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The Inhibition Effect of Some Organic Compounds on Corrosion of Brass and Carbon Steel in Aggressive Medium

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The surfactants Triton X100 and Triton A20 were studied as corrosion inhibitors for brass and carbon steel type OL37 in sulfuric acid medium using potentiodynamic polarization measurements, electrochemical impedance spectroscopy (EIS), FT-IR spectroscopy and metallurgical microscopy methods. We suppose that, these surfactants inhibit corrosion of metal electrodes by a protective mechanism can be owed to either the adsorption of inhibitor molecules forming a protective film or obtaining a insoluble compound and repairing the porous oxide layers. Experimental data showed that these surfactants achieved a significant inhibiting effect on brass and carbon steel corrosion and act that a mixed inhibitor. The adsorption of the non-ionic surfactants on the electrodes surface obeys to the Langmuir isotherm model. The temperature influence on the corrosion behaviour of the metal electrode in 0.5M H₂SO₄ with and without the inhibitor at 100 ppm and 800ppm was analyzed in the temperature domain from 293 to 313 K. The negative value of thermodynamic parameter like Gibbs free energy of adsorption shows the spontaneity of adsorption process. The experimental results indicate that these inhibitors established its corrosion protection ability. The best effectiveness is achieved at the inhibitor concentration of 100ppm for the system Triton X100/OL 37 and 800ppm for Triton A20/brass.

Keywords: organic inhibitor, brass, carbon steel, electrochemical methods, FT-IR spectroscopy

1. INTRODUCTION

Metals and its alloys are widely used in various industrial applications; this enhanced the investigation in corrosion protection in different corrosive media. It is appreciated that less active metals are less available and more expensive compared to common metals, which are too much exhibited at corrosion process to be utilized [1-8]. Protection of these metals can be obtained by numerous ways from which the treatment of the aggressive media and using of inhibitors is one of the most significant. The employment of inhibitors is one of the most practical techniques of anticorrosion

protection. In last years, the development of new organic compounds as acid inhibitors on active metals is one of the on a wide scale researched domain the area of anticorrosion protection [4-12]. Organic inhibitors are often used to protect these metals and its alloys against corrosion. The performance of these inhibitors which assure a barrier to the surface depends on various factors: chemical structure, molecular size, their charge density, by the distribution of charge in the molecule, temperature, way of interaction with the electrode surface, the nature of the metal surface and the aggressive medium. Acid media are intensively used in a diversity of industrial processes such as oil well acidification, acid pickling, chemical cleaning, and descaling, petrochemical processes and in numerous synthesis operations [6-19], which usually lead to severe metallic corrosion. Corrosion inhibitors are largely used to hinder or minimize material loss for metals that are in contact with acid media. In the principal, organic inhibitors containing polar groups with nitrogen, sulfur, oxygen and heterocyclic compounds with polar functional groups and/or conjugated double bond are appreciated as one of the effective chemicals for the hindering the metals corrosion due to their particular molecular structure [9-22]. Numerous studies demonstrated that most organic inhibitors operate by adsorption on the metal surface and in general, inhibitors can operate either by physical adsorption or chemisorption [10-27]. A lot of studies explained that the surfactants can be used as corrosion inhibitors for the corrosion protection of diverse metals in various media [13-29]. Surfactants are widely used in our daily life and in industrial practices. The surfactants are a large class of organic inhibitors that have been utilized for to achieve this anticorrosion protection [19-35]. The ionic and nonionic surfactants were significant to be considerable corrosion inhibitors for various metal materials. Many studies suggested that the best parts of surfactants are adsorbed on the metal materials surface by displaced water molecules from the electrode surface and forming a strong and strengthened barrier film. The ability of a surfactant molecule to adsorb is particularly directly related to its feature to aggregate and to form micelles [18-39]. The adsorption of a surfactant significantly influenced the corrosion resisting estate of a metal [25-42].

In this paper, the corrosion inhibition of two electrodes: brass and carbon steel in $0.5M H_2SO_4$ medium by some nonionic surfactants was examined by electrochemical techniques and the electrode surface was analyzed by Fourier transform infrared spectroscopy (FT-IR) and metallography analysis. As well, the influence of inhibitor concentration and temperature on the corrosion inhibition has been studied.

2. EXPERIMENTAL

In this research, the studied organic inhibitors were two nonionic surfactants: Triton X100 and Triton A-20 have been from Sigma-Aldrich products of pure quality (>97%). The corrosive medium was $0.5M H_2SO_4$ has been done by dilution of AG 96% H_2SO_4 (from Merck) with bi-distilled water. All chemicals were reagent grade and used as received without further purification.



Triton A-20, C17H28O3

Scheme 1 Chemical structure of the nonionic surfactants examined

Experimental tests have been effectuated on two electrodes like: carbon steel type OL 37 and brass. The composition of OL 37 is: C% 0.15; Si% 0.09; Mn% 0.4; P% 0.023; S% 0.02; Al% 0.022; Ni% 0.001; Cr% 0.001; Fe% 99.293; the brass has the chemical composition: Fe% 0.29, Cu% 65.60, Zn% 34, Si% 0.06, Pb% 0.05; and the corrosive medium was 0.5M H₂SO₄. Experiments have been effectuated in absence and presence of different concentrations of nonionic surfactants concentrations: 20, 50, 100, 300, 500, 800 and 1000 ppm at 25°C. The working electrode was: carbon steel OL 37 and brass in the shape cylindrical with an uncovered area of 0.5 cm^2 . This form is favorites, since it ensures an important surface and a decrease number of edges. The working electrode was mechanically polished with emery papers with different dimension (600, 1200, 2600, 4000 grid) up to mirror-luster, cleaned in benzene at boiling temperature in order to eliminate all traced of grease, after that, the working electrode has been washed with bi-distilled water and introduce in the electrochemical cell. All tests were effectuated at temperature of 25°C under atmospheric oxygen without agitation. All electrochemical methods have been carried out by using the electrochemical cell with a three conventional electrode: a platinum sheet like auxiliary electrode, a saturated calomel electrode as the reference electrode and a working electrode: brass and OL 37; this cell was connected to an automated model VoltaLab 40 potentiostat/galvanostat and a computer has been utilized with Voltamaster 4 software. The electrochemical behavior of an OL 37 and brass electrode in 0.5 M H₂SO₄ with and without of nonionic surfactants has been considered by potentiostatic, potentiodynamic and electrochemical impedance spectroscopy methods. The inhibiting effect has been studied from the polarization curves achieved using the galvanostatic and potentiodynamic techniques and calculation of the kinetic parameters for corrosion of electrodes in presence and absence of different concentration of inhibitors. On plotting the polarization curves consideration was kept of the case that long -drawn

anodic polarization might deliver rise to changes at the level of the surface asperities which would involve parallel translation of the Tafel slopes. This result can be removed by first tracing the cathodic polarization curves and then the anodic ones, method employed in this research. Investigation of Tafel polarization curves was accomplished by plotting the potential from cathodic to anodic potentials at a scan rate of 2mVs⁻¹ in the potential range from -850mv to -150mV versus to OCP-open circuit potential for OL 37 and -400 to +200mV versus OCP for brass. The electrochemical impedance spectroscopy (EIS) measurements have been realized at open circuit potential (OCP) disturbed with amplitude of 10mV AC sine wave and over a frequency domain of 100 kHz to 40 mHz. The experimental tests have been repeated with every solution until a good reproducibility of the data has been achieved. The electrochemical techiques were achieved utilizing VolaLab PGZ 301 instrument Potentiostat/Galvanostat. Surface analysis on the electrode of the obtaining film was investigated by FTIR spectroscopy (FTIR spectrometer Tensor 37 Bruker optik) and metallographic micrographies (Microscope Hund H660).

3. RESULTS AND DISCUSSION

3.1. Electrochemical studies

In this study, one of the best modes for corrosion protection of metal electrodes in corrosive medium is the application of the inhibitors, which control the corrosion of anodic or cathodic reaction and both. Figure 1 indicates the corrosion data of brass electrode in 0.5 M H₂SO₄ solution with and without various concentrations of Triton X 100- and Triton A-20. It was established that, both cathodic and anodic polarization curves indicated lower current density in the existence of nonionic surfactant inhibitors than those registered in noninhibting solutions. This comportment showed that all used surfactant had considerable influences on cathodic and anodic reactions of the electrochemical process.





Figure 1. Polarization curves of brass electrode in 0.5M H₂SO₄ with and without A) Triton X100 and B) Triton A-20

Table 1. Kinetic parameters of	corrosion of bras	s in solution of	of 0.5M H ₂ SO ₄ -	+ xppm Triton	X 100 at
temperature of 25°C					

Concentration (ppm)	i _{corr} (mAcm ⁻²)	R_p Ωcm^{-2}	R _{mpy}	P _{mm/year}	K _g g/m²h	E (%)	-E _{corr} (mV)	b _a (mVdec ⁻¹)	-b _c (mVdec ⁻¹)	θ
0	0.045	315	20.65	0.52	0.51		85	49	167	
20	0.031	377	14.22	0.361	0.350	32	104	56	106	0.32
50	0.029	462	13.31	0.33	0.32	36	40	58	113	0.36
100	0.022	516	10.09	0.25	0.24	50	163	90	108	0.50
300	0.021	611	9.63	0.24	0.23	54	53	60	128	0.54
500	0.020	679	9.17	0.23	0.22	56	151	80	105	0.56
800	0.015	907	6.88	0.17	0.16	67	160	85	102	0.67
1000	0.017	917	7.8	0.20	0.19	63	87	60	111	0.63

Table 2. Kinetic parameters of corrosion of brass in solution of 0.5M H₂SO₄ + xppm Triton A-20 at temperature of 25°C

Concentration (ppm)	i _{corr} (mAcm ⁻²)	R_p Ωcm^{-2}	R _{mpy}	P _{mm/year}	K _g g/m²h	E (%)	-E _{corr} (mV)	b _a (mVdec ⁻¹)	-b _c (mVdec ⁻¹)	θ
0	0.045	315	20.65	0.52	0.51	-	85	49	167	-
20	0.021	865	9.63	0.244	0.237	50	79	69	109	0.55
50	0.014	1030	6.42	0.163	0.158	69	88	61	76	0.69
100	0.013	1070	5.96	0.151	0.146	71	74	85	90	0.71
300	0.012	1230	5.50	0.140	0.135	73	76	84	107	0.73
500	0.0083	1651	3.81	0.097	0.093	82	88	62	113	0.82
800	0.008	1660	3.7	0.094	0.091	83	85	68	115	0.83
1000	0.009	1480	4.12	0.11	0.10	80	131	82	98	0.80

It can be noticed to the figure 1 that the anodic current density of brass has been meaningful low after the inhibitor added with relation to that of bare brass. The inhibitor influence of Triton X100

and Triton A-20 is noted on the cathodic reactions, where the cathodic current decreases at a constant potential whereas hydrogen evolution were hindered. The experimental results reveal that the created protective inhibitors layer achieved adsorbed on the brass surface, blocking the available reaction sites.

Corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic and cathodic Tafel slopes established by extrapolation of linear portions of the anodic and cathodic Tafel curves of brass electrode with and without inhibitor are exhibited in tables 1-2. It is obvious from Figure 1 and Tables 1-2 that both the anodic and cathodic current values have been noticeably decreased in inhibited solutions in comparison with the non-inhibited solution. The polarization kinetic parameters denoted that the Triton X 100 and Triton A-20 were a mixed type inhibitors with preponderance in the cathodic direction. The best efficacy is performed to the surfactant concentration of 800ppm and 500ppm for the system: Triton A-20/brass/H₂SO₄ and 800 ppm for the system: Triton X 100/brass/H₂SO₄.



Figure 2. Polarization curves of carbon steel electrode in 0.5M H₂SO₄ with and without different concentration of A) Triton X100 and B) Triton A-20

Figure 2 reveals the polarization curves for OL 37 in $0.5 \text{ M H}_2\text{SO}_4$ in the absence and presence of different concentrations of Triton X100 and Triton A-20. It is evident that the existence of nonionic

surfactants establish a significant reduction on the corrosion rate, it substantial modifications both the cathodic and anodic curves to lesser currents. This case shows that the inhibitors suppress of the anodic and cathodic reactions. This situation can be assigned to adsorption of surfactant on the electrode area. Tafel slopes getting from the polarization techniques are presented in figure 2 and the corresponding kinetic parameters (corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel constants, polarization resistance (R_p) and corrosion rates) are appeared in Tables 3-4. The electrochemical parameters indicated that the Triton X 100 and Triton A-20 have been a mixed type inhibitors with predominance in the anodic direction.

Concentration (ppm)	i _{corr} (mAcm ⁻²)	R_p Ωcm^{-2}	R _{mpy}	P _{mm/vear}	K _g g/m ² h	E (%)	-E _{corr} (mV)	b _a (mVdec ⁻¹)	-b _c (mVdec ⁻¹)	θ
0	1.020	15.16	476	12.081	10.74	-	556	101	83	
20	0.123	79	57.4	1.456	1.29	88	414	48	96	0.88
50	0.062	77	28.93	0.734	0.653	94	441	50	66	0.94
100	0.041	89	23.8	0.604	0.537	96	454	46	72	0.96
300	0.105	86	49	1.243	1.106	90	458	52	106	0.90
500	0.115	67	53.66	1.362	1.211	89	432	47	73	0.89
800	0.140	56	65.33	1.658	1.474	86	429	49	92	0.86
1000	0.147	50	68.60	1.741	1.548	85	452	48	90	0.84

Table 3. Kinetic parameters of corrosion of OL 37 of 0.5M H_2SO_4 + xppm Triton X 100 at temperature of 25°C

Table 4. Kinetic parameters of corrosion of OL 37 of 0.5M H₂SO₄ + xppm Triton A-20 at temperatureof 25°C

Concentration (ppm)	i_{corr} (mAcm ⁻²)	R _p Ocm ⁻²	R _{mpy}	P	$K_g g/m^2h$	E (%)	-E _{corr}	b_a (mVdec ⁻¹)	-b _c (mVdec ⁻¹)	θ
0	1.02	15.16	476	12.081	10.74	-	556	101	83	
20	0.113	58	52.73	1.338	1.19	89	450	40	56	0.89
50	0.095	70	44.33	1.125	1.00	91	462	44	65	0.91
100	0.050	84	21.46	0.544	0.484	95	460	46	69	0.95
300	0.109	80	50.86	1.291	1.148	89	442	42	57	0.89
500	0.140	67	65.33	1.658	1.474	86	447	59	104	0.86
800	0.145	71	67.66	1.717	1.527	85	441	49	75	0.85
1000	0.159	65	74.20	1.883	1.674	84	452	51	82	0.84

The inspection of figure 2 and Tables 3-4 indicated that the corrosion rate have been meaningfully reduced in inhibited solutions when in comparison with the corrosive medium and to increase of the protection effect. By examination in comparison the inhibition effectiveness and the corrosion rate (Rmpy, in mil per year; P, in mm per year and Kg, in $gm^{-2}h^{-1}$) for all inhibitors, in the same situation, one can see like, Triton X100 and Triton A-20 have an very good efficiency for anticorrosion performance of carbon steel in 0.5M H₂SO₄. The presence of nonionic surfactants establish a considerable decrease in corrosion current density, modification the anodic curves to more

positive potentials and the cathodic curves to more negative potentials. This case can be assigned to adsorption of surfactant on the electrode area. The adsorption of the nonionic surfactant molecules on the OL 37 surface diminutions the interaction of the electrode surface and the corrosive ions ($SO_4^{2^-}$) which great reduces the corrosion process and increases their protective effect. Surfactants congregate in particular way at the interface metal/electrolyte and modify the interfaces and so, verify, reduction or prevent reactions from a film and its electrolyte, when introduced in the medium. Moreover, the inhibition property increases with the hydrophobic chain length molecule and the highest inhibition effectiveness has been achieved at the concentration higher than the critical micelle concentration (CMC). The corrosion protection is established by the presence of the hydrocarbonate chains of the surfactants which competitively adsorb over the metal electrode surface stopping the active sites and hence the $SO_4^{2^-}$ anion is hindered from touching the metal surface and corrosion protection is realized [18-29].

Also, it can be noticed to figures 1-4 and tables 1-4 that the highest inhibition efficiency has been accomplished for Triton X $100/OL37/H_2SO_4$ at the 100ppm and 300ppm concentration and for Triton A-20/brass/H₂SO₄ at the 800ppm and 500ppm concentration.

By analyzing in comparison the protection effect for all inhibitors, in the all situation, one can notice as, the Triton X 100 on OL37 and Triton A-20 on brass have an excellent efficiency for the protective properties in $0.5M H_2SO_4$ while Triton A-20/OL37 and Triton X100/brass in same condition have a good inhibition effectiveness. The experimental tests establish that these nonionic surfactants may be considered as mixed type corrosion inhibitors and it could be proved by the influences of surfactants on the electrochemical properties of metal electrodes.

3.2. Electrochemical Impedance Spectroscopy (EIS)

The corrosion inhibition properties of nonionic surfactants on two working electrodes in H_2SO_4 solution have been as well considered by electrochemical impedance spectroscopy (EIS). Impedance tests were realized at open circuit potential on the frequency domain from 100 kHz to 40 mHz with an AC wave of \pm 10 mV (peak-to-peak) and the impedance influences have been achieved at a rate of 10 points per decade change in frequency [22-31]. EIS tests reveal about to research of the protection properties of a nonionic surfactants as a corrosion inhibitor of metal electrodes in aggressive medium. Nyquist plots for brass achieved at the interface with and without of varioust concentrations of Triton X 100 and Triton A-20 are presented in figure 3.



Figure 3. Nyquist plots for brass in 0.5M H₂SO₄ solutions in the absence and presence of different concentrations of Triton X 100 and Triton A-20 at temperature of 25°C

Figure 3 indicates Nyquist plots for brass in 0.5M H₂SO₄ solutions in the absence and presence of different concentrations of Triton X 100 and Triton A-20 at temperature of 25°C. It can be observed from figure 3 the Nyquist impedance spectroscopy for brass with and without surfactants indicates one capacitive loop that is typical for a charge transfer reaction. Figure 3 too displays that the diameters of the capacitance loops in the existence of the nonionic surfactants are greater than those in the absence of surfactants, proposing that these inhibitors has very good anticorrosion properties on brass electrode in 0.5 M H₂SO₄. In all situations, it is establish that the diameter of the semicircle increases with increasing concentration of these inhibitors, assuring that the obtained protection film was realized by the existence of these surfactants [19-24, 28-36]. Figure 3 presents that the diameters of the capacitance loops with 800ppm and 1000ppm Triton X100-brass-H₂SO₄, and for 500ppm and 1000ppm Triton A-20-bass-H₂SO₄ are greater than those in the absence of inhibitors, proposing that provide a excellent anticorrosion protection over the brass in acid medium.



Figure 4. Nyquist plots for carbon steel in 0.5M H₂SO₄ solutions in the absence and presence of different concentrations of Triton X 100 and Triton A-20 at temperature of 25°C

Figure 4 appears the Nyquist impedance plots registered for various concentrations of Triton X 100 and Triton A-20 surfactants of the OL 37 electrode in sulfuric acid environment. The impedance spectra of OL 37 electrode display one capacitive loop and the dimension of the semicircles improves with increasing the inhibitor concentration. It is evident from the Nyquist plots that the impedance reaction of OL 37 has been meaningfully modified by the plus of the nonionic surfactants which proposing that the achieved inhibitive layer was strengthened by the plus of surfactants. In this study, for all the cases investigated, the electrochemical impedance spectra are presented by one semicircle, with a high frequency capacity loop and low frequency inductive loop. The semicircular occurrence reveals that the OL 37 is verified by charge transfer reaction and the existence of inhibitor does not change the mechanism of dissolution. Moreover, these capacitive loops are not precise semicircles and

this event is ascribed to frequency dispersion, largely assigned to rugosity and inhomogeneities of the electrode area [20-35]. Figure 4 shows that the diameters of the capacitance loops with 1000 ppm and 500ppm Triton X100/OL $37/H_2SO_4$, and for 1000ppm and 300ppm Triton A-20/OL $37/H_2SO_4$ are higher than these in the absence of surfactants, proposing that assure a high inhibition effect for OL 37electrode in corrosive medium.



Figure 5. The Bode diagrams of OL 37 in 0.5M H₂SO₄ at various concentrations of Triton X100 and Triton A-20



Figure 6. The Bode diagrams of brass in 0.5M H₂SO₄ at various concentrations of Triton X100 and Triton A-20

In figures 5-6 are presented Bode plots are in accord with Nyquist plots figures 3-4. It can be noticed that in absence of surfactant the metal electrode exhibits one time constant appropriate to a phase angle of about -25° for OL 37 and -40° for brass at average and low frequencies, this event indicates an inductive comportment with low diffusive disposition. As well, in the presence of the nonionic surfactants, on the graphs- phase angle against log frequency indicates a maximum appropriate to a phase angle of about -70° for Triton X100/ OL37, -65° for Triton A-20/ OL37, -70° for Triton X100/ Triton A-20/brass (see figures 5-6) which establish that in this event the electrode has a pronounced capacitive behaviour, in conformable with the Nyquist diagrams and in agreement with the results achieved by electrochemical polarization.

Concentration	Rs	R _{ct}	C _{dl}	E0/
(ppm)	(ohm.cm ²)	(ohm.cm ²)	$(\mu F \text{ cm}^{-2})$	E%
0	1.18	172	126	
50	1.215	302	860	43
100	2.05	468	780	63
300	1.923	470	660	64
500	1.855	475	522	64
800	1.713	586	486	71
1000	1.516	690	323	75

Table 5. Electrochemical parameters of brass in solution of 0.5M $H_2SO_4 + xppm$ Triton X 100 at temperature of 25°C

Table 6. Electrochemical parameters of brass in solution of 0.5M $H_2SO_4 + xppm$ Triton A-20 at temperature of 25°C

Concentration	R _S	R _{ct}	C _{dl}	E0/
(ppm)	(ohm.cm ²)	(ohm.cm ²)	$(\mu F \text{ cm}^{-2})$	E%
0	1.18	172	126	
50	1.75	512	982	64
100	2.668	595	932	71
300	3.593	930	868	82
500	3.97	1029	285	83
800	3.74	957	472	82
1000	6.34	1158	270	85

Table 7. Electrochemical parameters of OL 37 in solution of 0.5M H₂SO₄ + xppm Triton X 100 at temperature of 25°C

Concentration	Rs	R _{ct}	C _{dl}	E0/	
(ppm)	(ohm.cm ²)	(ohm.cm ²)	$(\mu F \text{ cm}^{-2})$	E%	
0	1.056	20.34	460		
50	1.22	44	758	54	
100	1.58	57	538	64	
300	0.92	59	498	66	
500	2.28	62	347	67	

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800	1.15	103	226	80
1000	1.52	147	126	86

Table 8. Electrochemical parameters of OL37 in solution of 0.5M H₂SO₄ + xppm Triton A-20 at temperature of 25°C

Concentration	Rs	R _{ct}	C _{dl}	E0/
(ppm)	(ohm.cm ²)	(ohm.cm ²)	$(\mu F \text{ cm}^{-2})$	E%
0	1.056	20.34	460	
50	1.57	39.47	450	49
100	2.43	45.52	409	55
300	2.42	53.60	374	62
500	1.74	89.17	308	77
800	2.53	99.05	254	80
1000	2.74	137	181	85

Investigation of the experimental results (see table 5-8) was made by fitting the data to the adequate equivalent circuit determined in figure 7 and this equivalent circuit contains the solution resistance (Rs), the charge transfer resistance (R_{ct}) which is located parallel at the capacitance of double layer (Cdl). The data revealed that the increase in charge transfer resistance values can be assigned because to the substitution of water molecules by the adsorption of the surfactant molecules on the electrode area and the obtained of a protective film on the metal surface [23-26, 28-39]. The decrease of the capacitance of double layer (Cdl) can ensue by the decrease of the local dielectric constant and by the increase of thickness of the electrical double layer confirming the obtaining of adsorbed surfactant film [35-45]. This case looks again that these inhibitors assure optimal corrosion protection. The Nyquist and Bode diagrams indicate that the mechanism of corrosion hindering by used these nonionic surfactants is by accomplished as a diffusion blockade and by a charge transfer reaction.



Figure 7. Equivalent circuit

3.3. Effect of temperature

The consequence of temperature on the protection properties of these surfactants at a concentration of 100ppm for OL 37 and 800ppm for brass in 0.5M H₂SO₄ at 298, 303, 313, 323 and 333 0 K was examined by potentiodynamic polarization technique. It can be observed that, the corrosion rate increased with increasing temperature in inhibited and non-inhibited medium. The protection result of these nonionic surfactants decrease with increasing temperature, while the corrosion inhibition of OL 37 and brass in H₂SO₄ environment with of these organic inhibitors is achieved by the adsorption of inhibitor, but, at higher temperature establish the desorption of these organic compounds molecules from the metal area. The dependence of corrosion rate on temperature can be presented by the Arrhenius equation and transition equation: [23, 27-30, 40-51]

$$\begin{split} i_{corr} &= A \exp\!\left(\frac{-E_a}{RT}\right);\\ i_{corr} &= \frac{RT}{Nh} \exp\!\left(\frac{\Delta S_a^*}{R}\right) \!\exp\!\left(\frac{\Delta H_a^*}{RT}\right) \end{split}$$

where i_{corr} is the reaction rate, A is a pre-exponential factor, E_a the apparent activation energy of OL 37 and of brass dissolution process, R the universal gas constant and T the absolute temperature, ΔH_a^* the apparent enthalpy of activation, ΔS_a^* the apparent entropy of activation, h Planck' constant, N the Avogadro number.

Figure 8 exhibited the Arrhenius plot, corrosion rate versus of 1/T for OL 37-Figure 8a and for brass-Figure 8b in 0.5M H₂SO₄ in presence and absence of the nonionic surfactants. The data of E_a with and without of the nonionic surfactants were getting by plotting corrosion rate versus of 1/T wherein straight lines have been achieved in Figure 8, from the slope of these lines are calculated activation energy (see table 9-10). Figure 9 display a graph of logarithm corrosion rate/T against of 1/T. Straight lines are accomplished with a slope of (- Δ H*/R) and an intercept of (ln(R/Nh)+(Δ S*/R), from which the values Δ H* and Δ S* were considered (see tables 9-10).

Table 9. The values of Ea, ΔH^0 and ΔS^0 for two nonionic surfactants on OL 37 in 0.5M H₂SO₄

Inhibitor	E _a (KJ/mol K	ΔH ⁰ (KJ/mol K)	ΔS^0 (J/mol K)
TRITON X100	65	63	-62
TRITON A20	52	49	-97
H ₂ SO ₄	40	37	-129

Table 10. The values of Ea, ΔH^0 and ΔS^0 for some nonionic surfactants on Brass in 0.5M H₂SO₄

Inhibitor	E _a (KJ/mol K	$\Delta H^0 (KJ/mol K)$	ΔS^0 (J/mol K)
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TRITON X100	21	19	-224
TRITON A20	23	20	-219
H_2SO_4	22	20	-204

It can be observed from table 5 and figure 8 for OL 37 that the values of E_a increased in the existence of inhibitors than in the absence of surfactants, so the value of E_a could explain the influence of temperature on corrosion protection. This comportment is denoted that the adsorption of the Triton X 100 and Triton A-20 on the metal area in 0.5 M H₂SO₄ is physical adsorption reveals in the first stage. From adsorption experimental results it can be established we have a mixed type of adsorption: physorption and chemisorption of the inhibitors onto the metal surface. The evident increase in the activation energy with the inhibitor suggests the bigger protection action of these nonionic surfactants, which implied the making of an energy barrier to the corrosion process and the surfactant molecules adsorption on the metal surface which decreases the interaction from the corrosive medium and the metal area. The higher Ea value in the inhibited medium is considered with the increases thickness of the double layer which enhances the activation energy of the corrosion process. Moreover, evidences effectiveness decreases with rise in temperature may be assigned to the increased desorption of surfactant molecules from electrode surface. The positive value of ΔH^0 with and without of surfactant represents the endothermic type of the dissolution reaction for the OL 37 in corrosive medium and that the dissolution of this electrode is complex [23, 27-30, 39-52]. The great and negative date of ΔS^0 for the inhibited and uninhibited solution and this suggest that the activated complex in the ratedetermining stage constitutes association first than dissociation, mentioning that a decrease in disorder occurs, going from reactant to the activated complex by the obtaining of steady adsorption film of the surfactant molecules on the metal surface [30-36].



Figure 8. Arrhenius plot for OL 37 in 0.5M H₂SO₄ in presence and absence of Triton X100 and Triton A-20 at different temperature



Figure 9. Arrhenius plot for brass in 0.5M H₂SO₄ with and without of Triton X100 and Triton A-20 at different temperature

Investigation the table 10 and figure 9, for brass that the value of E_a for the corrosion with and without of 800 ppm of surfactant is almost the same. The approximate value of E_a of the corrosion process in the existence of the surfactant compared without of surfactant can be assigned to their physical adsorption on the brass area. The positive signal of enthalpies implies that the dissolution of brass electrode is an endothermic phenomenon. The large and negative date of ΔS^0 for the inhibited and uninhibited solution may be the effect of the adsorption of the Triton X100 and Triton A-20 molecules onto brass in the 0.5M H₂SO₄ medium –quasi-substitution. As well, the negative values of ΔS^0 suggest association process in the constitution of activated intermediate complex [23, 30-39, 46-55].

3.4. Adsorption isotherms

Adsorption isotherm is important in established the mechanism of organo-electrochemical reactions [8,23-25,32-38]. Likewise, the greater inhibitor efficacy is a result of the adsorption process. The adsorption isotherm provides important acquaintance at the interaction of inhibitor and metal surface. To evaluate the result of organic inhibitor concentration on the corrosion rate, it is utilized to fit the rate data to equilibrium adsorption expressions, like Langmuir isotherm model.



Figure 10. Langmuir plot for Triton X100and Triton A-20 on OL 37 and brass in 0.5M H₂SO₄

The adsorption isotherm relation of Langmuir is depicted employment the subsequent equation: $\theta/(1-\theta) = KC$, where θ is the degree of the coverage on the working electrode area by the inhibitor and K is the adsorption equilibrium constant, θ is obtained by: $\theta = (i_{corr}-i_{.inh})/i_{corr}$ where i_{inh} and i_{corr} are the corrosion current density in 0.5M H₂SO₄ with and without of the inhibitor. Every correlation factor (R²) exceeded 0.99 (Triton X100/OL 37 R²=0.9979; Triton A-20/OL 37 R²=0.9945; Triton X100/brass R²=0.9916 and Triton A-20/brass R²=0.9932) exhibits that the protection was ascribed to adsorption of these inhibitors onto the metal surface. It can be said that, the corrosion protection effect of nonionic-surfactants is associated with their adsorption performance and fact is demonstrated by utilization of the Langmuir isotherm. The reaction in the first stage of the corrosion process of the electrode surface in 0.5M H₂SO₄ in existence of inhibitors is: Me + INH \leftrightarrow Me(INH)_{ads} \leftrightarrow Meⁿ⁺ +ne⁻+INH. When, it existence a great inhibitor concentration, a dense and strong layer is achieved onto metal surface that decreases aggression over the metal.

Plotting C/ θ against C give a straight line with a slope closed to unity and this shows that the adsorption of these surfactants can be accomplishes to a Langmuir adsorption isotherm see figure 10. The pronounced correlation of the Langmuir adsorption isotherm can verify the availability of this mod. The equilibrium constant (K_{ads}) for the adsorption process of these surfactants can be estimated from reciprocal of the intercept and their data are indicated in Table 11. It is obvious that the grant

values denote an intensive adsorption of the inhibitors on the electrode surface in $0.5MH_2SO_4$. The great value of the adsorption equilibrium constant considers the high adsorption capacity of this organic inhibitor on brass and on OL 37 surface. The adsorption of a surfactant particularly changed the corrosion resisting estate of a metal.

The system	K _{ads} , M ⁻¹	$\Delta G^{\circ}_{ads}\mathrm{KJmol}^{-1}$	The adsorption
TritonX100/OL37/0.5M H ₂ SO ₄	2 x10 ⁵	-40	Chemisorptions and physical adsorption
TritonA-20/OL37/0.5M H ₂ SO ₄	1 x10 ⁴	-33	Physical adsorption and chemisorptions
TritonX100/Brass/0.5M H ₂ SO ₄	4 x10 ³	-31	Physical adsorption and chemisorptions
TritonA-20/Brass/0.5M H ₂ SO ₄	8x10 ³	-32	Physical adsorption and chemisorptions

Table 11. The values of K_{ads} and ΔG_{ads}° of the nonionic surfactants on OL 37 and brass in 0.5M H₂SO₄

The equilibrium constant of the adsorption process (K_{ads}) is presented by the standard adsorption free energy (ΔG_{ads}°) achieved by the equation: $\ln K_{ads} = -(\Delta G_{ads}^{o} / RT)$

The determined value of ΔG_{ads}° achieved is negative and depicts that the adsorption of nonionic surfactants is a spontaneous process, and further the negative values of ΔG_{ads}° as well reveal the powerful interaction of the inhibitor molecule with the electrode surface.

The getting values about -20Kjmol⁻¹ or lower appears the electrostatic interaction between the charged molecules (the nonionic surfactants) and the charged electrode surface (physical adsorption)-see Table 11, when those more negative than -40KJmol⁻¹, implicate charge sharing or charge transfer from the surfactant molecules at the electrode area for constitute a co-coordinative type of bond (chemisorptions)-see Table 11[23-35, 42-48, 52-54].

The mechanism of protection can be described from the experimental data, it was deduced that all the surfactants (Triton X100 and Triton A-20) hinder the corrosion of OL 37 and brass in 0.5M H₂SO₄ by adsorption of surfactants to electrode/solution interface. Adsorption of these surfactants may be realized by physical adsorption and chemisorption process. This case is affected of the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte [8, 19-24, 32-37, 43-51]. The inhibition efficacy of these surfactants for the corrosion metal surface in 0.5M H₂SO₄ may be considered on the number of adsorption sites, molecular size and the manner of interaction with the electrode area, the interaction of heterocyclic compounds and existence of lone pairs of the oxygen atoms in the polyethylene oxide chains and electrons of heterocyclic atoms and the free d-orbital of Fe surface atom and possession of vacant, reduced energy electron orbital (Cu⁺ and Cu²⁺) are especially significant elements establish the adsorption of surfactant molecules onto electrode surface [17-23, 26-45]. Physical adsorption necessities the presence of both electrically charged surface of the metal and charged species in the bulk of the environment and the chemisorptions process suppose charge sharing or charge transfer from the inhibitor molecules to the metal surface to get a coordinate bond [17-24, 29-42, 51-55].

3.5. Surface analysis by FTIR spectroscopy

In present paper, FT-IR spectrometry has been employed to identify the existence of the important absorption bands remarked for Triton X100 and Triton A-20 adsorbed on electrode surface by immersion in the aggressive medium. All spectra in these measurements have been getting at a resolution 4cm⁻¹ in the range 4000-650 cm⁻¹ [8, 17-23, 36-39,40-47,51-53]. In order to estimate the protective film established on the electrode surface in presence of inhibitors, as well to give new bonding information on the electrode surface has been investigated by FT-IR spectra.

The important peaks in the transmittance spectrum for Triton X100 and Triton A-20 have been presented in figures 11 a-b are the consequence: in the spectrum of Triton X100, the bond is attributed to the stretching vibration of the OH can be observed at 3354cm⁻¹. The peak at approximately 2949 and 2866 cm⁻¹ is ascribed to symmetrical and asymmetrical stretching vibration of C-H. The spectrum in the 1500- 1700 cm⁻¹ region exhibit benzene ring vibration bands. The peak appearing at 1456cm⁻¹ is related to the CH₂ group. The peak observed at 1349 cm⁻¹ is assigned to stretching vibration of CH₃. The sharp band at 1245 cm⁻¹ and 1102 cm⁻¹ represents the C-O and C-C stretching vibration. The band at 1100-800 cm⁻¹ is attributed to C-O-C vibration in (CH₂CH₂O).





Figure 11. FT-IR spectra of (a) Triton X100, (b)Triton A-20, c) Brass+800 ppm Triton X 100, d) Brass+1000 ppm Triton A-20, e) OL 37+100 ppm Triton X 100 and f) OL37+50 ppm Triton A-20

At the spectrum from figure 11b, it can be seen the main feature of absorption bands of Triton A20, at 3365cm⁻¹ shows the presence of the OH group, at almost 2959 and 2902 cm⁻¹ are ascribed to the to the aliphatic -CH symmetric and asymmetric stretching vibration.

The band presented at 1786 and 1631 cm⁻¹ is appropriated to the C=O stretching mode and another small peak assigned to 1296 cm⁻¹ depicts C-O stretching vibration. The peaks determined to in plane and out of plane of the CH chains at 1248, 1101 and 1087 cm⁻¹ are noted in the surfactant.

It can be see all considerable peaks of surfactant-Triton X100 shown up in adsorption film on the brass surface (figure 11c). The band at 3369cm⁻¹ is attributed to O-H stretching; a band at approximately 2879 and 2821 represents C-H stretching vibration. The peak about 1680 cm⁻¹ and 1288 cm⁻¹ correspond to C=O and the C-O stretching vibration. The asymmetrical bending vibration of CH₃ was established at 1339 cm⁻¹ and at 1433cm⁻¹ related to CH₂. The band at 1109, 985, 808 cm⁻¹ are assigned to C-O-C vibration in (CH₂CH₂O). A band at almost 1170, 1090, 985 and 775cm⁻¹ are assigned to the in plane and out plane C-H of the aromatic rings. The FT-IR spectrum of 1000 ppm Triton A-20/Brass is shown in figure 11d. The main feature bands to the aromatic ring in Triton A-20 is obvious at 1773 and 1663 cm⁻¹ for C=O stretching and peak at 1278cm⁻¹ for C-O bond, being clearly demonstrated, the peak at 3397cm⁻¹ assumed to the stretching vibration of the OH and the peak at 2982-2879 cm⁻¹ corresponds to the aliphatic -CH stretching vibration . The presence bands at 1216, 1115, 1068, 1003 and 908 cm⁻¹ are assigned to in plane and out of plane of the CH chains. Comparing figures 11a, 11b, 11c and 11d, it can be considered that Triton X100 and Triton A-20 are adsorbed on the brass surface.

The FT-IR spectrum of protective film achieved on the OL 37 electrode by immersion in corrosive medium with optimum concentration of inhibitor 100ppm Triton X100 and 50ppm Triton A-20 is presented in Figure 11e and 11f. It can be noted all meaning peaks of inhibitor-Triton X100 shown up in protective film on the metal surface (see-figure 11e). The band at 3364 cm⁻¹ is assigned to O-H stretching. The existence bands placed at 2970 and 2878 cm⁻¹ is displayed in stretching vibration of the aliphatic C-H. The peak at almost 1678 and 1287 cm⁻¹ is due the existence of C=O and the C-O stretching vibration. The spectrum at the 1513, 1678 and 1713 cm⁻¹ indicate benzene ring vibration bands. The peaks at 1463 and 1340 cm⁻¹ is associated to the stretching vibration of the CH₂ and CH₃

groups in the nonionic surfactant. The peaks at 1112, 1059, 971 and 861 cm⁻¹ are assigned to C-O-C vibration in $(CH_2CH_2O)_n$. The bands 3837 cm⁻¹ and 3729 cm⁻¹ are attributed to Fe-O bending [8, 17-21, 36-39].

From figure 11f, it can be said the principal characteristics of 50ppm Triton A-20/OL37, a broad peak at 3436cm⁻¹ shows the presence of the OH stretching. The band at 2982-2872 cm⁻¹ is assumed to the aliphatic CH₂ symmetric and asymmetric stretching vibration. The existence of C=O and C-O is denoted by their stretching ways at 1714, 1681 cm⁻¹ and 1215cm⁻¹. The band appearing at 1081, 1163, 608 and 619 cm⁻¹ is associated to in plane and out of plane of the CH chains are noticed in the surfactant. Also, this FT-IR spectrum showed up at 3867cm⁻¹ the direct bonding from Fe atoms and Triton A-20 molecules via O atoms and the getting Fe-inhibitor complex and this determines that there is just chemical adsorption achieved on the surface of OL 37 [8, 17-24, 37-49, 51-55]. Comparing figures 11a, 11b, 11e and 11f, it can be proposed that Triton X100 and Triton A-20 are formed on the OL 37 area.

3.6. Surface analysis by metallographic spectroscopy

The achievement of the protective surface film of Triton X 100 and Triton A-20 as corrosion inhibitors on the brass and OL 37 surface was established by metallurgical exploration microscope inspection on the working metal surface.



d)1000ppmTriton X-100 e)300ppm Triton A-20

c) Brass+0.5M H₂SO₄



f) OL37+0.5M H₂SO₄

g) 100ppm and 50ppm Triton X-100/OL37



h) 100ppmTriton-A20/OL37

Figure 12. Micrographies of brass and OL 37 in 0.5M H₂SO₄ in presence and absence of some nonionic surfactants as corrosion inhibitor

Figure 12 indicates some micrographies which were examined for our systems: surfactant/0.5M $H_2SO_4/OL37$ and surfactant/0.5M $H_2SO_4/brass$ before and by a some period immersion in aggressive medium.

It can be noticed from figure 12 c and f that the working electrode area has been significant affected in absence of the surfactants. Looking at Figure 12 it can be seen that the all micrographs examined with of these surfactants showed the area becomes more smooth, uniform and compact than the non-inhibited surface. Also, figure 12 reveals a considerable inhibiting capacity to corrosion on metal surface; it is observed that there is a very good prevention layer formed over metal surface which is able for the protection at corrosion. It can be said that these films act as a barrier from aggressive environment and electrode surface and as an effect the corrosion process is hindered. Some research and surface examination such as FT-IR and metallographic spectroscopy have been made in order to confirm the formation of protective film onto the working electrode area and showed the adsorption process for all surfactants over metal surface in $0.5M H_2SO_4$ environment.

4. CONCLUSIONS

Triton X100 and Triton A-20 inhibitors exhibited very good inhibition properties for OL 37 and brass electrode in $0.5M H_2SO_4$ medium while the corrosion current density decreased and the inhibitor efficiency increased with increasing inhibitors concentrations.

Electrochemical measurements reveal that the nonionic surfactants act as mixed-type inhibitor.

The results of EIS reveal that the charge transfer resistance increases with inhibitor concentration, which denotes the obtaining of a protective film on the electrode surface by the adsorption of surfactant molecules which establish increase in the inhibition effect.

The adsorption of the nonionic surfactants investigated over the metal electrode is in according the Langmuir adsorption isotherm model.

The adsorption process is an endothermic phenomenon followed by increase in entropy.

The data of FTIR also showed the adsorption of surfactant molecules onto the metal surface and blocking the active sites.

Investigation and surface examination by FTIR and metallographic spectroscopy prove the obtaining of a protective layer on the metal area and indicate the adsorption mechanism of all nonionic surfactants over electrode surface in 0.5M H₂SO₄ environment.

So Triton X100 has better inhibition properties than Triton A-20 on the OL 37and Triton A-20 has higher protection effect than Triton X100 onto brass surface.

The inhibition effectiveness follows the order: Triton X100/OL37> Triton A-20/brass > Triton A-20/OL37 > Triton X100/brass as a result the existence of these surfactants induces a meaning decrease in corrosion rate.

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