

## CORROSION INHIBITION OF CARBON STEEL BY SOME ANIONIC SURFACTANTS IN 0.5M H<sub>2</sub>SO<sub>4</sub>

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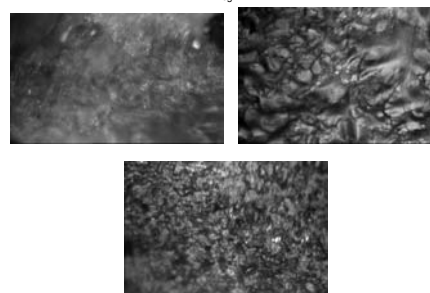
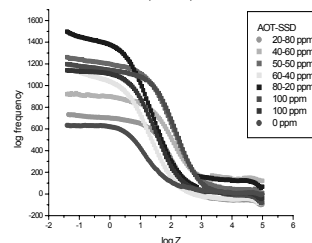
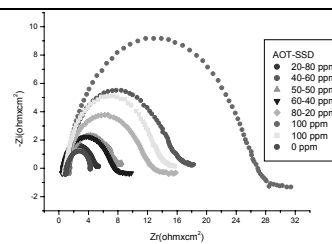
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The inhibitory effect of some anionic surfactants as 1 Dodecane sulfonate sodium (SSD) and Dioctyl sulfosuccinate sodium (AOT) at various combinations of these organic compounds (AOT/1-Dodecane sulphonate sodium: 20/80 ppm, 40/60 ppm, 50/50 ppm, 60/40 ppm, 80/20 ppm and 100 ppm) on the corrosion behavior of carbon steel in 0.5M H<sub>2</sub>SO<sub>4</sub> medium at temperature of 25°C was studied by potentiostatic and potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FT-IR) and metallurgical microscopy techniques. The effect of inhibitor concentration on the corrosion rate, surface coverage and inhibition efficiency was investigated. Results show that these organic inhibitors exert a great inhibiting effect on carbon steel corrosion and act as a mix-type inhibitor. The inhibition efficiency of organic inhibitors may be due to either the adsorption of inhibitor molecules building a protective film or the formation of an insoluble complex of the inhibitor adsorption obeys the Langmuir model. The negative value of thermodynamic parameter like Gibbs free energy of adsorption  $\Delta G_{ads}^{\circ}$  indicates the spontaneity of adsorption process. Moreover, characterization using FT-IR demonstrates the adsorption of inhibitors and the formation of corrosion products on the carbon steel surface. EIS and potentiodynamic results confirm its corrosion inhibition ability.



### INTRODUCTION

Carbon steel is one of the important materials used in different industries. It has excellent mechanical properties and cost effectiveness. Corrosion of carbon steel in various aggressive

media is of practical importance. The study of carbon steel corrosion phenomena has become significant especially in acidic media because of the increased industrial applications of acid solutions. Acid solutions are generally used in many industrial processes. H<sub>2</sub>SO<sub>4</sub> and other acid

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solutions (HCl, H<sub>3</sub>PO<sub>4</sub> and so on) are aggressive solutions used in numerous industrial synthesis processes. The main problem in using carbon steel in aggressive environments is that of uniform corrosion. Treatment of the corrosive medium for the protection of metals and alloys can be realized through elimination of the corrosive species or through use of inhibitors. An eventual solution to protect carbon steel in aggressive environments is the application of corrosion inhibitors or coatings. Adding an inhibitor to the electrolyte is known as one method of inhibiting corrosion. Many studies on the addition of inhibitors have been done in the field of carbon steel corrosion inhibition in different environments.<sup>1-9</sup> Organic heterocyclic compounds have been used for the corrosion inhibition of iron copper, aluminum, and other metals in various aggressive media.<sup>3-13</sup> In general, organic compounds containing polar groups including nitrogen, sulfur and oxygen and heterocyclic compounds with polar functional groups and/or conjugated double bond. Some researches have reported the inhibiting effects of alkyl amines, phenyl-alkyl amines, imines derivatives and polymer inhibitors.<sup>5-15</sup> Several studies suggested that most organic surfactant inhibitors are adsorbed on the metal surface by displacing water molecules from the surface and forming a compact barrier film.<sup>9-17</sup> The ability of a surfactant molecule to adsorb is generally directly related to its ability to aggregate and to form micelles. Among all the inhibitors the most important are the organic ones, also called adsorption inhibitors. They check the corrosion action on the cathodic or anodic response or both of them. When they present sufficient concentration, they usually affect the whole metal surface and therefore they cannot be called anodic or cathodic inhibitors. Therefore, the interaction of organic compounds and metal surface can be proved by adsorption isotherm and in general, inhibitors can function either by physical adsorption or chemisorption with the metal.<sup>5-13</sup>

In our study, the corrosion inhibition of carbon steel in 0.5M H<sub>2</sub>SO<sub>4</sub> medium at different concentrations of these surfactants and of several combinations inhibitors has been studied by electrochemical technique, electrochemical impedance spectroscopy measurements, FT-IR and metallographic analysis. Electrochemical measurements are used to evaluate the anticorrosive properties of these organic inhibitors.

## EXPERIMENTAL

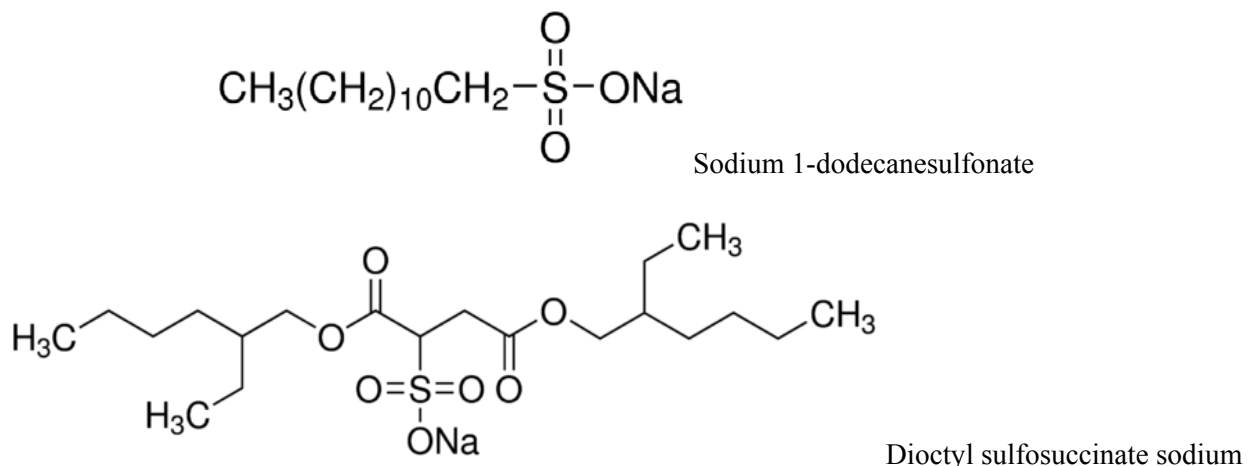
Experiments were performed on carbon steel type OL 37 electrode with composition: C% 0.15; Si% 0.09; Mn% 0.4; P% 0.023; S% 0.02; Al% 0.022; Ni% 0.001; Cr% 0.001; Fe% 99.293; and the corrosive medium used was 0.5M H<sub>2</sub>SO<sub>4</sub>.

The investigated inhibitors have been of some anionic surfactants of 1 Dodecane sulfonate sodium (SSD) and Dioctyl sulfosuccinate sodium (AOT) at different concentration and at various combinations of these organic inhibitors. Experiments were carried out in the absence and presence of different concentrations of anionic surfactants and at their combinations AOT/1-Dodecane sulfonate sodium at 20/80, 40/60, 50/50, 40/60, 80/20, 100 ppm concentrations at 25°C. Electrochemical techniques achieved a conventional three electrode cell with a platinum auxiliary electrode and a saturated calomel electrode as the reference electrode. The working electrode for electrochemistry measurements was made of carbon steel type OL37; it was prepared from a cylindrical carbon steel rod with of area an 0.5 cm<sup>2</sup>. This shape is preferred, because it assures a greater surface and a reduced number of edges. The working electrode was mechanically polished on wet silicon carbide (SiC) papers (1200, 2500, 4000 grid) rinsed with bidistilled water, degreased with acetone and ethanol and dried at room temperature.

The polarization behavior of carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in presence and absence of organic inhibitors has been studied by potentiostatic and potentiodynamic methods. The inhibitory action was studied through tracing the polarization curves obtained using the, potentiodynamic method calculation of the kinetic parameters of corrosion in case of solutions with inhibitors, especially the corrosion current densities, and their comparison with the kinetic parameters of the solution without inhibitors. Potentiostatic, potentiodynamic and EIS measurements were carried out by using the electrochemical cell connected to an automated model VoltaLab 40 potentiostat/galvanostat. All the potential values given in this study were measurements with respect to this electrode at a temperature of 25°C. Fourier transform infrared spectroscopy (FT-IR) was used to identify whether there was adsorption of organic inhibitor on the surface of the metal was performed with Bruker Optics. A metallographic/metallurgical microscopy technique was obtained with Hund H600 microscope.

## RESULTS AND DISCUSSION

The electrochemical behaviour of the carbon steel OL37 in absence and presence of the organic inhibitors was investigated by electrochemical polarization methods. In this study, the inhibition of the corrosion is the result of the adsorption of the organic compound on the metal surface forming an invisible layer of a few molecular diameter thickness. The effect of different concentrations and various combinations of anionic surfactants (see in Scheme 1) was investigated as corrosion inhibitors for carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



Scheme 1 – Chemical structures of organic inhibitors studied.

Figs. 1-3 show the polarization curves for carbon steel OL 37 in 0.5 M  $\text{H}_2\text{SO}_4$  in absence and presence of different concentrations and various combination of 1-Dodecane sulfonate sodium (SSD) and Diocetyl sulfosuccinate sodium (AOT). It can be seen from figures 1-3 the addition of organic inhibitors reduces the anodic and cathodic

polarization curves. This case indicated that the inhibition repress anodic dissolution of metal and cathodic reaction of hydrogen evolution with increase of the inhibitor concentrations. This fact suggests that the inhibitor molecules have been adsorbed on active sites of the OL 37 surface.

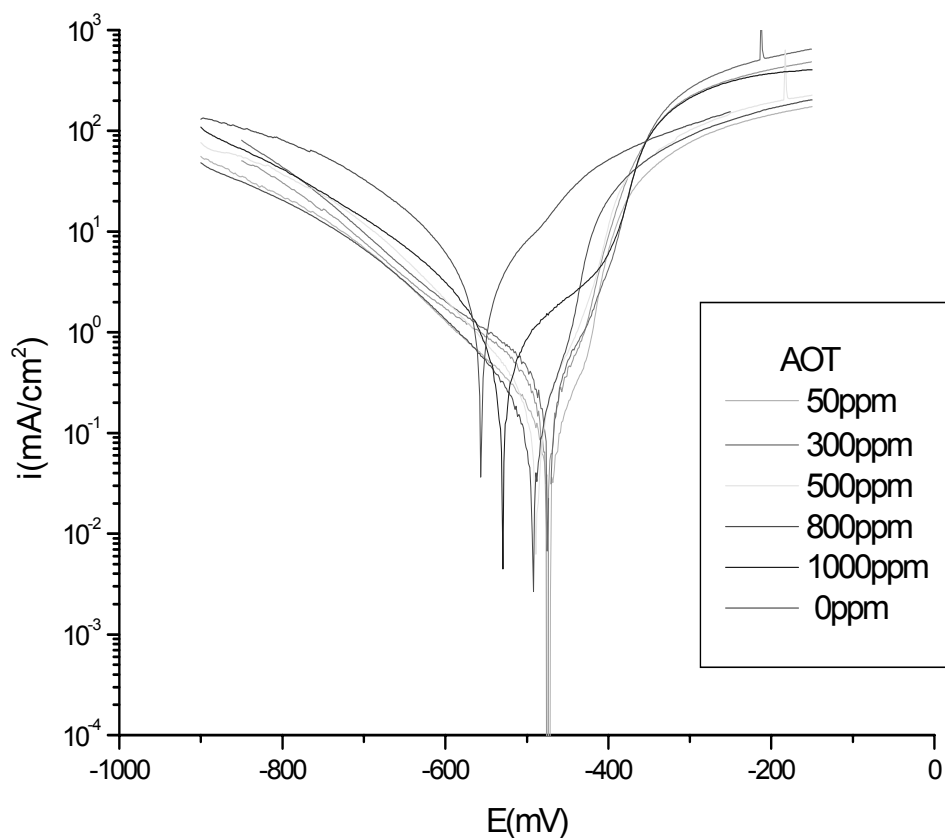


Fig. 1 – Potentiodynamic polarization curves of OL 37 in 0.5 M  $\text{H}_2\text{SO}_4$  in the presence and absence of inhibitors AOT at temperature of 25 °C.

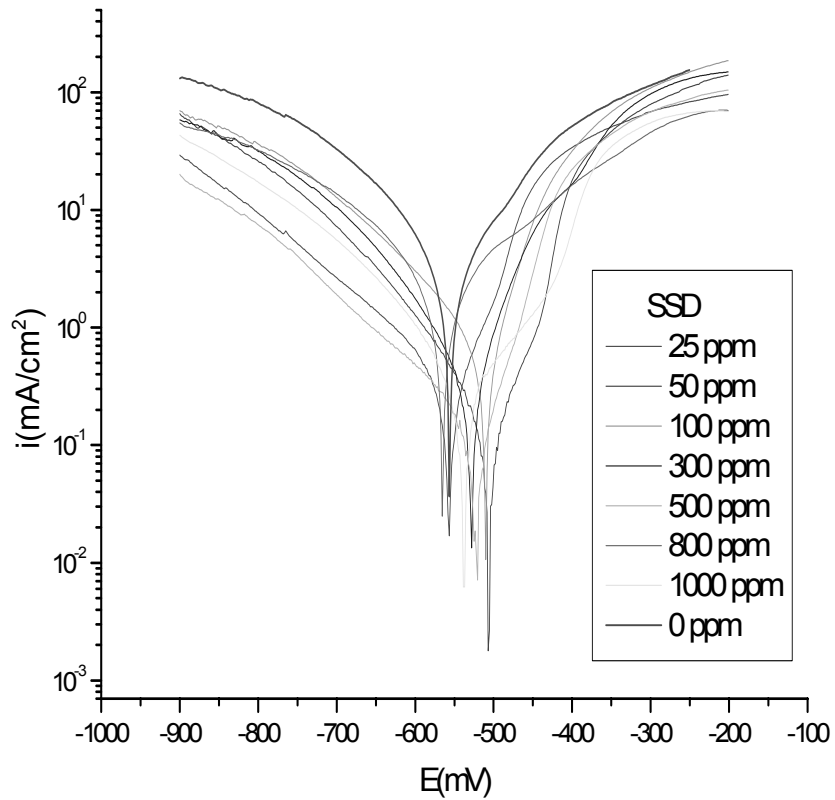


Fig. 2 – Potentiodynamic polarization curves of OL 37 in 0.5 M  $H_2SO_4$  in presence and absence of inhibitors SSD at temperature of 25°C.

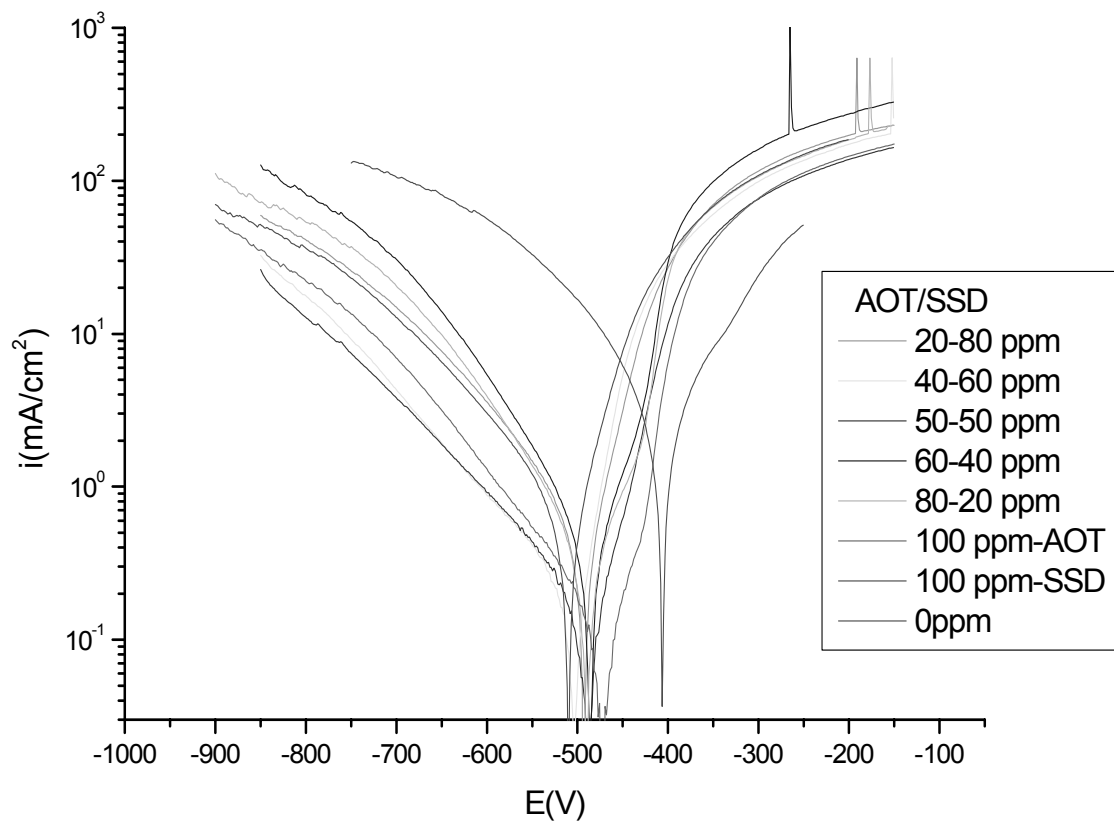


Fig. 3 – Potentiodynamic polarization curves of OL 37 in 0.5 M  $H_2SO_4$  in presence and absence of inhibitors AOT/SSD at temperature of 25°C.

Figs. 1-3 exhibit Tafel plots for OL 37 in 0.5 M  $H_2SO_4$  with and without different concentrations and various combinations of organic polymers (AOT, SSD, AOT/SSD). Examination of these figures depict that the addition of AOT, SSD and AOT/SSD in this acid solutions decreases the corrosion current density and increases the efficiency of these organic inhibitors. In this way, the presence of anionic surfactants inhibits especially the anodic dissolution reaction of OL 37 and also delays the cathodic reduction of the

hydrogen ion reaction. These results show that the SSD, AOT and AOT/SSD act like mixed inhibitors. Electrochemical corrosion kinetics parameters (corrosion rate, inhibition efficiency, corrosion current density, corrosion potential, cathodic and anodic Tafel slopes) of different concentrations and various combinations of anionic surfactants as corrosion inhibitors was determined by potentiodynamic polarization technique and these electrochemical parameters are given in Tables 1-3.

Table 1

Electrochemical parameters of OL 37 in 0.5M  $H_2SO_4$  in the presence and absence of dioctyl sulfosuccinate sodium (AOT) at temperature of 25°C

Concentration (ppm)	$i_{corr}$ (mAcm <sup>-2</sup> )	$R_p$ Ωcm <sup>-2</sup>	$R_{mpy}$	$P_{mm/year}$	$K_g$ g/m <sup>2</sup> h	E (%)	-E <sub>corr</sub> (mV)	$b_a$ (mVdec <sup>-1</sup> )	$-b_c$ (mVdec <sup>-1</sup> )	$\theta$
0	1.484	10.16	717.26	18.204	16.19	-	556	101	83	-
50	0.231	47	111.6	2.8	2.5	84.44	555	86	95	0.844
100	0.1107	131	53.5	1.3	1.2	92.54	475	56	107	0.925
300	0.1106	69	53.4	1.3	1.2	92.44	478	56	68	0.924
500	0.205	53	99	2.5	2.2	86.18	476	59	95	0.862
800	0.122	78.4	59	1.5	1.3	91.77	491	53	76	0.918
1000	0.07	113	34	0.87	0.77	95.12	492	57	63	0.951

Table 2

Electrochemical parameters of OL 37 in 0.5M  $H_2SO_4$  in the presence and absence of 1-Dodecane sulfonate sodium (SSD) at temperature of 25°C

Concentration (ppm)	$i_{corr}$ (mAcm <sup>-2</sup> )	$R_p$ Ωcm <sup>-2</sup>	$R_{mpy}$	$P_{mm/year}$	$K_g$ g/m <sup>2</sup> h	E (%)	-E <sub>corr</sub> (mV)	$b_a$ (mVdec <sup>-1</sup> )	$-b_c$ (mVdec <sup>-1</sup> )	$\theta$
0	1.484	10.16	717.26	18.204	16.19	-	556	101	83	-
25	0.197	69.57	95.2	2.41	2.14	86.7	555	71	82	0.867
50	0.1127	109	54.4	1.4	1.2	93	506	63	76	0.93
100	0.37	46.83	178	4.58	4	75	510	66	86	0.75
300	0.28	55.02	135	3.4	3	81	530	65	88	0.81
500	0.072	145	34.8	0.89	0.9	95	525	67	81	0.95
800	0.238	67.37	115	2.9	2.6	83	558	100	88	0.83
1000	0.223	66.14	108	2.7	2.4	84.6	539	112	89	0.84

Table 3

Electrochemical parameters of OL 37 in 0.5M  $H_2SO_4$  in the presence and absence of various combinations of organic inhibitors type AOT/SSD at temperature of 25°C

Concentration AOT/SSD(ppm)	$i_{corr}$ (mAcm <sup>-2</sup> )	$R_p$ Ωcm <sup>-2</sup>	$R_{mpy}$	$P_{mm/year}$	$K_g$ g/m <sup>2</sup> h	E (%)	-E <sub>corr</sub> (mV)	$b_a$ (mVdec <sup>-1</sup> )	$-b_c$ (mVdec <sup>-1</sup> )	$\theta$
0	1.484	10.16	717.26	18.204	16.19	-	556	101	83	-
20/80	0.255	53	123	3.1	2.7	84.4	496	59	73	0.844
40/60	0.103	74	50	1.3	1.1	83	506	50	79	0.83
50/50	0.07	112	34	0.87	0.77	95	492	62	78	0.95
60/40	0.15	67	72	1.84	1.63	89	489	63	72	0.89
80/20	0.22	58	106	2.7	2.4	85	493	65	79	0.85
100/AOT	0.111	131	54	1.3	1.2	92	475	56	107	0.92
100/SSD	0.37	46.83	178	4.6	4	75	510	66	86	0.75

It could be said that from Figs. 1-3 and Tables 1-3, the anodic and cathodic reaction was modified by the adding of AOT, SSD and AOT/SSD inhibitors. Both anodic and cathodic curves moving toward smaller current densities; it recorded that the adding of inhibitors can reduce the OL 37 anodic dissolution and likewise slowed the hydrogen reduction. All the studied organic inhibitors (AOT, SSD and AOT/SSD) showed a very good inhibition properties for the corrosion of OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub> and the corrosion current density decreased considerably and the inhibitor efficiency increased with increasing inhibitors concentrations and combinations of these inhibitors due to the increase in the blocked sites of the OL 37 electrode surface by adsorption. By examining, in comparison, the inhibition efficiency and the corrosion rate ( $R_{mpy}$ , in mil per year; P, in mm per year and Kg, in gm<sup>-2</sup>h<sup>-1</sup>) of all inhibitors, in the same condition, it could be observed that, the AOT and AOT/SSD have a greater efficiency for anticorrosion protection of OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub> and SSD have a good inhibition efficiency. Occasionally, the anodic curves display oxidation peaks followed by the narrow passive range and a decrease of the current density (this behaviour can be explained due to formation of oxo-hydroxo-complexes of iron). The maximum efficiency is obtained when the inhibitor concentration for AOT is 100ppm, 300 ppm and 1000ppm, for SSD is 50 ppm and 500 ppm and for AOT/SSD is 40-60 ppm, 50-50 ppm and 60-40 ppm. These dates

demonstrate that these surfactants can be classified as mixed type corrosion inhibitors.

Adsorption isotherm is very important in determining the mechanism of organo-electrochemical reactions. Also, the greater inhibitor efficiency is an effect of the adsorption process. The adsorption isotherm can give important information on the interaction of inhibitor and metal surface. To measure the influence of organic inhibitor concentration on the corrosion rate, it is used to match the rate data to equilibrium adsorption expressions, as Langmuir equation:<sup>5-11</sup>  $\theta/(1-\theta) = KC$ , where  $\theta$  is the degree of the coverage on the electrode surface by the inhibitor and K is the equilibrium constant of the adsorption process,  $\theta$  is determined by:  $\theta = (i_{corr} - i_{inh})/i_{corr}$  where  $i_{inh}$  and  $i_{corr}$  are the corrosion current density in 0.5M H<sub>2</sub>SO<sub>4</sub> with and without inhibitor.<sup>6-13</sup> All correlation coefficient ( $R^2$ ) exceeded 0.99 (AOT  $R^2=0.9977$ ; and SSD -  $R^2=0.9964$ ), which indicates that the inhibition was attributed to adsorption of these compounds on the metal surface. Utilization of the Langmuir behavior is frequently justified with the argument that inhibition shall include adsorption.

In this study, straight lines were obtained when concentration  $C_{inh}/\theta$  was plotted against  $C_{inh}$  with a slope of unity. The linear relationship suggests that the adsorption of inhibitors obeys the Langmuir adsorption isotherm (Fig. 4). The high value of the adsorption equilibrium constant reflects the high adsorption ability of this inhibitor on carbon steel surface.

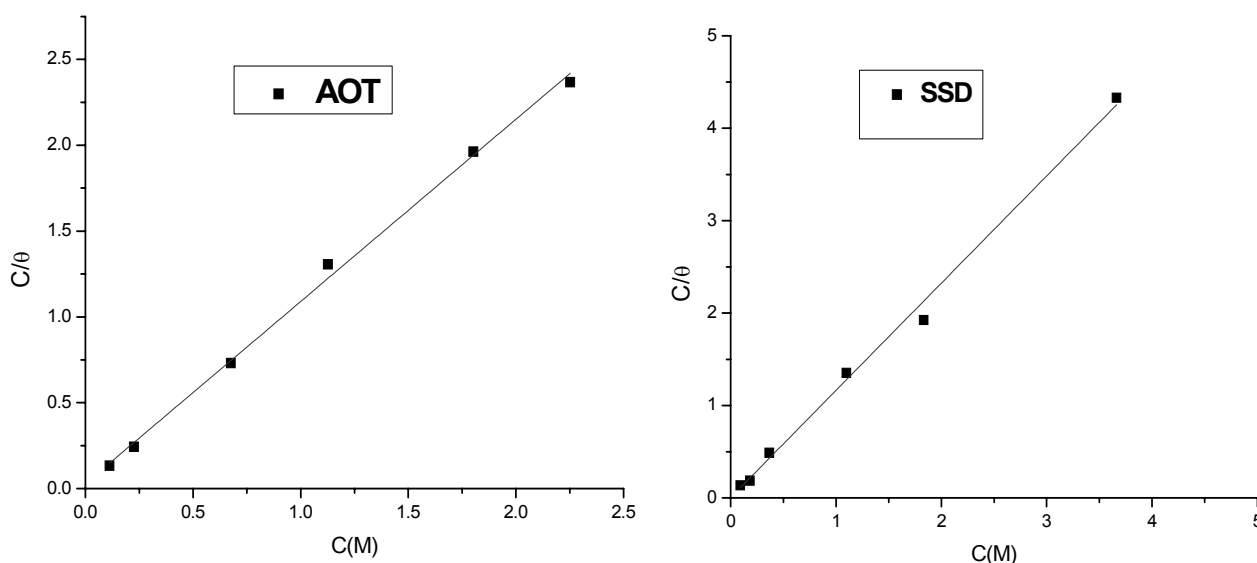


Fig. 4 – Langmuir plot for (a) AOT, (b) SSD and (c) AOT/SSD on OL 37+ 0.5M H<sub>2</sub>SO<sub>4</sub>.

Table 4

The values of  $K_{ads}$  and  $\Delta G_{ads}^{\circ}$  for anionic surfactants + 0.5M H<sub>2</sub>SO<sub>4</sub>

The system	Type of metallic material	Values of $K_{ads}$ , M <sup>-1</sup>	Values of $\Delta G_{ads}^{\circ}$ KJmol <sup>-1</sup>	Type of adsorption
AOT +0.5M H <sub>2</sub> SO <sub>4</sub>	OL 37	35.19	-8.854	Physical adsorption
SSD +0.5M H <sub>2</sub> SO <sub>4</sub>	OL 37	259	-13.762	Physical adsorption

The equilibrium constant of the adsorption process ( $K_{ads}$ ) is related to the standard adsorption free energy ( $\Delta G_{ads}^{\circ}$ ) obtained by the relation:  $\ln K_{ads} = -(\Delta G_{ads}^{\circ} / RT)$ .<sup>5-7, 11-15</sup>

The deduced value of  $\Delta G_{ads}^{\circ}$  obtained is negative and means that the adsorption of organic inhibitor is a spontaneous process, and furthermore the negative values of  $\Delta G_{ads}^{\circ}$  also show the strong interaction of the inhibitor molecule with the surface.

The obtained values  $\Delta G_{ads}^{\circ}$  around -20 KJmol<sup>-1</sup> or lower indicate the electrostatic interaction between charged metal surface and charged in the bulk of the solution, while those around -40KJmol<sup>-1</sup> or higher involve charge sharing or charge transfer between the metal surface and organic molecules (see Table 4).

The inhibition activity analysis of the organic compound was made by assuming that the mechanism of inhibition by organic molecules is physical adsorption.

Mechanism of inhibition can be explained from the results obtained, it was concluded that all the organic inhibitors (AOT, SSD, AOT/SSD) inhibit the corrosion of OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub> by adsorption of inhibitors at metal/solution interface. Adsorption of organic compounds can be reached by a physical adsorption process. This process is influenced by the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte. The inhibition efficiency of organic inhibitors AOT, SSD, AOT/SSD for the corrosion OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub> can be interpreted on the basis of the number of adsorption sites, molecular size and the way of interaction with the metal surface. Physical adsorption needs presence of

both electrically charged surface of the metal and charged species in the majority of the solution.

The corrosion behavior of OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub> in the presence and absence of AOT, SSD and AOT/SSD at temperature of 25°C was investigated by electrochemical impedance spectroscopy (EIS). Impedance measurements were performed at open circuit potential on the frequency range between 100 kHz and 40 mHz with an AC wave of  $\pm 10$  mV (peak-to-peak).

Fig. 5 showed a typical set of Nyquist plots of OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub> in the presence and absence of different concentrations and various combinations of organic inhibitors.

Anticorrosive properties of the inhibitor adsorption on the metal surface determining a greater increase in impedance of the electrochemical system, thus creating an increase in the resistance to the charge transfer process.<sup>7-11</sup>

The impedance spectra of OL37 electrode show one capacitive loop. In all cases, it is found that the size of the capacitive loop increases with increase in concentrations AOT, SSD, AOT/SSD resulting that the formed protective film has been accomplished by the addition of organic inhibitors. But, these capacitive loops are not perfect semicircles and this fact is attributed to frequency dispersion, largely attributed to roughness and inhomogeneities of the solid surface.

Fig. 5 as well shows that the diameters of these semicircles in the presence of 100ppm and 300ppm, 1000ppm AOT/OL 37/0.5M H<sub>2</sub>SO<sub>4</sub>, 50ppm and 500ppm SSD/OL 37/0.5M H<sub>2</sub>SO<sub>4</sub> and for 80-20ppm, 60-40ppm and 50-50ppm, AOT/SSD/OL 37/0.5M H<sub>2</sub>SO<sub>4</sub> are much higher than those in the absence of organic compounds, resulting that has good anticorrosion protection on the OL 37 in acid solutions.

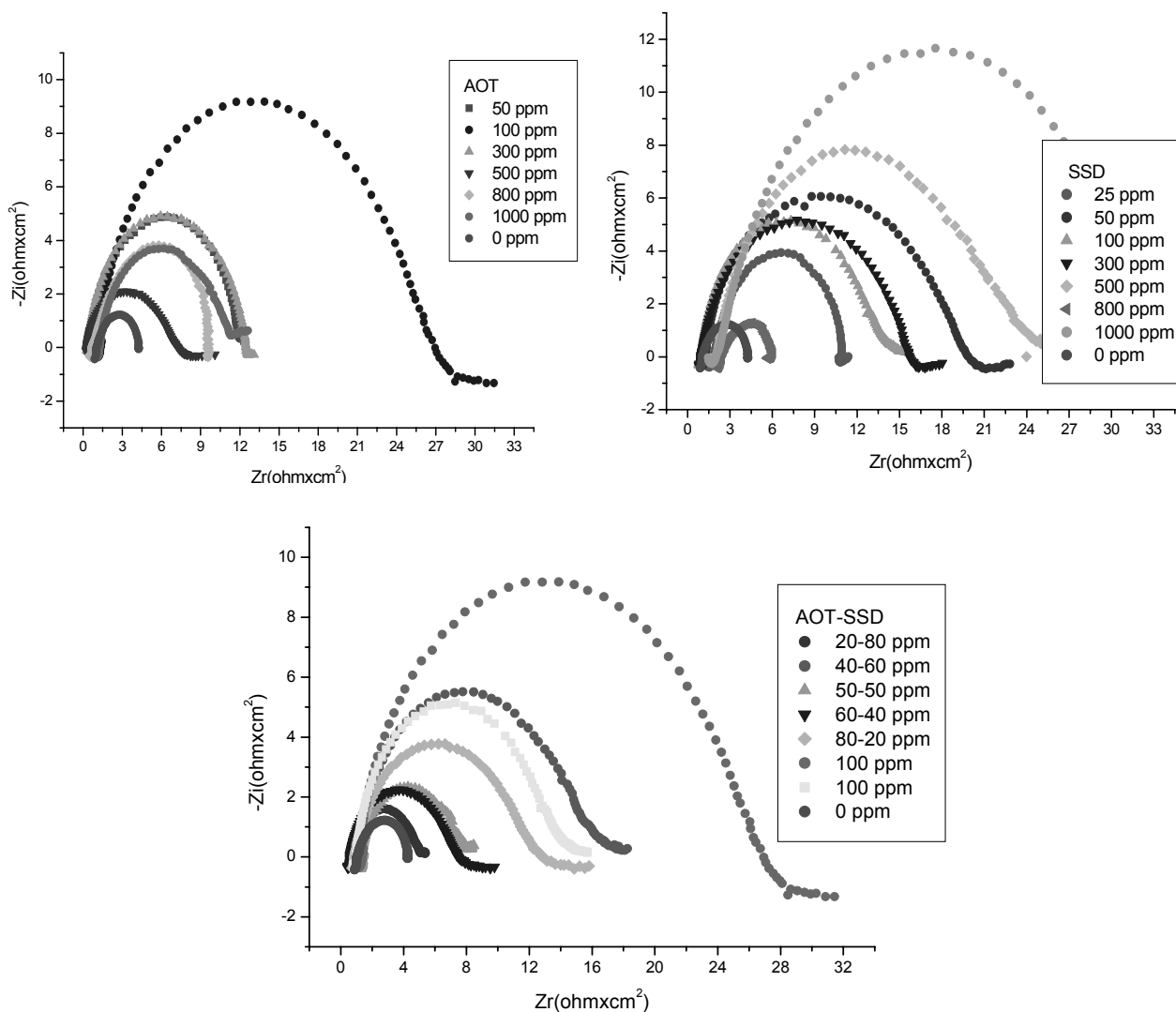


Fig. 5 – The Nyquist diagrams for OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub> in the presence and absence of different concentrations and various combinations of organic inhibitors.

Bode diagrams presented in Fig. 6 are in accordance with Nyquist diagrams. It could be observed that in the absence of inhibitor the carbon steel has only one time constant for 25° phase angle at medium and low frequencies, presenting an inductive behaviour with low diffusive predisposition.

From Fig. 6 it could be noticed that with the inhibitor, to seem a top corresponding to a phase angle of 65° which means where the electrode has an intense capacitive behaviour, in accordance with the results obtained by electrochemical polarization and in concordance with the Nyquist diagrams

Some impedance parameters like charge transfer resistance (R<sub>ct</sub>), double layer capacitance

(C<sub>dl</sub>) and inhibition efficiency were calculated and given in Tables 5-7. It can be observed that from Tables 5-7 the R<sub>ct</sub> values increase while C<sub>dl</sub> values decrease with the inhibitor concentration increase. This fact due to the increase in the surface coverage ( $\theta = E/100$ ) by means of the inhibitor, which resulted in an increase in the inhibition efficiency (see Tables 5-7).<sup>9-16</sup>

%E is calculated using the equation:

$$\%P = [(R_{ct} - R_{0ct})/R_{ct}] \times 100,$$

where R<sub>0ct</sub> and R<sub>ct</sub> are the values of the charge transfer resistance ( $\Omega \text{ cm}^2$ ) without and with the organic inhibitors.



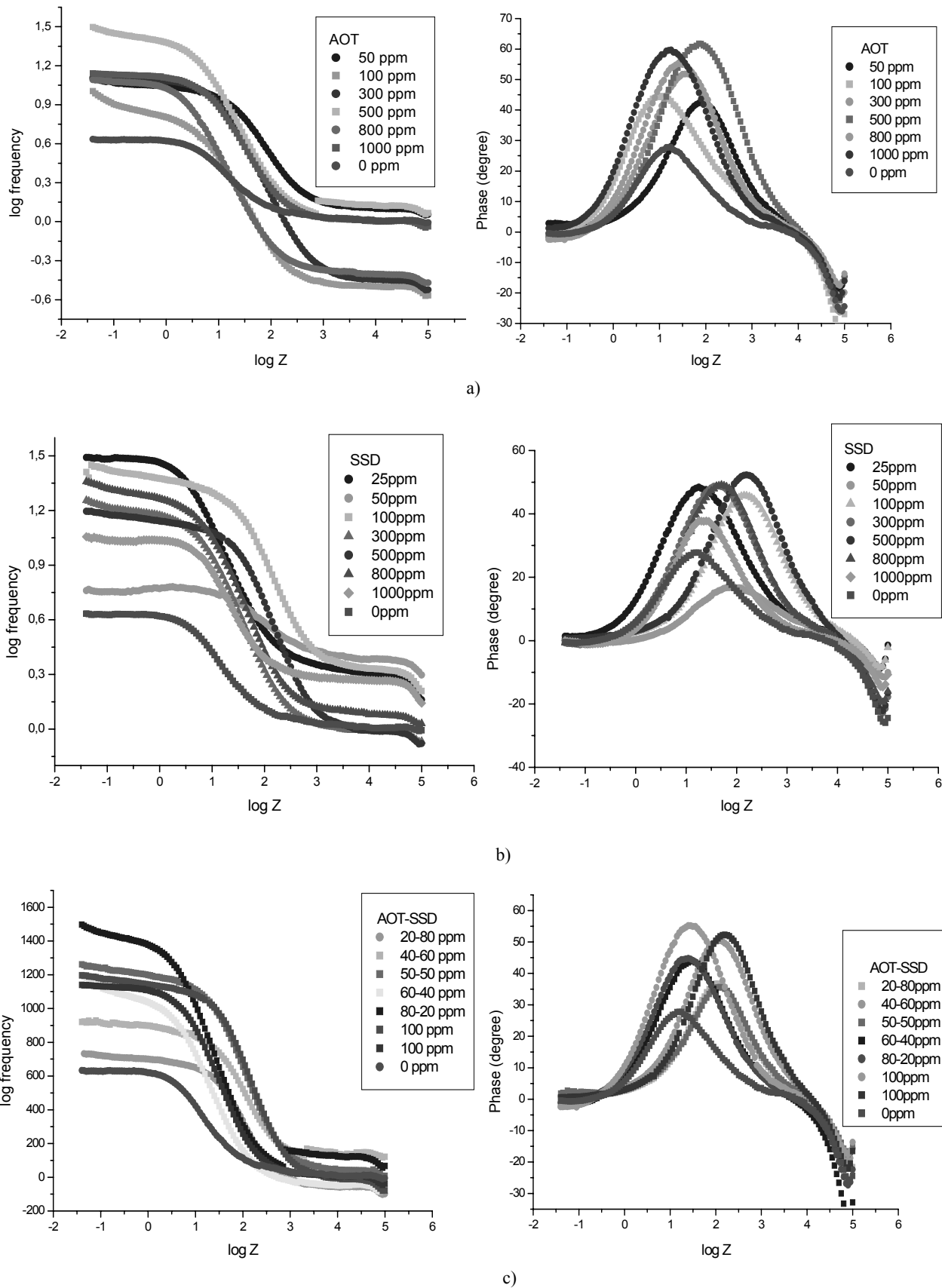


Fig. 6 – The Bode diagrams for OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub> in presence and absence of different concentrations and various combinations of organic inhibitors (a-AOT, b-SSD, c-AOT/SSD).

Table 5

EIS parameters for corrosion of OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub> with AOT

Concentration (ppm)	R <sub>ct</sub> (Ωcm <sup>2</sup> )	Cdl (mF/cm <sup>2</sup> )	Efficiency (%)
0	3.244	6.280	-
50	13.07	1.98	75
100	22.19	1.66	86
300	26.51	0.944	89
500	19.52	1.415	83
800	21.04	1.305	85
1000	47.63	0.561	93

Table 6

EIS parameters for corrosion of OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub> with SSD

Concentration (ppm)	R <sub>ct</sub> (Ωcm <sup>2</sup> )	Cdl (mF/cm <sup>2</sup> )	Efficiency (%)
0	3.244	6.280	-
25	11.08	1.74	71
50	19.27	1.4	83
100	14.59	1.924	78.9
300	15.25	1.916	79
500	23.29	0.820	87
800	23.455	0.616	87.5
1000	29	0.602	88.8

Table 7

EIS parameters for corrosion of OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub> with AOT/SSD

Concentration (ppm)	R <sub>ct</sub> (Ωcm <sup>2</sup> )	Cdl (mF/cm <sup>2</sup> )	Efficiency (%)
0	3.244	6.280	-
20/80	14.29	1.927	77
40/60	18.84	1.26	83
50/50	16.80	1.380	81
60/40	17.38	1.286	81
80/20	19.43	1.205	83
100 AOT	22.19	1.66	86
100 SSD	14.59	1.924	78.9

The equivalent circuit that describes our metal/electrolyte interface is shown in Fig. 7, where for analysis of the impedance spectra containing a single capacitive semicircle, the standard Randle's circuit is used (Fig. 7), as the circuit is composed of R<sub>s</sub>, refer to solution resistance, R<sub>ct</sub> charge transfer resistance and CPE constant phase element, respectively.<sup>6-17</sup> The high frequency limits correspond to R<sub>s</sub>, while the lower frequency limits correspond to R<sub>s</sub>+R<sub>ct</sub>. The

resistor R<sub>s</sub> capacitance is in series to R<sub>ct</sub> and R<sub>ct</sub> is in parallel to the double layer capacitance.

In this study of all various combinations of organic inhibitors in the studied concentration interval, the electrochemical impedance spectra are characterized by one semicircle and they were fitted using one time constant equivalent model with capacitance (CPE1), the charge transfer resistance R<sub>ct</sub> (R<sub>2</sub>) and R<sub>s</sub> (R<sub>1</sub>) solution resistance were obtained using the Nyquist diagrams.

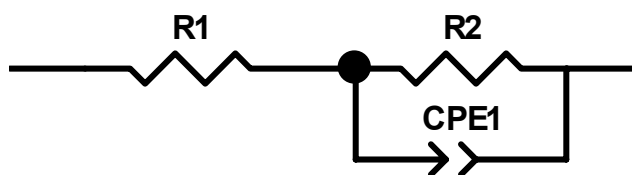
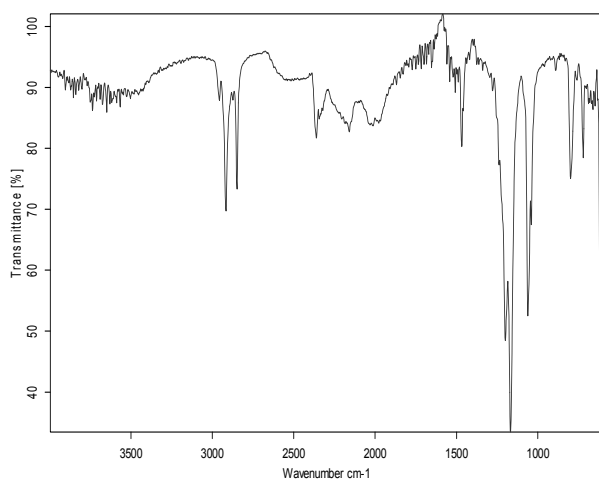
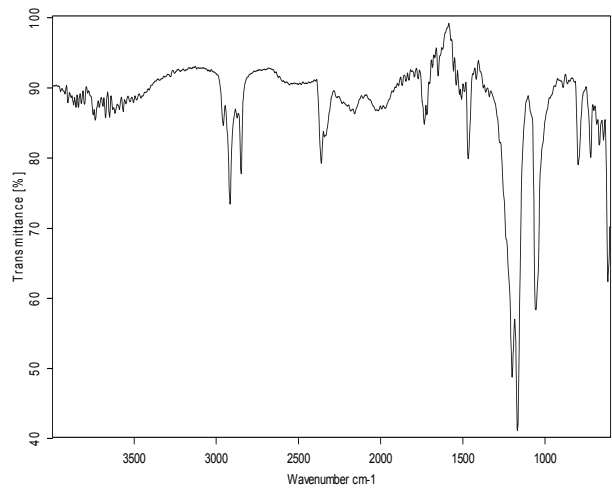


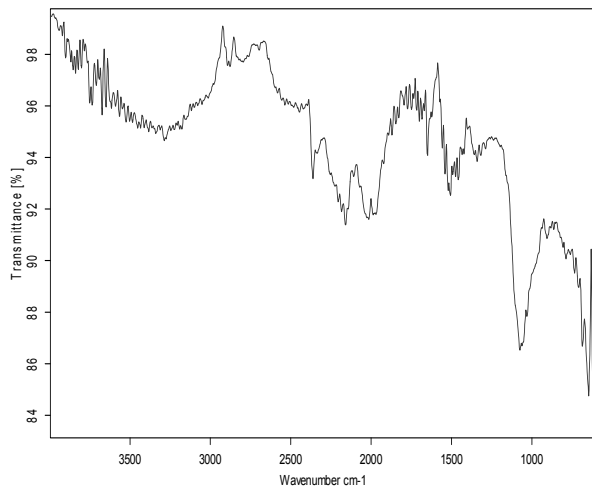
Fig. 7 – Equivalent circuit.



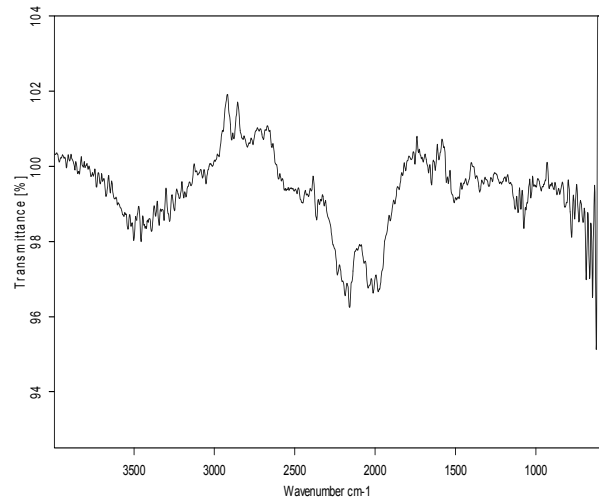
a) SSD



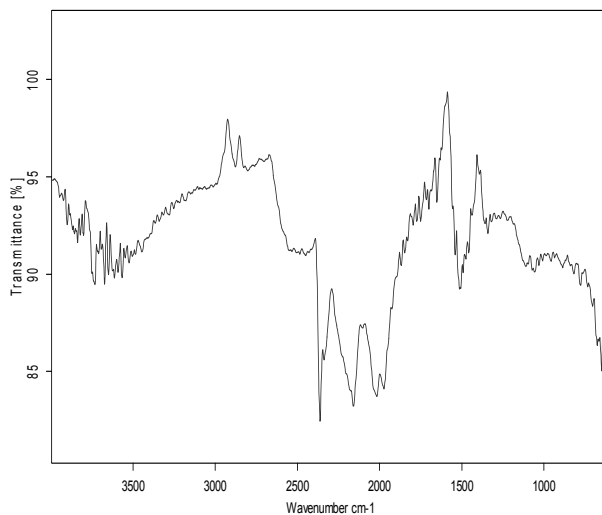
b) AOT



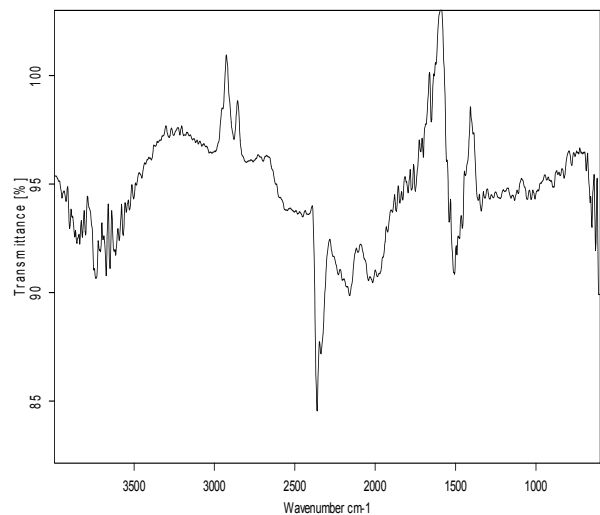
c) 500ppmSSD



d)100ppm AOT



e) 50-50ppm AOT/SSD



f) 60-40ppm AOT/SSD

Fig. 8 – FT-IR transmittance spectrum of AOT pur(a), SSD pur (b), 100ppm AOT/OL 37/0.5M H<sub>2</sub>SO<sub>4</sub> (c), 500ppm SSD/OL 37/0.5M H<sub>2</sub>SO<sub>4</sub> (d) and (e)-(f) 50-50 ppm 60-40ppm AOT/SSD/OL 37/ 0.5M H<sub>2</sub>SO<sub>4</sub>.

Inhibition efficiency obtained from EIS method is in good concordance with polarization technique.

A few researchers have confirmed that FT-IR spectrometry is a powerful tool that can be used to obtain the type of bonding for organic inhibitors adsorbed on the electrode surface.<sup>18-20</sup> In this study, FT-IR spectra showed that these organic inhibitors (AOT, SSD, AOT/SSD) were adsorbed on the carbon steel surface. All spectra in this paper were obtained at a resolution  $4\text{cm}^{-1}$  in the range  $4000\text{-}600\text{ cm}^{-1}$ . To assess the protective layer formed on the electrode surface in presence of inhibitors on the carbon steel surface was analyzed by FT-IR technique.

Fig. 8 show the FTIR spectra of AOT, SSD, AOT/SSD and the corrosion surface of carbon steel in  $0.5\text{M H}_2\text{SO}_4$  in presence of diferent concentratiois and various combination of these inhibitors.

Transmission spectra of surfactant SSD is shown in Fig. 8a. FT-IR transmittance spectrum of protective film adsorbed on the carbon steel surface in  $0.5\text{M H}_2\text{SO}_4$  containing of 500ppm SSD is presented in Fig. 8c. From Fig. 8a and c it can be observed that all important peaks of organic compounds SSD appeared in the protective film. A broad band in the range from  $3600\text{-}3200\text{ cm}^{-1}$  is attributed to O-H stretching, which indicates that the protective film contains  $\text{H}_2\text{O}$ .<sup>18-20</sup> The band in the region  $3000\text{-}2700\text{ cm}^{-1}$  corresponds to the aliphatic C-H stretching vibration of the  $\text{CH}_2$  and  $\text{CH}_3$  groups, the band at  $1190$  and  $1348\text{ cm}^{-1}$  corresponds to the S=O. The presence of C-O is indicates stretching at  $900\text{-}800\text{ cm}^{-1}$ . Comparing figures 8a and c, it can be suggested that SSD is adsorbed on the electrode surface.

The transmission FT-IR spectra obtained for AOT and 100ppm AOT anionic surfactant is presented in Figs. 8b and 8d. From Figs. 8b-d it can be observed that all important peaks for the adsorbed inhibitor AOT on the electrode surface. The peak appearing near  $1467$  and  $1348\text{ cm}^{-1}$  is attributed to the C-H stretching of  $\text{CH}_3$  group. The peaks can be seen at  $1718$  and  $1649\text{ cm}^{-1}$  is ascribed stretching vibrations of C=O. The band at  $2916$ ,  $2846$  and  $3051\text{ cm}^{-1}$  is attributed O-C=O. The peak at approximately  $1317$ ,  $1306$ ,  $1167$  and

$1154\text{ cm}^{-1}$  is due to the existence of the S=O and S-C stretching mode. A medium band in the region at  $3600\text{-}3100\text{ cm}^{-1}$  is attributed to O-H stretching and at  $3051$  and  $3057\text{ cm}^{-1}$  is related to C-H stretching vibration.

The characteristic peaks in the transmittance spectrum for 50-50 ppm AOT/SSD and 60-40 ppm AOT/SSD were presented in Fig. 8e and 8f are the following: the peak at approximately  $3000\text{-}2500\text{ cm}^{-1}$  and  $1457$ ,  $1337$  and  $1317\text{ cm}^{-1}$  correspond to the aliphatic C-H stretching vibration of the  $\text{CH}_2$  and  $\text{CH}_3$  groups. The peaks observed at  $1749$  and  $1657\text{ cm}^{-1}$  is ascribed stretching vibrations of C=O. The band at  $2991$  and  $3061\text{ cm}^{-1}$  is attributed O-C=O. The peak at approximately  $1323$ ,  $1074$ ,  $1067$  and  $1154\text{ cm}^{-1}$  is due the existence of the S=O and S-C stretching mode. A sharp peak in the region at  $3600\text{-}3100\text{ cm}^{-1}$  is attributed to O-H stretching mode. The peaks can be seen at  $3892$ ,  $3853$ ,  $3851$ , and  $3839\text{ cm}^{-1}$  is assigned to Fe-O bending which indicate that the bond is formed by the movemat of electrons from the polar atom O of anionic surfactants at the electrode surface. Comparing Figs. 8a-c, 8b-d and 8a-b-e-f it can be suggested that these organic inhibitors (AOT, SSD and AOT/SSD) are adsorbed on the carbon steel OL 37 surface.

The formation of the protective surface film of organic inhibitor on the electrode surface was confirmed by metallurgical research microscope findings on the electrode surface. Fig. 9 shows a few micrographies obtained by us for the systems OL 37+ $0.5\text{M H}_2\text{SO}_4$  and after polarization technique in  $0.5\text{ M H}_2\text{SO}_4$  with and without an optimum concentration of organic inhibitor. Likewise in the presence of organic inhibitors the surface becomes more smooth and homogeneous. Analyzing in comparison the Figs. 9a-h, it can be observed that on the surface of micrographies there are adsorbed films of inhibitor and corrosion products.

From Figs. 9a-h it is evident that the inhibited electrode surface is smoother than the uninhibited surface where showing protective layers are formed of adsorbed films of inhibitor and corrosion products. These films act as a barrier between aggressive medium and metal surface and as a result the corrosion process is protected.

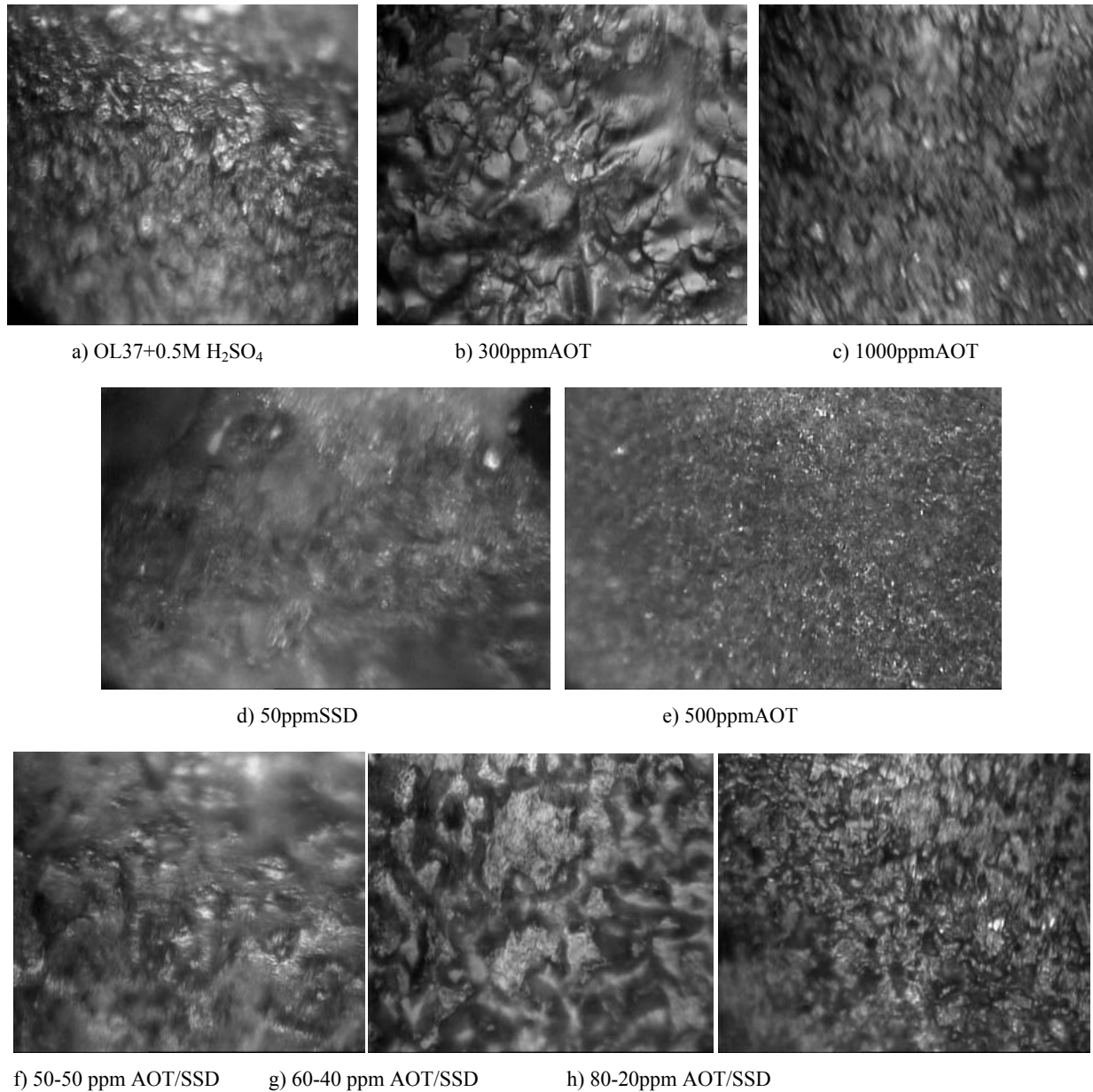


Fig. 9 – Micrographies of the carbon steel in 0.5M H<sub>2</sub>SO<sub>4</sub> with organic inhibitor: a) OL37+0.5 M H<sub>2</sub>SO<sub>4</sub>, b) 300 ppm AOT, c) 1000 ppm AOT, d) 50 ppm SSD, e) 500 ppm SSD, f) 50-50 ppm AOT/SSD, g) 60-40 ppm AOT/SSD, h) 80-20ppm AOT/SSD.

## CONCLUSIONS

The organic inhibitors: 1 Dodecane sulfonate sodium (SSD) and Dioctyl sulfosuccinate sodium (AOT) which were studied by us have presented higher anticorrosive properties and a considerable efficiency for decreasing of the rate corrosion of the studied carbon steel type OL 37 in 0.5M H<sub>2</sub>SO<sub>4</sub>;

The organic inhibitors were adsorbed on the carbon steel surface according to a Langmuir isotherm. The inhibition activity analysis of the organic compound was made by assuming that the mechanism of inhibition by organic molecules is physical adsorption.

FT-IR spectroscopy shows very clearly that these organic inhibitors were adsorbed on the metal surface.

The adsorption of the analyzed organic inhibitor obeyed the Langmuir isotherm and the FT-IR results as well demonstrate the adsorption of the inhibitor molecule on the metal surface and blocking the active sites.

EIS results are in very good concordance with results obtained by potentiodynamic and potentiostatic experiments.

The formation of the protective surface film of organic inhibitor on the electrode surface was confirmed by the metallurgical microscope technique.

AOT, SSD and AOT/SSD acted as mixed type corrosion inhibitor.

The inhibition efficiency follows the order: AOT>AOT/SSD>SSD.

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