG°_{ads}), was calculated from the equilibrium constant of adsorption using the following equation [14]:

$$k = \frac{1}{55.5} \exp\left[\frac{-\Delta G^{o}_{ads}}{RT}\right] \qquad (5)$$

where, R is the universal gas constant, T is the absolute temperature and 55.5 represents the concentration of water in mole L^{-1}

The plot of log θ/(1- θ) versus logarithm of polysorbate concentration give straight lines with slopes very close to unity for these compounds (Fig. 2). These results suggest that the adsorption of the polysorbate compounds on C-steel surface follows Langmuir adsorption isotherm. This isotherm postulates that there is no kind of interaction forces that could arise between the molecules adsorbed at the metal surface. Thus, the values of free energy of adsorption (ΔG^{o}_{ads}) are calculated using these equations. It was found that ΔG^{o}_{ads} values are -24, -23and -21 kJ for polysorbate 20, polysorbate 40 and polysorbate 80 respectively. The negative ΔG^{o} values suggest that the adsorption process is spontaneous.

Table 2. Electrochemical parameters for C-steel corrosion in free and inhibited 2.0M HCl solution.

| Inhibitor system	Conc. (PPM)	β_a (mV dec^{-1})	$-\beta_c$ (mV dec^{-1})	E_{corr}, mV (SCE)	I_{corr} (mA/cm^2)	θ	%I.E
HCl (2M)	-----	78	113	-433	0.48	-----	------
Polysorbate 20	100	151	173	-460	0.22	0.55	54.20
	200	161	188	-465	0.19	0.60	60.40
	300	180	198	-468	0.17	0.65	64.60
	400	189	213	-474	0.13	0.73	73.00
	500	203	236	-479	0.09	0.82	81.30
Polysorbate 40	100	156	178	-488	0.21	0.57	56.30
	200	163	189	-494	0.18	0.63	62.50
	300	173	197	-499	0.15	0.69	69.20
	400	195	224	-501	0.11	0.76	75.80
	500	211	240	-504	0.087	0.82	82.20
Polysorbate 80	100	158	176	-491	0.20	0.59	58.40
	200	164	188	-498	0.17	0.65	64.90
	300	174	199	-506	0.14	0.71	70.90
	400	192	218	-511	0.12	0.75	75.20
	500	207	251	-521	0.08	0.84	83.70
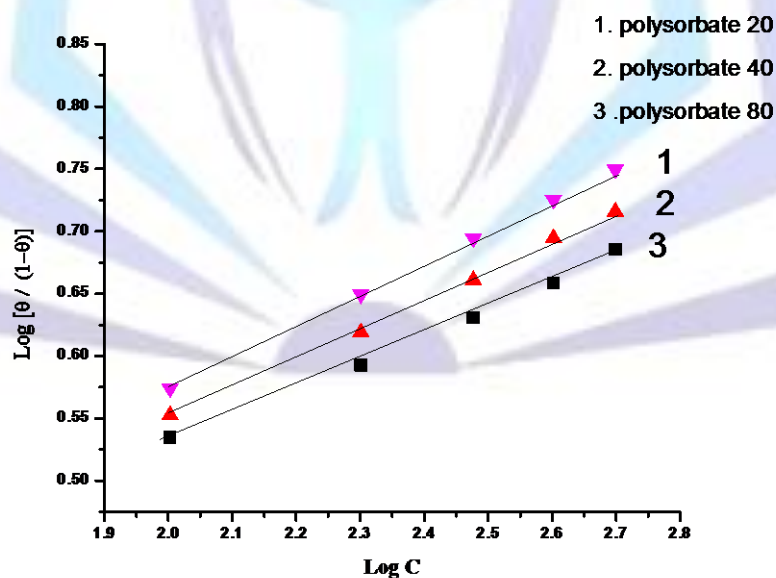
Fig. 2. Langmuir adsorption isotherms of different polysorbate compounds.

## 3.3. Electrochemical impedance studies

Electrochemical impedance measurements were carried over the frequency range from 10 kHz to 100 mHz at open circuit potential. The sample equivalent Randle circuit for studies is shown in Fig. 3, where Rs (Ωcm^2) represents the

solution and corrosion products film; the parallel combination of resistor, R_{ct} (charge transfer resistance) and capacitor C_{dl} (double layer capacitance) which represents the corroding interface.
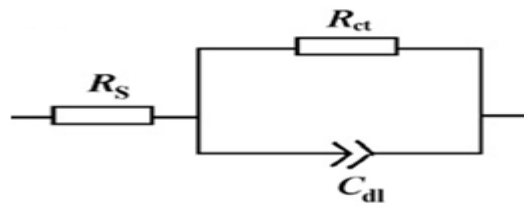
Fig.3. Electrical equivalent circuit ($R_s\Omega$ = uncompensated solution resistance, R_{ct} = charge transfer resistance and C_{dl} = double layer capacitance).

The Nyquist representation of the impedance behavior of carbon steel in 2.0M HCl with and without addition of various concentrations of inhibitor is given in Fig.4. It is seen that addition of inhibitor increases the value of R_{ct} and reduces C_{dl}.
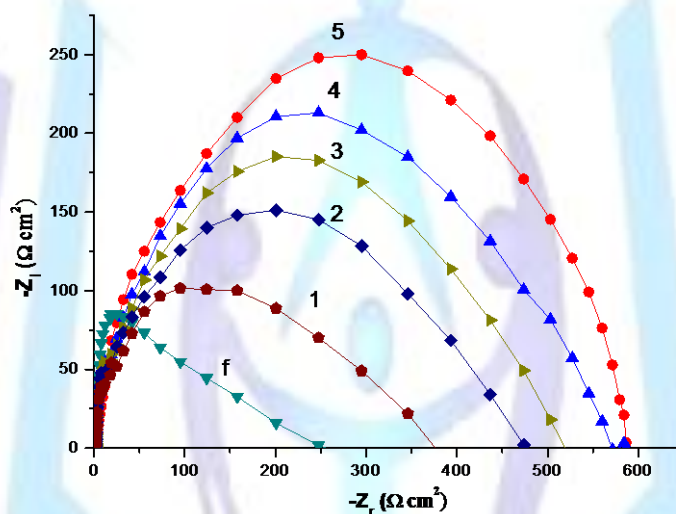
Fig.4. Nyquist plot of C-steel in 2.0M HCl solution in absence and presence of different concentrations of polysorbate 80: (1) 0.00 ppm (2) 100 ppm (2) 200 ppm (3) 300 ppm (4) 400 ppm (5) 500 ppm.

The R_{ct} values of the investigated compound increase with increasing inhibitor concentration. At the same time the C_{dl} has opposite trend in the whole concentration range. These observations clearly bring out the fact that the corrosion of carbon steel in 2.0M HCl is controlled by a charge transfer process. The decrease in C_{dl} is due to the gradual replacement of water molecules by the adsorption of the organic molecules at metal / solution interface, leading to a protective film on the steel surface, and then decreasing the extent of dissolution reaction [15]. The characteristic parameters associated to the impedance diagrams (R_{ct}, C_{dl}), θ and IE (%) are given in Table 6. The IE (%) and θ were calculated from the following equations.

$$\theta = \left[\frac{(1/R_{ct})_0 - (1/R_{ct})}{(1/R_{ct})_0}\right] \qquad (6)$$

$$\%I.E = \left[\frac{(1/R_{ct})_0 - (1/R_{ct})}{(1/R_{ct})_0}\right] \times 100 \qquad (7)$$

where $(R_{ct})_0$ and (R_{ct}) are the uninhibited and inhibited charge transfer resistance, respectively [16].

Table 3: Impedance data and surface coverage for carbon steel in 2M HCl in absence and presence of different concentrations of polysorbate compounds.

Inhibitor	(M)	R_s (Ωcm^2)	R_{ct} (Ωcm^2)	C_{dl} ($\mu f.cm^2$)	θ	IE (%)
	0	1.2	65	-----	-----	-----
	0.01	1.1	448	41.2	0.8549	85.49
	0.02	1.8	500	36.13	0.8700	87.00
Polysorbate 20	0.03	2.1	551	34.14	0.8820	88.20
	0.04	2.3	570	28.26	0.8860	88.60
	0.05	2.7	585	20.4	0.8889	88.89
	0.001	1.2	420	40.88	0.8452	84.52
	0.002	1.7	433	37.18	0.8499	84.99
Polysorbate 40	0.003	1.9	538	33.2	0.8792	87.92
	0.004	2.2	565	26.15	0.8850	88.50
	0.005	2.6	580	21.4	0.8879	88.79
	0.01	1.1	385	40.33	0.8312	83.12
	0.02	1.3	470	36.45	0.8617	86.17
Polysorbate 80	0.03	1.6	520	32.14	0.8750	87.50
	0.04	1.9	560	26.28	0.8839	88.39
	0.05	2.3	585	14.25	0.8889	88.89

3.4. Mechanism of inhibition

The inhibition mechanism of the corrosion of carbon steel in hydrochloric acid by some polysorbate compounds (non-ionic surfactants) was studied. The percentage inhibition efficiency was calculated by chemical techniques e.g. weight loss measurement, and electrochemical techniques e.g. potentiodynamic polarization, electrochemical impedance spectroscopy and potentiodynamic anodic polarization technique at scan rate of 1mV/sec, to measure the pitting corrosion. It was found that the percent of inhibition efficiency of polysorbate compounds is dependent on its concentration.

These observations indicate that the corrosion inhibition is due to the adsorption of the inhibitors at the metal / solution interface. The nature of interaction of inhibitor on the metal surface during corrosion inhibition can be explained in terms of its adsorption characteristics.

However, the inhibition efficiency depends on many factors, which include the number of adsorption active centers in the molecule and their charge density, molecular size, mod of adsorption, temperature, heart of hydrogenation and formation of metallic complexes. The adsorption of these compounds on the metal surface cans retard the anodic or cathodic reaction by one or more of the following mechanisms.

i)   Formation of physical barrier layer between metal and inhibitor.

ii)   Reducing the metal reaction through alternating the nature of metal surface.

iii)   Changing the structure of the metal /solution interface.

The inhibiting effect of some polysorbate compounds is due to its adsorption on the steel surface. The adsorbed layer acts as a barrier between the metal surface and the aggressive solution leading to a decrease in corrosion rate. The surface activity of polysorbate compounds as well as the presence of function groups, such as carbonyl group, in their structures facilitates such adsorption. The surfactant molecules adsorb on the metal surface via their function groups, while their hydrocarbon chains are oriented toward the aqueous solution. Since these hydrocarbon chains are hydrophobic in nature, they repel the aqueous aggressive anions away from the metal surface and therefore inhibit the corrosion

reaction. The obtained results by different techniques indicate that the order of inhibition efficiency of the polysorbate compounds depending on the chemical structure of these compounds and decreases in the following order

Polysorbate 20 < Polysorbate T40 < Polysorbate T80

This sequence reflects the effect of type of the fatty acid included in the chemical structure of polysorbate on their inhibitive action.

Now, one can rewrite the above sequence according to the alkyl chain as following:

Oleate (C18) > Palmitate (C16) > Luarate (C12)

This new sequence illustrates the effects of both hydrocarbon chain length and the presence of double bond in the inhibitor structure. The values of the percentage inhibition efficiency of some polysorbate compounds toward the corrosion of carbon steel in hydrochloric acid using different techniques show an agreement and conformity of the experimental results. However, there is a small difference in the values obtained. This observed discrepancy could be attributed to the difference of the experimental conditions

4. Conclusions

1- The tested polysorbate compounds inhibit the corrosion of C-steel in 2.0 M HCl solution.

2- Polysorbate compounds inhibit the C-steel corrosion by adsorption on its surface and act better than the passive oxide film.

3- The inhibition efficiency increases as the length of the polysorbate hydrocarbon chain is increased.

4- The inhibition efficiencies of the tested polysorbate compounds increase with increasing of their concentrations.

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