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Adsorption and Inhibitive Corrosion Properties of Some New Polymeric Compounds as Green Inhibitors on Carbon Steels in Cooling Water Systems

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1. Introduction

Carbon steel, the most widely used engineering material, accounts for approximately 85% of the annual steel production world wide. Carbon steel is used in large tonnages in chemical processing, construction and metal –processing equipment, in marine applications and petroleum production and refining [1-4 and 4-7]. The use of organic inhibitors to decrease the rate of corrosion processes of carbon steels is quite varied [7-11 and 11-15]. Corrosion is a major problem in cooling water industrial systems, in oil and gas production systems. Therefore, the prevention from the corrosion of metals used in industrial applications is an important issue that the must be dealt with. Metal corrosion in water-conveying systems such as cooling water circuits is of major concern in industrial applications. It is well known that, in all the cases of cooling water systems at the metal/water interface contact appear frequent corrosion processes which determine deposition of corrosion products, like scales. Due to the scales formation the heat exchange becomes more difficult, that disturbs the normal function of industrial installation [15-18 and 18-22]. In this regard, aspects like cost of treatment versus cost of corrosion damages as well as process safety and the impact of corrosion and corrosion treatment on the environment have to be taken into account [22-26]. It is well known that, excessive corrosion does not only lead to serious damage of installations, it also causes considerable environmental pollution [26-31]. Most previous research into their usage has concentrated on relationships between chemical structure and inhibition performance [31-37 and 37-41]. Recent investigations have additionally emphasized the importance of the nature of the metal surface in inhibition performance [41-47 and 47-52]. In order to evaluate compounds as corrosion inhibitors and to design novel inhibitors, much more research works were concentrated on the

studies of the relationship between structural characteristics of the organic compounds and their inhibiting effects [52-56]. It had been suggested that the most effective factors for the inhibiting effects are the electronegative atoms such as, N, S, P etc, the unsaturated bonds such as, double bonds or triple bonds etc., and the plane conjugated systems including all kinds of aromatic cycles, of which they can offer special active electrons or vacant orbital to donate or accept electrons [56-59 and 59-61]. A large number of organic molecules have at least one of the above-mentioned characteristics in their molecular structure according to the diversity of organic compounds [61-65 and 65-69]. Heterocyclic compounds, kind of effective inhibitors, have at least two factors within their structures, which is the reason of their structures, which is the reason of their effective inhibiting [69-73 and 73-75]. The ability of an inhibitor to provide corrosion protection therefore depends to a large extent upon the interaction between the inhibitor and the metal surface under corrosion conditions [75-81 and 81-84]. The adsorption of organic molecules at the metal/solution interface is of a great interest in surface science and can markedly change the corrosion resisting properties of metals [84-89, 89-91 and 91-96]. The protection of corroding surfaces prevents the waste of both resources and money during the industrial applications and it is vital for extension of the equipment and limiting the dissolution of the toxic metals from components into the environment [96-112]. Generally, it is assumed that strong adsorption of the inhibitors is a prerequisite [112-117]. The adsorption of inhibitors leads to the formation of a physical barrier that reduces the metal reactivity in the electro-chemical reaction of corrosion [117-119]. Early studies considered the adsorption of inhibitors on metal surfaces to be primarily physical adsorption and/or chemisorptions [119-121]. New investigations have shown that adsorption could also occur through hydrogen bonding [121-123]. Most of these studies made use of sensitive surface analysis tools such as X-ray photoelectron spectroscopy (XPS) to resolve the nature of inhibitor adsorption [123-125]. Some earlier works has however been carried out under conditions that are not representative of on actual application. In this study, the inhibition of carbon steel corrosion in cooling waters by organic compounds was investigated by potentiodynamic polarizations, electrochemical impedance spectroscopy (EIS) measurements, FT-IR and metallography analysis. This study presents some attempts of analyzing of corrosive phenomena, which occur in cooling water systems, and relates to the protection of metallic surfaces from corrosion using these new polymers obtained in microwaves field. The use of inhibitors is one of the most practical methods for protecting against the corrosion and it is becoming increasingly popular.

The used organic inhibitors were six polymers, which were obtained by radicalic polymeri-zation in presence of microwave field: PASAC-4 (maleic anhydride and urea molar ratio 1:0.8 at t=120°C), PASAC-5 (polyaspartic acid at t=120°C and reaction without catalyst), and PASAC-6 (polyaspartic acid and phosphoric acid molar ratio 1:0.04 at t=190°C), PASAC-7 (polyaspartic acid and phosphoric acid molar ratio 1:0.06 in ammonium salt at t=200°C), PASAC-8 (polyaspartic acid and H_3PO_4 molar ratio 1:0.025 at t=200°C in propylene carbonate), and PASAC-9 (maleic anhydride and urea molar ratio 1:0.6 at t=200°C) (These organic compounds are not commercial names-is abbreviation). The studied metals were the carbon steels type OL 37 and OLC 45.

Electrode	C%	Si%	Mn%	Fe%	P%	S%	Al%	Ni%	Cr%	Cu%	Sn%	As%
OLC 45	0.48	0.03	0.79	98.32	0.02	0.025	0.027	0.05	0.06	0.18	0.012	0.006
OL 37	0.15	0.09	0.4	99.293	0.023	0.02	0.022	0.001	0.001	-	-	-

Table 1. The chemical composition of the working electrodes

The working electrode was made from these metals materials and had a cylindrical shape. This shape is preferred, because it assures a greater surface and a reduce number of edges. Prior to each determination, the working electrode was mechanically ground and polished with emery paper of varied granulation up to mirror-luster, degreased in benzene at boiling temperature in order to remove all traced of fat and remained abrasive powder on the electrode surface after polishing. After that, the working electrode was washed with distilled water and inserted in the polarization cell, which was the usually three-electrode cell. All tests have been performed at 25°C under atmospheric oxygen without agitation.

The corrosion medium was industrial cooling water with the following chemical composition:

Indicators	UM	Water type SC_1, values of parameters
PH		8.42
Conductivity	μs/cm	1061
Alcalinity p	mval/L	0.1
Alcalinity m	mval/L	3.3
total Hardness	mval/L	8.3
calciu Hardness	mval/L	3.0
Chloride, Cl^-	mg/L	117.01
Sulfate	mg/L	155
Solid substances	mg/L	2.75
organic compounds	mg/L	11.37
Iron	mg/L	0.073
Aluminium,	mg/L	0.0175
Nitrite, NO_2^-	mg/L	<0.1
Nitrate, NO_3^-	mg/L	10
Phosphate, PO_4^{3-}	mg/L	0.046
Copper, Cu^{2+}	mg/L	<0.015
Zinc, Zn^{2+}	mg/L	<0.1

Table 2. The chemical composition of the cooling water type SC_1

Indicators	UM	Water type SC$_2$, values of parameters
PH		7.95
Conductivity	μs/cm	665
Alcalinity	mval/L	4.2
total Hardness	mval/L	4.18
calciu Hardness	mval/L	4.16
Chloride, Cl$^-$	mg/L	95.74
Sulfate	mg/L	73.15
Solid substances	mg/L	0.95
organic compounds	mg/L	3.47
Iron	mg/L	0.099
Aluminium,	mg/L	0.02
Nitrite, NO$_2^-$	mg/L	<0.1
Nitrate, NO$_3^-$	mg/L	35
Phosphate, PO$_4^{3-}$	mg/L	<0.04
Copper, Cu^{2+}	mg/L	<0.02
Zinc, Zn^{2+}	mg/L	<0.1

Table 3. The chemical composition of the cooling water type SC$_2$

In this study, we have been used as organic inhibitors the following polymers: PASAC-4, PASAC-5, PASAC-6 PASAC-7, PASAC-8 and PASAC-9. The inhibition activity analysis of these organic compounds was made by assuming that the mechanism of inhibition by organic molecules is chemisorptions and that the energetic of the corrosion process per se is unaffected by the addition of substituent on the parent compound.

2. Results and discussion

2.1. Potentiodynamic polarization

as, it is well known; less active metals are less accessible and more expensive in comparison with ordinary metals, which are too much exposed to corrosion process to be used. Protection of these metals can be achieved by multiple ways from which the treatment of the corrosive

media is one of the most important. The treatment of the corrosive media can be achieved by removing the aggressive chemical agents or by using inhibitors, which control the corrosion of anodic or cathodic reaction of both. Here, the inhibition of the corrosion is the result of the adsorption of the organic compound on the metal surface forming an invisible film of a few molecular diameters thickness. The inhibition activity analysis of the organic compound was made by assuming that the mechanism of inhibition by organic molecules is chemisorption

The polarization behaviour of carbon steels mentioned above was studied through the plotting of the polarization curves obtained using the potentiodynamic method, finding the kinetic parameters of corrosion (especially the density of the corrosion current) from solutions without inhibitors and their comparison with the kinetic parameters from solutions with different concentrations of inhibitor. The corresponding Tafel parameters were obtained by Mansfeld's method, employing polarization data near the corrosion potential. In the present study, when values of E-E_{cor} are higher than about 70 mV, slight but significant changes in the anodic and cathodic Tafel slopes were found. Figures 1-4 show a series of potentiodynamic polarization curves of two-carbon steels electrode in industrial cooling water type SC_1 and SC_2 (it was not aerated) in absence and presence of different concentrations of inhibitors PASAC-4, PASAC-5, PASAC-6, PASAC-7, PASAC-8 and PASAC-9.

The corrosion parameters were calculated on the basis of potentiodynamic potential-current characteristics in the Tafel region (E=E_{corr} ± 150mV) and the vicinity of the corrosion potential ((E=E_{corr} ± 15mV) according to Mansfield's theory.

$$\log i_a = \log i_{corr} + \left(E_i - E_{corr} \right) / b_a \tag{1}$$

$$\log i_c = \log i_{corr} + \left(E_{corr} - E_i \right) / b_c \tag{2}$$

This equation corresponded to linear anodic and cathodic Tafel lines. Current density i_{corr} was determined by extrapolating the Tafel lines to E=E_{corr} or according to the Stern-Geary equation. This resulted in:

$$i_{corr} = b_a b_c / 2.303 \left(b_a + b_c \right) R_p \tag{3}$$

Where R_p was the polarization resistance, defined as the tangent of a polarization curve at E_{corr}.

$$R_p = \left(\frac{dE}{di} \right)_{E=E_{corr}} \tag{4}$$

In the present study when the values of E-E_{corr} are higher than 70mV, slight but significant changes in the anodic and cathodic Tafel slopes were found.

| Inhibitor) (ppm)	i_{corr} ($\mu A/cm^2$)	Rp KΩ/cm^2	R_{mpy}	$P_{mm/year}$	K_g g/m^{2}h	E(%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	13.01	1.78	6.07	0.15	0.137	-	-513	110	-215	-
50	4.011	6.56	1.8718	0.0475	0.0422	69.16	-366	108	-210	0.6916
100	4.319	4.71	2.0155	0.0511	0.0454	66.80	-467	108	-146	0.6680
300	0.942	17.57	0.4386	0.0111	0.0099	92.77	-326	80	-84	0.9277
500	0.992	17.86	0.462	0.0117	0.0104	92.39	-360	81	-76	0.9239
800	0.835	29.50	0.3896	0.0098	0.0087	93.58	-307	189	-109	0.9358
1000	1.001	21.91	0.4671	0.0118	0.0105	92.30	-332	153	-106	0.9230

Table 4. Kinetic corrosion parameters of carbon steel OL-37+ X ppm PASAC 4 +S$_1$ at 25°C

Inhibitor) (ppm)	i_{corr} ($\mu A/cm^2$)	Rp KΩ/cm^2	R_{mpy}	$P_{mm/year}$	K_g g/m^{2}h	E(%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	13.01	1.78	6.07	0.15	0.137	-	-513	110	-215	-
50	7.62	2.93	3.556	0.0901	0.0802	41.42	-515	109	-1430	0.4142
100	7.08	2.70	3.304	0.0838	0.0745	45.58	-518	107	-150	0.4558
300	4.476	3.48	2.086	0.0529	0.0470	65.64	-709	81	-181	0.6564
500	2.64	4.84	1.232	0.0312	0.0278	79.70	-710	56	-54	0.7970
800	1.6	6.43	0.746	0.0189	0.0168	87.70	-760	85	-49	0.8770
1000	8.384	2.01	3.912	0.0993	0.0883	35.55	-694	78	-160	0.3555

Table 5. Kinetic corrosion parameters of carbon steel OL-37+ X ppm PASAC5+S$_1$ at 25°C

| Inhibitor) (ppm)	i_{corr} ($\mu A/cm^2$)	Rp KΩ/cm^2	R_{mpy}	$P_{mm/year}$	K_g g/m^{2}h	E(%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	13.01	1.78	6.07	0.15	0.137	-	-513	110	-215	-
100	3.34	3.11	1.558	0.0395	0.0351	74.32	-520	62	-76	0.7432
300	4.63	3.36	2.1606	0.0548	0.0487	64.41	-550	82	-124	0.6441
500	4.56	3.19	2.204	0.0559	0.04971	64.95	-533	99	-151	0.6495
800	5.04	2.82	2.436	0.05498	0.0741	62.18	-552	88	-133	0.6218

Table 6. Kinetic corrosion parameters of carbon steel OL-37+ X ppm PASAC 6 +S$_1$ at 25°C

The figures 1-5 show a series of potentiodynamic polarization curves for two carbon steel electrodes in a cooling water type S1, in absence and presence of different concentrations of inhibitor.
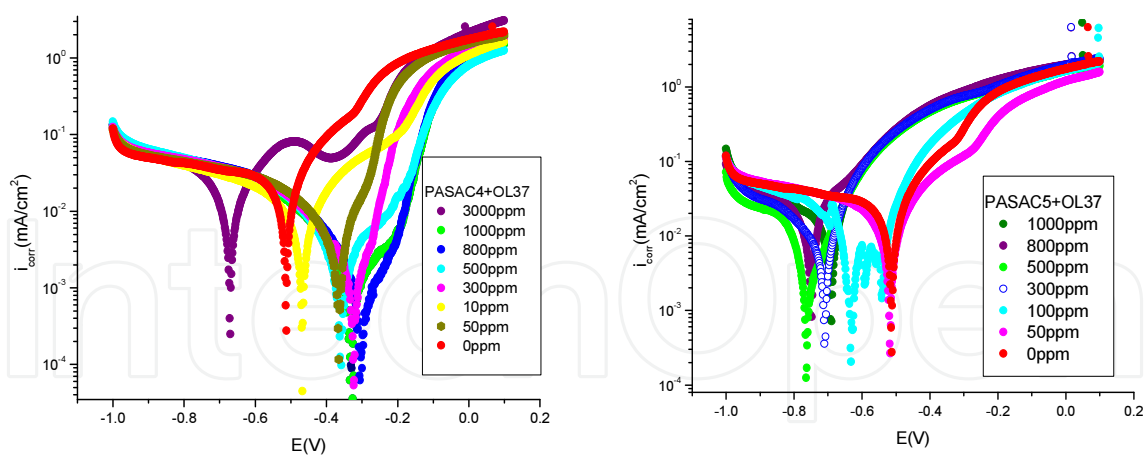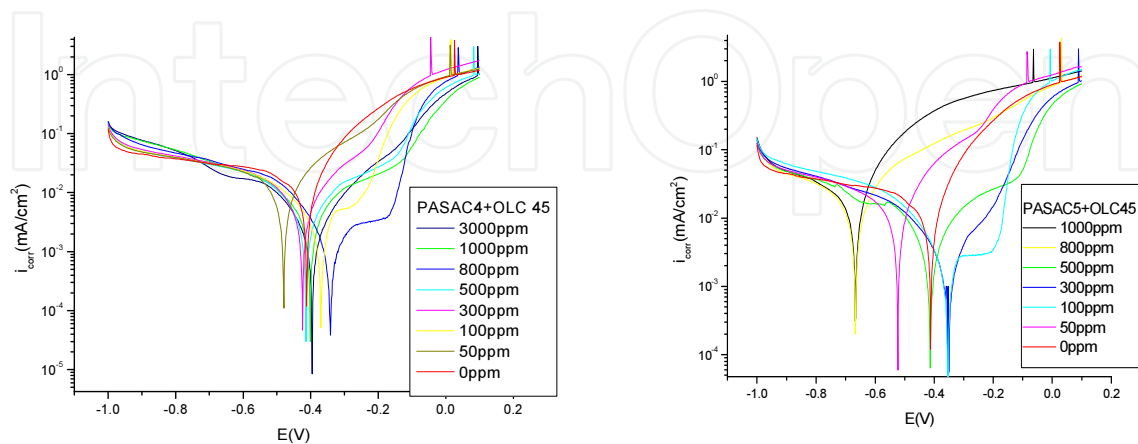
Figure 1. The polarization curves of OL-37 carbon steel in cooling water type S1 in presence of PASAC4 and PASAC5 at 25°C
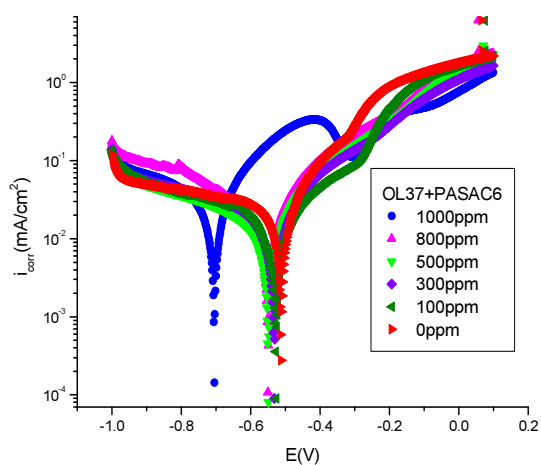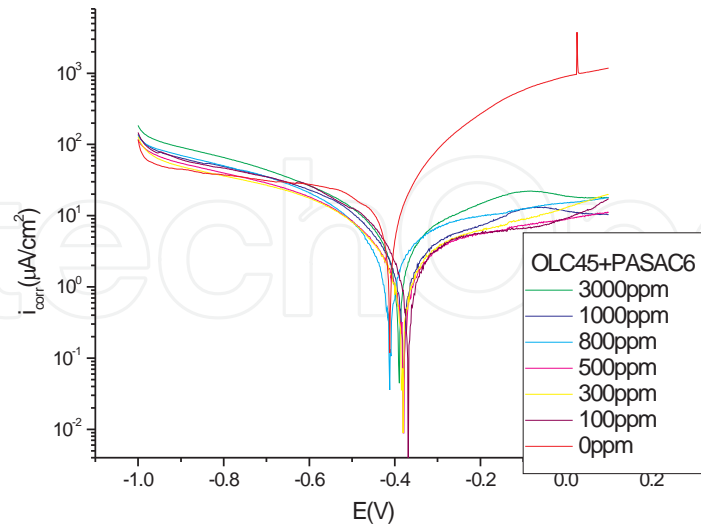

Figure 2. The polarization curves of OL-37 carbon steel in cooling water type S1 in presence of PASAC6 at 25°C

Figure 3. The polarization curves of OLC-45 carbon steel in cooling water type S1 in presence of PASAC4 and PASAC5 at 25°C

Figure 4. The polarization curves of OLC-45 carbon steel in cooling water type S1 in presence of PASAC6 at 25°C

Analysis of the polarization curves from figures 1-5 indicates that at low overvoltages, the Tafel relationship are followed, showing that both anodic and cathodic reactions are activation-controlled. At higher overvoltages a limiting current appears on the anodic and cathodic polarization curves showing that, the transport of ions towards the electrode surface becomes the rate-determining step (concentration polarization). Analyzing figures 1-5 it can be observed that on the anodic curves there is a low active range of potential where the relation Tafel is verified. After this range the current densities slightly increases and tends to a limit value. This behaviour points out that on this range the corrosion process is controlled by diffusion. Sometimes on the anodic curves appears 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 Fe). The maximum efficiency is obtained at the inhibitory concentration for PASAC 4 is 800ppm (OL37 and OLC 45), for PASAC5 is 500ppm (OLC45) and 800ppm (OL37) and for PASAC6 is 500ppm (OL37 and OLC 45). At the increasing inhibitor concentration over these concentrations (500 and 800 ppm) the inhibitor efficiency starts to decrease, respectively the corrosion current densities begin to decrease. Analyzing the cathodic polarization curves from figures 1-5 it can be observed that, on the large range of the potential the carbon steel electrodes behave very close to a passive behaviour. Practically, we can say that, in this potential range the electrode surface is passivated. We consider that, in this potential range, the cathodic reaction is hindered by the oxide film (passive film) from the electrode surface. In this potential range takes place the oxygen reduction cathodic reaction according to equation:

$$\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2HO^- \tag{5}$$

After this like passive range potential the cathodic current increases again and this increasing is due to the hydrogen evolution. From polarization curves obtained by potentiodynamic method were calculated all kinetic corrosion parameters which are given in tables 4-12.

Inhibitor(p pm)	i_{corr} ($\mu A/cm^2$)	Rp $K\Omega/cm^2$	R_{mpy}	$P_{mm/year}$	K_g g/m^2h	E(%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	7.12	2.62	3.32	0.084	0.075	-	-414	91	-188	-
50	5.59	3.55	2.608	0.066	0.0588	21.48	-482	113	-141	0.2148
100	3.263	5.62	1.5227	0.0386	0.0343	54.17	-424	106	-128	0.5417
300	2.1678	8.02	1.01164	0.0256	0.0228	69.55	-414	109	-106	0.6955
500	1.68	10.37	0.784	0.0198	0.0176	76.40	-372	94	-116	0.7640
800	1.027	20.43	0.479	0.0121	0.0108	85.57	-345	158	-106	0.8557
1000	1.17	13.43	0.546	0.0138	0.0123	83.56	-399	94	-94	0.8356

Table 7. Kinetic corrosion parameters of carbon steel OLC-45+ X ppm PASAC 4 +S1 at 25°C

Inhibitor) (ppm)	i_{corr} ($\mu A/cm^2$)	Rp $K\Omega/cm^2$	R_{mpy}	$P_{mm/year}$	K_g g/m^2h	E(%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	7.12	2.62	3.32	0.084	0.075	-	-414	91	-188	-
100	6.392	3.02	2.9829	0.0757	0.0673	10.22	-526	102	-166	0.1022
300	1.412	13.29	0.659	0.0167	0.0148	80.16	-357	145	-116	0.8016
500	1.234	14.14	0.5758	0.0146	0.0129	82.66	-355	101	-111	0.8266
800	2.356	8.75	1.0994	0.0279	0.0248	66.91	-416	121	-124	0.6691

Table 8. Kinetic corrosion parameters of carbon steel OLC-45+ X ppm PASAC5 +S1 at 25°C

Inhibitor (ppm)	i_{corr} ($\mu A/cm^2$)	Rp $K\Omega/cm^2$	R_{mpy}	$P_{mm/year}$	K_g g/m^2h	E(%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	7.12	2.62	3.32	0.084	0.075	-	-414	91	-188	-
100	1.34	17.12	0.6253	0.0158	0.0141	81.17	-371	169	-109	0.8117
300	1.08	19.86	0.4946	0.0125	0.0111	85.11	-385	95	-80	0.8511
500	1.18	20.77	0.5506	0.0139	0.0124	83.42	-384	146	-112	0.8342
800	1.305	15.89	0.609	0.0154	0.0137	81.67	-415	117	-100	0.8167
1000	1.45	14.11	0.6766	0.0171	0.0152	79.63	-390	130	-99	0.7963

Table 9. Kinetic corrosion parameters of carbon steel OLC-45+ X ppm PASAC 6 +S1 at 25°C

Analyzing these tables, it can be observed that, the addition of the organic inhibitor to the amounts shown in the tables 4-12 leads in all the cases to inhibition of the corrosion process.

Inhibitor ppm	i_{corr} µA/cm²	R_p kΩ/cm²	R_{mpy}	P mm/year	K_g g/m²h	E %	E_{corr} mV	ba mV	b_c mV	θ
0	13.01	1.78	6.07	0.15	0.137	-	-513	110	-215	-
50	4.46	4.53	2.081	0.0528	0.0469	65.71	-529	104	-160	0.6571
100	4.14	4.17	2.072	0.0525	0.0467	65.87	-563	89	-150	0.6587
300	3.01	5.85	1.404	0.0356	0.0316	76.86	-589	105	-94	0.7686
500	3.95	4.43	1.843	0.0467	0.0416	69.63	-680	80	-154	0.6963
800	4.44	3.94	2.072	0.0525	0.0467	65.87	-690	79	-148	0.6587

Table 10. Kinetic corrosion parameters of OL 37+ X ppm PASAC 7+S1 at 25°C

Inhibitor ppm	i_{corr} µA/cm²	R_p kΩ/cm²	R_{mpy}	P mm/year	K_g g/m²h	E %	E_{corr} mV	ba mV	b_c mV	θ
0	13.01	1.78	6.07	0.15	0.137	-	-513	110	-215	-
50	6.88	2.97	3.211	0.0814	0.0724	47.10	-550	100	-159	0.4710
100	6.55	2.96	3.056	0.0775	0.0689	49.65	-504	102	-158	0.4965
300	3.53	5.67	1.647	0.0418	0.0371	72.86	-446	111	-156	0.7286
500	2.67	7.88	1.248	0.0316	0.0281	79.43	-511	102	-208	0.7943
800	4.90	3.88	2.608	0.0661	0.0588	57.03	-633	349	-118	0.5703

Table 11. Kinetic corrosion parameters of OL 37+ X ppm PASAC 8+S1 at 25°C

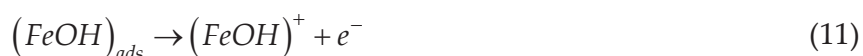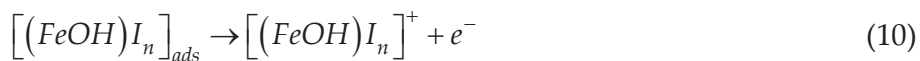| Inhibitor ppm	i_{corr} µA/cm²	R_p kΩ/cm²	R_{mpy}	P mm/year	K_g g/m²h	E %	E_{corr} mV	ba mV	b_c mV	θ
0	13.01	1.78	6.07	0.15	0.137	-	-513	110	-215	-
50	6.36	2.87	2.968	0.0753	0.0669	51.11	-483	98	-134	0.511
100	6.27	3.29	2.661	0.0675	0.0600	56.16	-520	107	-167	0.561
300	5.703	3.24	2.926	0.0742	0.0660	51.80	-495	101	-137	0.518
500	3.683	5.11	1.718	0.0436	0.0387	71.69	-640	96	-143	0.717
800	3.55	5.12	1.656	0.0420	0.0373	72.71	-512	90	-133	0.7271

Table 12. Kinetic corrosion parameters of OL 37+ X ppm PASAC 9+S1 at 25°C

It can be observed from tables 9-12 that, the inhibitor PASAC8 has a higher efficiency for corrosion system OL37+S1, PASAC7 had a good efficiency for corrosion system OL 37 in S1 than for PASAC9 in same condition. The maximum efficiency is obtained at the inhibitor concentration for PASAC 7 is 300ppm, for PASAC8 is 500ppm and for PASAC9 is 800ppm. At the increasing inhibitor concentration over these concentrations (500 and 800 ppm) the inhibitor efficiency starts to decrease, respectively the corrosion current densities begin to increase again.

Analyzing in comparison the corrosion rate of organic inhibitors, in the same condition, one can see that, the PSAC-4 had a higher efficiency for corrosion system OL 37 in S1 and OLC 45 in S1, PASAC6, PASAC5, PASAC8, and PASAC7 had a good efficiency for corrosion system OL 37 in S1 than PASAC-9.

Analyzing these tables, it can be observed that, the addition of the organic inhibitor to the amounts shown in the tables 4-12 leads in all the cases to inhibition of the corrosion process.

This fact can be explained taking into account the effects of organic compounds on the electrochemical properties of the carbon steels in concordance with Donahue's theory [17]. According to this theory, the corrosion process of carbon steel could takes place thus:

$$Fe + OH^- \Leftrightarrow \left(FeOH\right)_{ads} + e^- \tag{6}$$

$$\left(FeOH\right)_{ads} + nI \Leftrightarrow \left[FeOH\right]In_{ads} \tag{7}$$

$$I + S_{ads} \Leftrightarrow Iads + S \tag{8}$$

$$\left(FeOH\right)_{ads} + nI_{ads} \Leftrightarrow \left[\left(FeOH\right)I_n\right]_{ads} \tag{9}$$

$$\left[\left(FeOH\right)I_n\right]_{ads} \rightarrow \left[\left(FeOH\right)I_n\right]^+ + e^- \tag{10}$$

$$\left(FeOH\right)_{ads} \rightarrow \left(FeOH\right)^+ + e^- \tag{11}$$

$$\left(FeOH\right)^{+} \rightarrow Fe^{2+} + OH^{-} \tag{12}$$

$$\left[\left(FeOH\right)I_{n}\right]^{+} \rightarrow \left[FeIn\right]^{2+} + OH^{-} \tag{13}$$

The symbol 'S' denotes the electrolyte or any specifically adsorbed ions and the symbol 'I' denotes the organic inhibitor. The step (9) would be the mode of inhibition, which has been designated as "blocking"or adsorption, while the steps (8) and (10) are the surface chelate modes. If the process described by (10) is the dominant mechanism for the production of chelate, then the formation of chelate would be enhanced by increased coverage of both adsorbed inhibitor and reaction intermediate. Since increased coverage of intermediate leads to product formation via step (12), the chelation process, i.e., step (10), must be fast or the surface coverage of adsorbed inhibitor must be high for inhibition to be maintained. Assuming the foregoing to be correct, i.e., chelate forms by (10) and that the equilibrium of (7) and (9) are shifted toward the right as adsorption sites are generated by dissolution, then importance of chelate ought to be increased with increasing immersion time [117]. The extent to which the steps (7) and (9) are shifted to the right relative to each other and the stoichiometry of (10), i.e., whether n ≥1, will determine whether inhibition will increase, decrease, or remain constant. Thus, until one may ascertain the critical parameters associated with (7), (9) and (10), only a qualitative discussion of the causes of the observed phenomena can be made. From the foregoing discussion, it should not be assumed that the mechanism given by (8) has been ruled out. On the contrary, such a mechanism is still attractive since organic compound is more readily available from the solution than it would be via some sort of surface diffusion mechanism. On the other hand, the fact that adsorbed organic compound is indeed present and the organic inhibitor and intermediate are assumed to gravitate toward the same surface sites suggests a preference for (10). We presume that both adsorption and surface chelate function in a more or less concerted manner to achieve inhibition (see tables 4-12 and figures 1-5).

The variation curves of the corrosion current density function of the inhibitor concentration are presented in figures 1-5. From figures, one can see much better the influence of these parameters on the polarization behaviour of the two carbon steels in cooling water system.

From polarization curves obtained by potentiodynamic method were calculated all kinetic corrosion parameters which are given in tables 4-12.

The variation curves of the corrosion current density and efficiency function of the inhibitor concentration are presented in figures 6-8. From figures, one can see much better the influence of these parameters on the polarization behaviour of the carbon steel OL 37 in cooling water system.
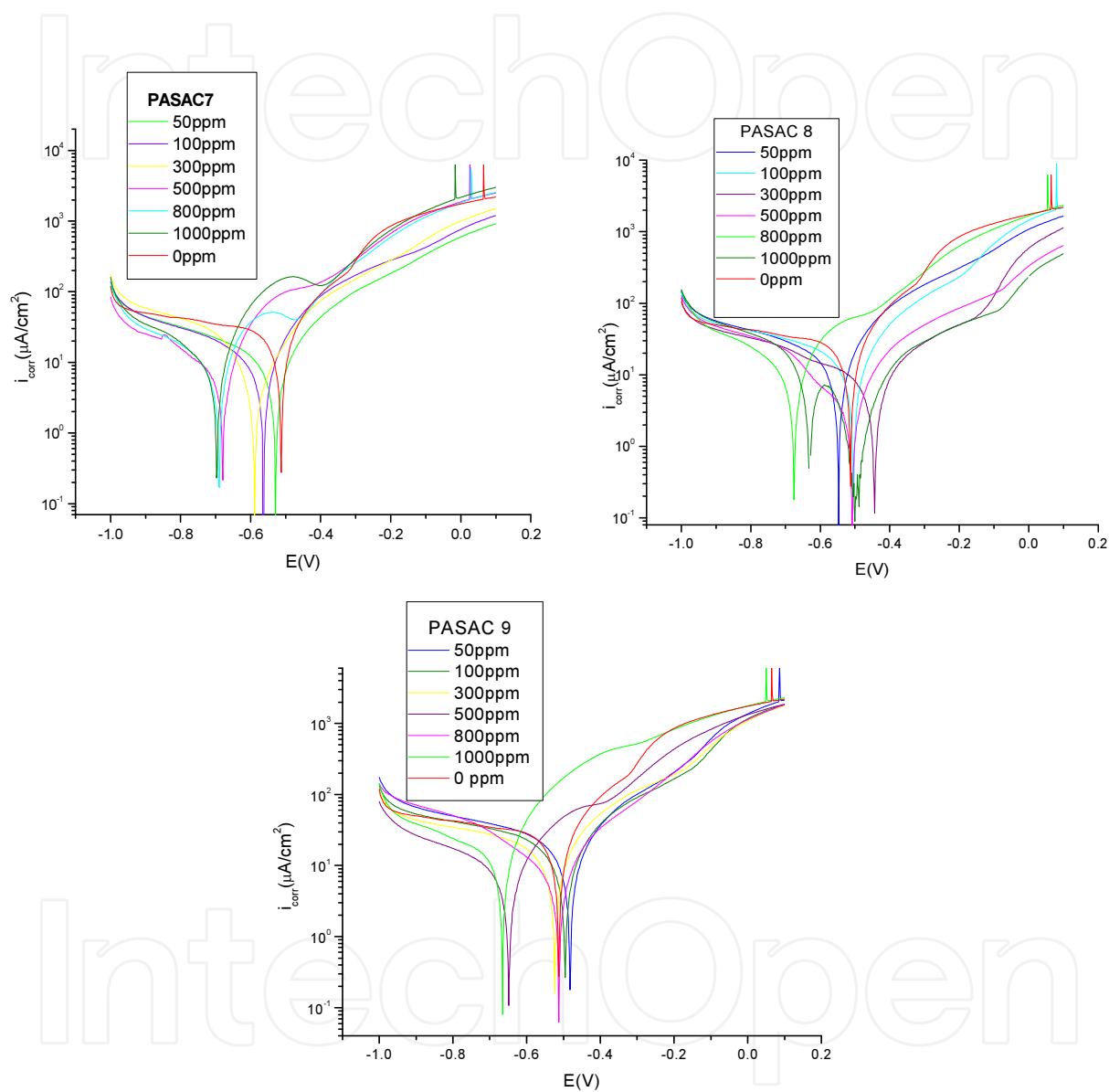
Figure 5. The polarization curves of OL 37 carbon steel in cooling water type S1 in presence of PASAC7, PASAC8 and PASAC9 at 25°C
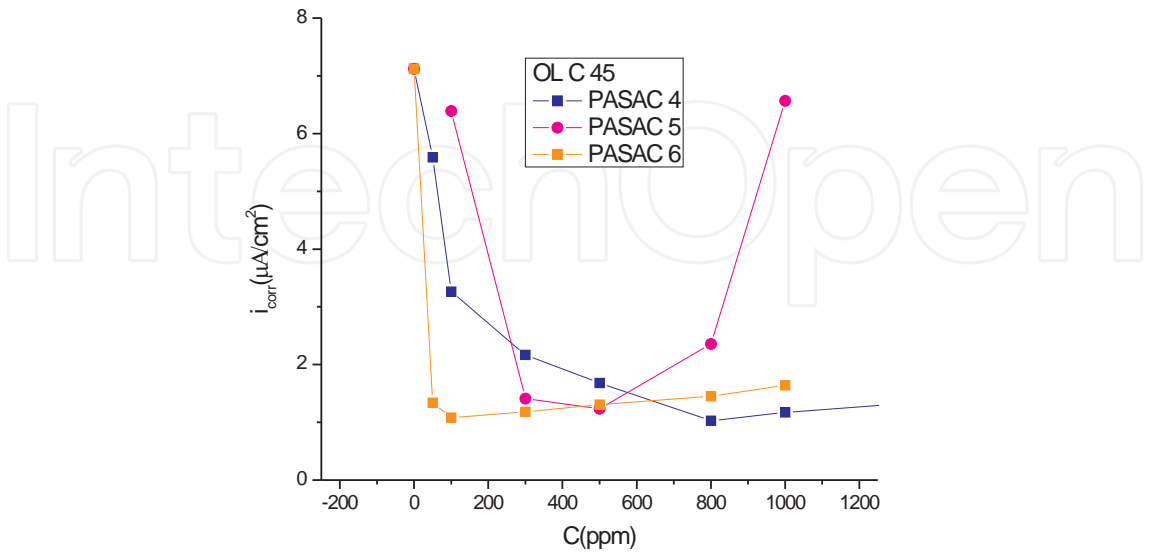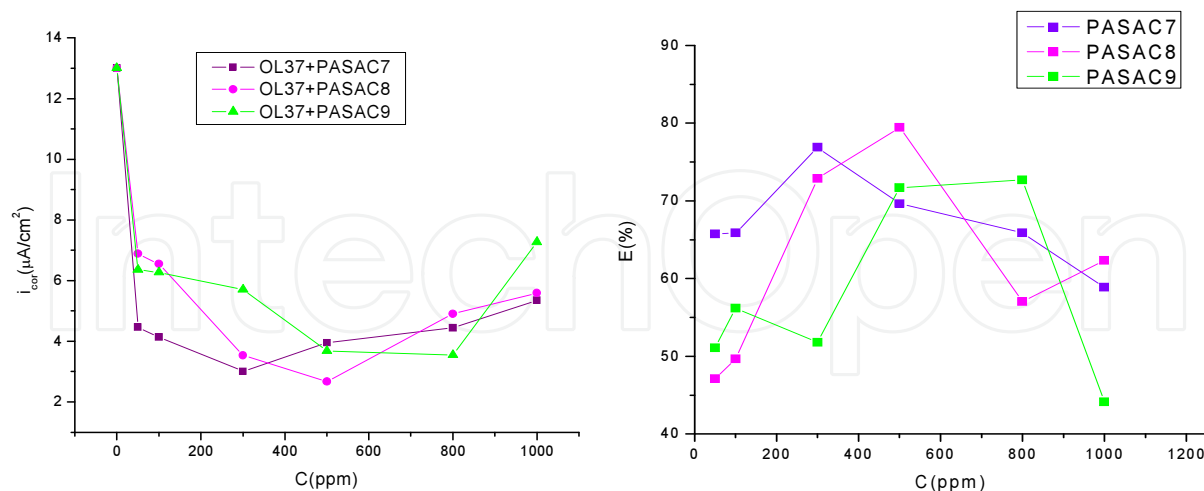
Figure 6. The influence of the inhibitor PASAC4, PASAC5 and PASAC6 concentration on the corrosion rate of carbon steel OLC 45 in cooling water type S_1 at 25^0
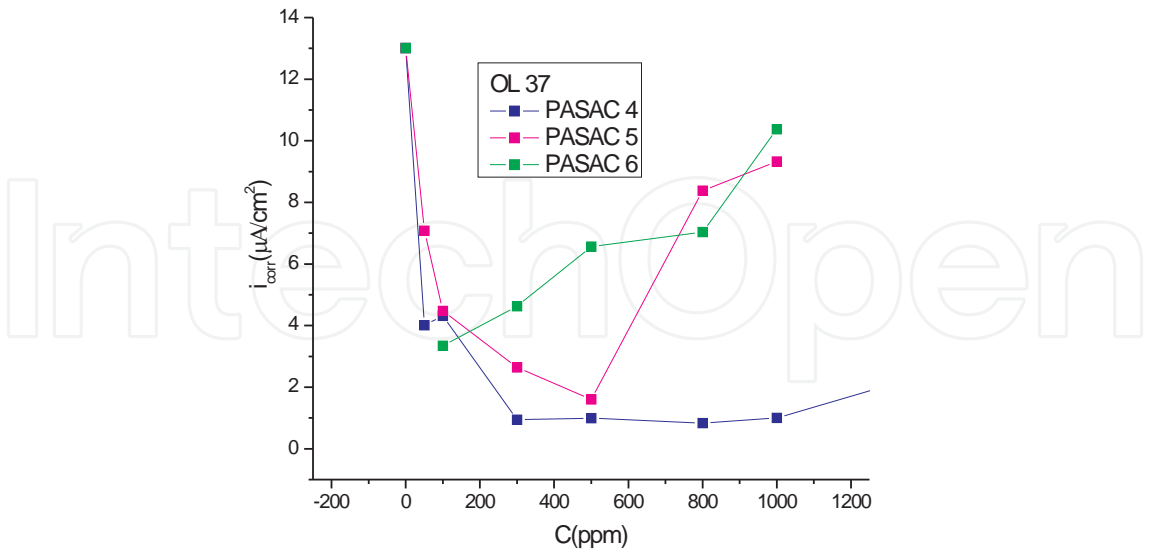
Figure 7. The influence of the inhibitor PASAC4, PASAC5 and PASAC6 concentration on the corrosion rate of carbon steel OL-37 in cooling water S_1 at 25^0

Figure 8. The influence of the inhibitor PASAC7, PASAC8 and PASAC9 concentration on the corrosion rate and efficiency of carbon steel OL-37 in cooling water type S_1 at 25^0. The inhibition efficiency follows the order: $\mathbf{E_{PASAC4} > E_{PASAC6}}$ $\mathbf{> E_{PASAC5}\ E_{PASAC8} > E_{PASAC7} > E_{PASAC9}}$

2.2. The adsorptions of the organic compounds on the carbon steels surface obeyed Langmuir's isotherm

We presume that, the higher inhibitor efficiency is a consequence of the stronger adsorption process. The molecules of organic inhibitor are adsorbed on the metal surface and form a barriere film, which hindered the corrosion process. To quantify the effect of inhibitor concentration on the corrosion rate, it is common to fit the rate data to equilibrium adsorption expression, such as Langmuir equation:

$$\theta / \left(1 - \theta\right) = Kc \tag{14}$$

Where θ is the fraction of surface coverage by the inhibitor and K is the equilibrium constant for the adsorption reaction. θ is given by:

$$\theta = \left(i_{corr} - i_{corr.inhib}\right) / i_{corr} \tag{15}$$

Where $i_{corr,\ inh}$ and i_{corr} are the corrosion rates in the industrial cooling water SC1 with and without inhibitor. Usage of the Langmuir treatment is often justified with the argument that inhibition must involve adsorption. In this study, the Langmuir isotherm is rearranged to give:

$$c\big/\theta = c + 1\big/K \tag{16}$$

c /θ is plotted against c, when a linear relationship is obtained for organic inhibitor and a slope of near unity which indicates an approximate Langmuir behaviour. The adsorption equilibrium constants (K) for our corrosion systems are given in table 13.

These values of K point out the adsorption process of organic inhibitors on the electrode surface and consequently the decrease of the corrosion rate. Further, we shell try to show what kind type of adsorption process takes place on the electrode surface. The adsorption equilibrium constant (K_{ads}) is related to the standard free energy of reaction by the equation:

$$\ln K_{ads} = -\left(\Delta G_T^\circ / RT\right) \tag{17}$$

The obtained values ΔG_{ads} up to -20Kjmol^{-1} are consistent with electrostatic interaction between the charged molecules (in our case, the inhibitor molecules) and the charged metal surface (physical adsorption), while those more negative than -40KJmol^{-1}, involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-coordinative type of bond (chemisorptions see table 13) [119-121].
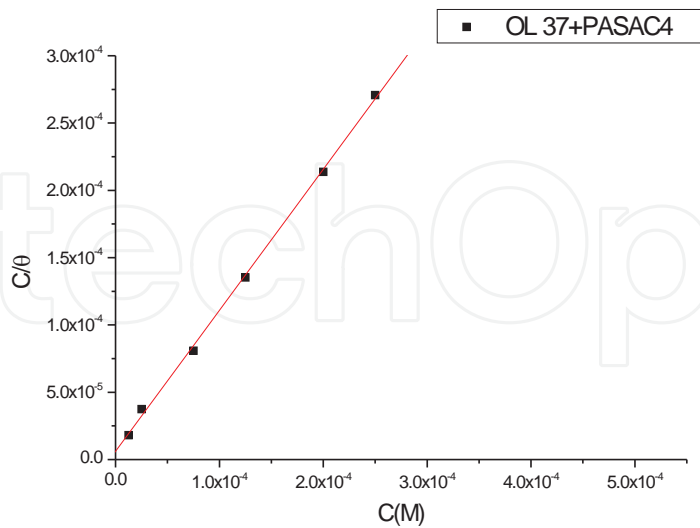
Figure 9. Langmuir plot for PASAC4+OL37 at different inhibitor concentrations
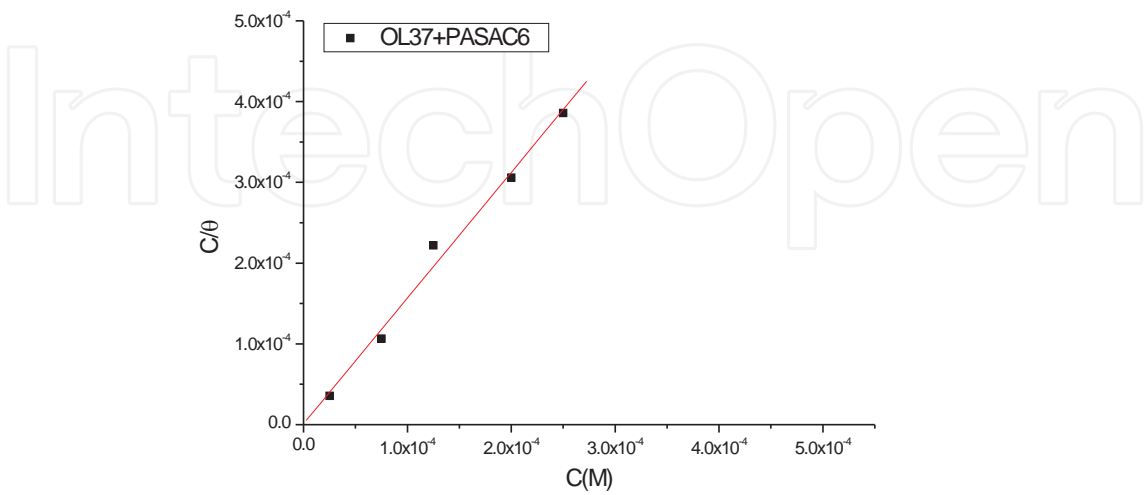
Figure 10. Langmuir plot for PASAC6+OL37 at different inhibitor concentrations
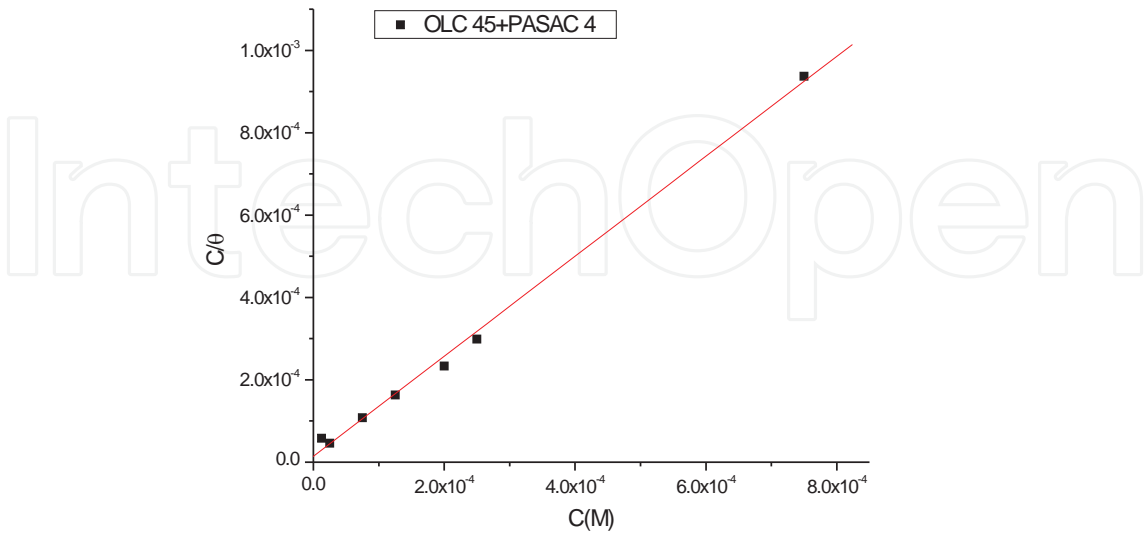
Figure 11. Langmuir plot for PASAC4+OLC-45 at different inhibitor concentrations
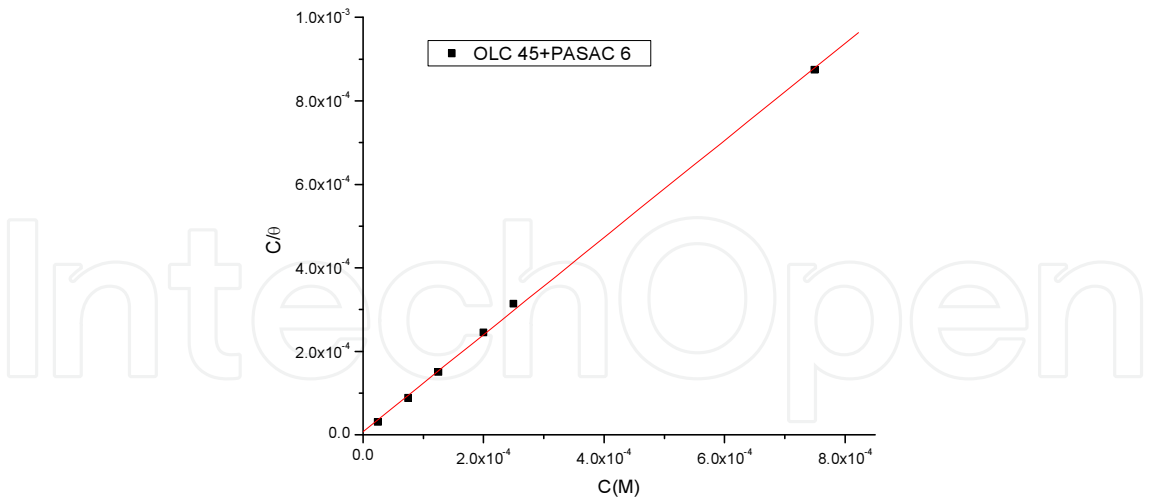
Figure 12. Langmuir plot for PASAC6+OLC-45 at different inhibitor concentrations
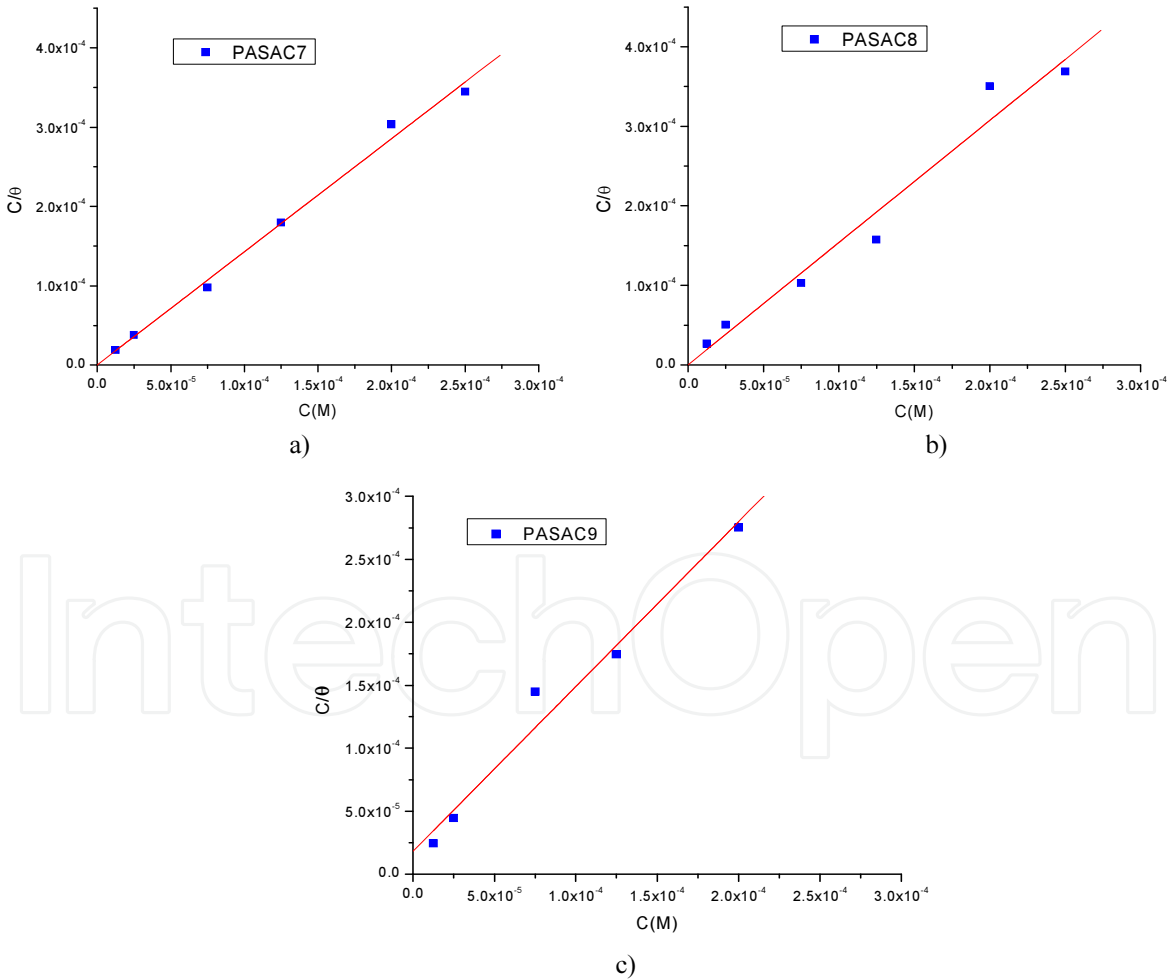
Figure 13. Langmuir plot for a)PASAC 7, b)PASAC 8 and c)PASAC 9 on OL 37 in S1 at different inhibitor concentrations

The system	Type of metallic material	Values of K_{ads}, M^{-1}	Values of ΔG°_{ads} KJM^{-1}	Type of adsorption
Cooling water type S_1+PASAC4	OL-37	1.675×10^5	-29.789	chemisorption and Physical adsorption
	OLC-45	6.959×10^4	-27.613	chemisorption and Physical adsorption
Cooling water S_1+PASAC6	OL-37	0.5981×10^4	-21.5356	Physical adsorption and chemisorption
	OLC-45	1.33547×10^5	-29.226	chemisorption and Physical adsorption
Cooling water S_1+PASAC7	OL-37	3.7703×10^6	-37.499	chemisorption and Physical adsorption
Cooling water S_1+PASAC8	OL-37	6.1846×10^6	-38.724	chemisorption and Physical adsorption
Cooling water S_1+PASAC9	OL-37	5.4895×10^4	-27.025	chemisorption and Physical adsorption

Table 13. The values of K_{ads} and ΔG°_{ads} for studied systems

2.3. FT-IR studies (Fourier transform infrared spectroscopy)

In this study, FT-IR spectrometry was used to identify whether there was adsorption and to provide new bonding information on the steel surface after immersion in the cooling water system containing organic inhibitor [120-122]. All spectra in these experiments were obtained at a resolution 4cm^{-1} in the region 650- 4000 cm^{-1}.

The FT-IR spectrum of pure organic polymer PASAC 4 is depicted in figure 14a and the FT-IR spectrum obtained for the carbon steel specimens (ol 37, OLC 45) immersed in cooling water systems type S1 containing 800ppm PASAC4 inhibitor organic is presented in figure 14b. A broad peak at 3345 cm^{-1} indicates the presence of the C-H bond of the pASAC4 and the appearance of the peak in region 1636 cm^{-1} and 1570 cm^{-1} corresponds to the C=O and N-H symmetric and asymmetric stretching vibration of the carbonyl group. The presence of C-N stretching frequency is clearly manifest in the region 1315 to 1200 cm^{-1}.

The FT-IR spectra obtained for the carbon steel specimens (ol 37, OLC 45) immersed in cooling water systems type S1 containing 800ppm PASAC4 inhibitor organic is presented in figure 14b. This shows the characteristics the bands for the adsorbed pasac 4 on the metal surface. A weak band in the range from 3674 cm^{-1} is attributed to C-H, the appearance of the peak in region

1596cm^{-1} is assigned to N-H symmetric stretching vibration. The peaks for C-N stretching modes can be assigned in the region around 1459 cm^{-1}.The bands 1170 cm^{-1}and 1060 cm^{-1}are attributed to C-O and C-N. moreover, these FT-IR measurements indicated at 3840 cm^{-1} the direct bonding between Fe atoms and Pasac 4 molecules via O and N atoms, and the formation Fe-inhibitor complex and this reveal that there is only chemical adsorption occurred on the surface of the metal.
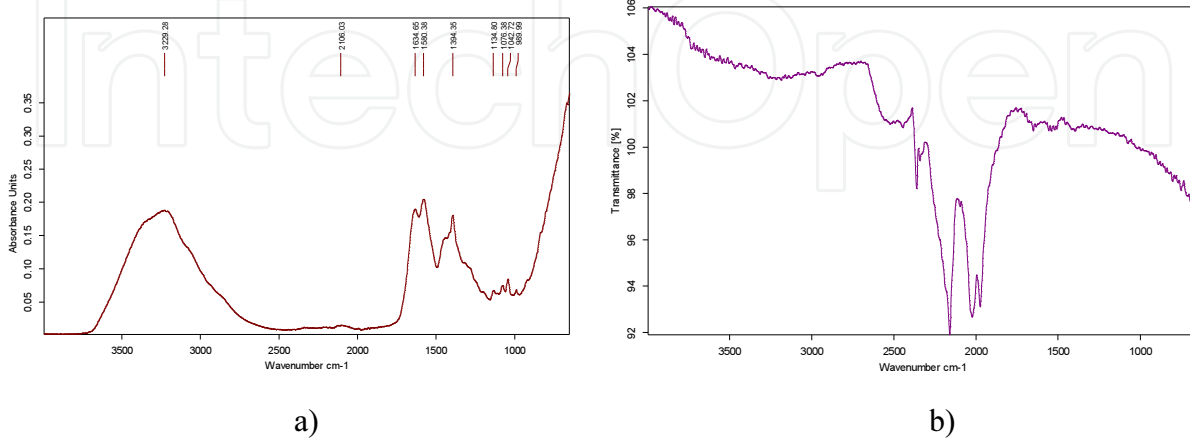
The FT-Ir spectrum of organic polymer PASAC6 and of carbon steel immersed in cooling water S1 containing 500ppm PASAC6 is show in figure 15a and 15b. In the spectra of PASAC6, the characteristics peaks at 1076 and 3291 cm^{-1} correspond to the C-O and O-H stretching of the COOH, peak at 1637 cm^{-1} indicates the presence of the C=O, the band at 1578 cm^{-1} is assigned to the bending of N-H. The band at 1393 cm^{-1} is ascribed to the stretching vibration C-N. The weak band at 1200-1000 cm^{-1} is attributed to C-H bending. The Ft-Ir spectra of adsorbed protective layer formed on the surface after immersion in S1 containing optimum concentration of inhibitor PASAC6 is shown in figure 15b. As can be seen all important peaks in pure compounds appeared in adsorption layer on the metal surface. The band around 3347 cm^{-1} is attributed to O-H stretching, which indicates that the protective film contains H$_2$O. The peak around 2978 cm^{-1} are assigned to C-H stretching vibration, the peaks at 1659 and 1433 cm^{-1} corresponds to the C=O and N-H.. The presence of C-N, C-O is indicated by their starching modes at 1078 and 820 cm^{-1}. The bands 3820 cm^{-1}and 3760 cm^{-1}are attributed to are assigned to Fe-O bending. This is already confirmed from the Langmuir adsorption isotherm studies
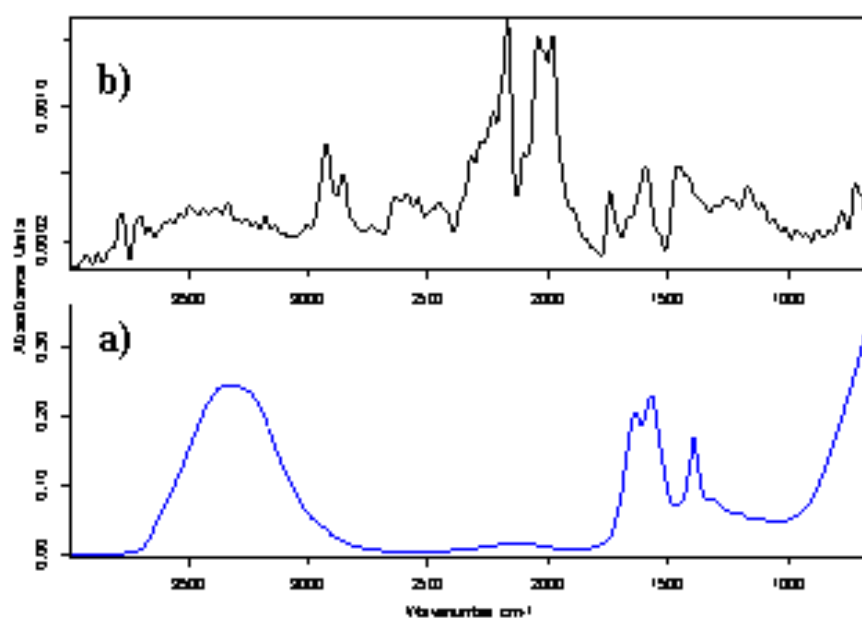
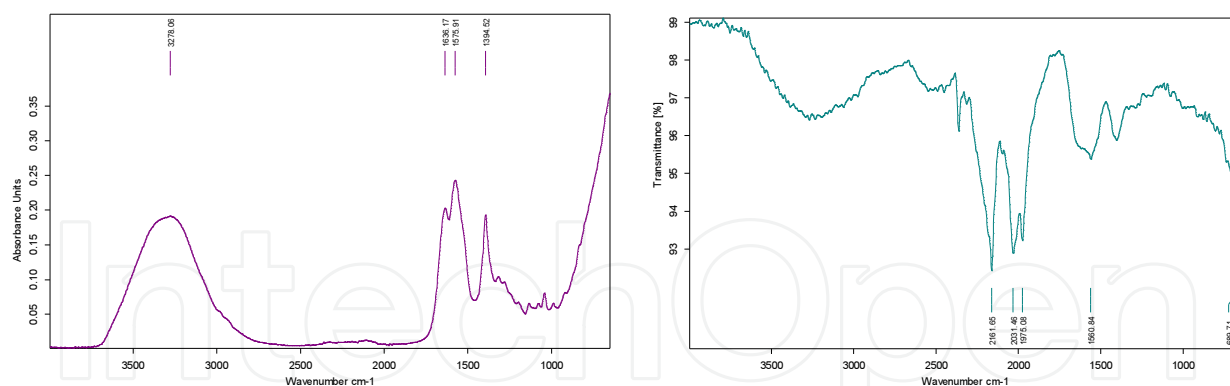**Figure 14.** FT-IR spectra of (a) PASAC 4 and (b) OL 37+800 ppm PASAC 4
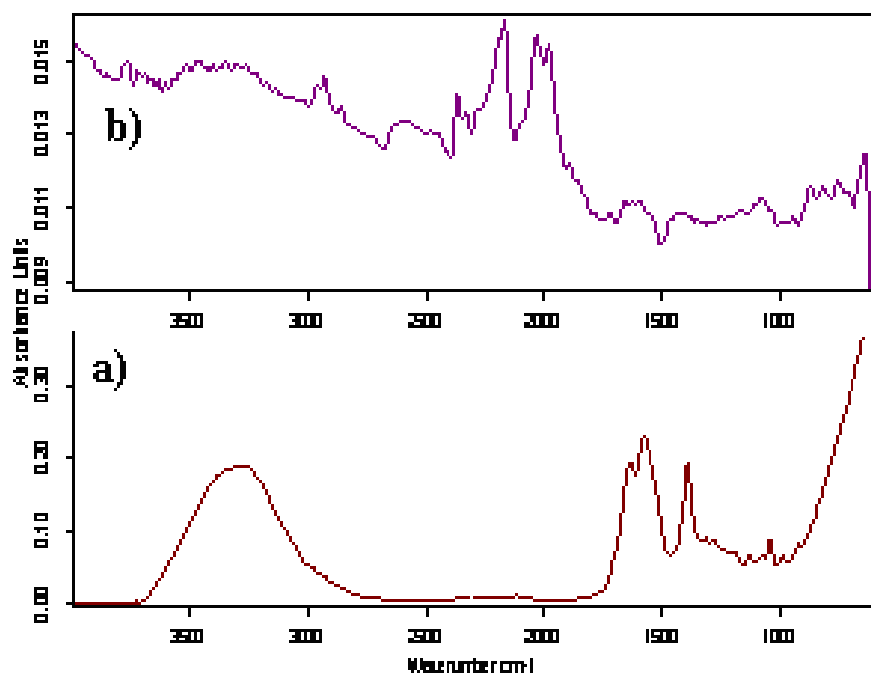
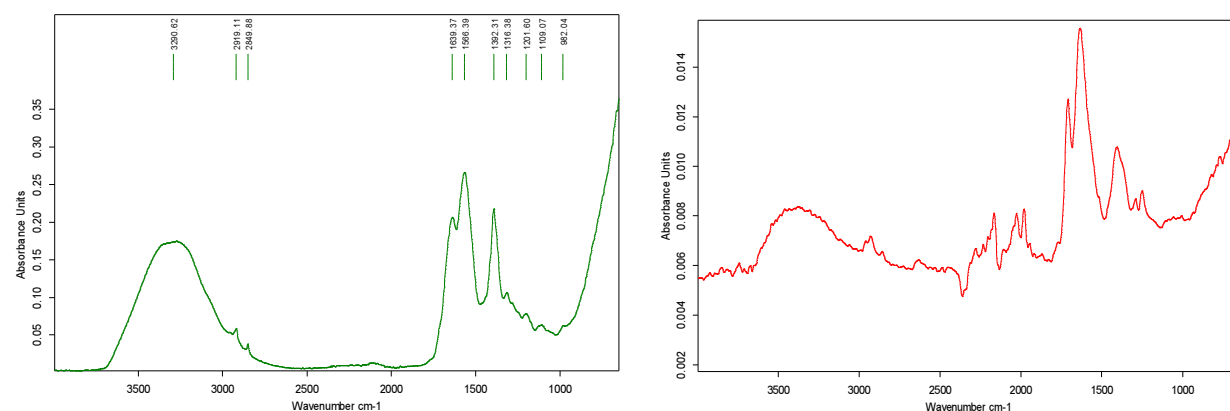**Figure 15.** FT-IR spectra of (a) PASAC 6 and (b) OLC 45+500 ppm PASAC 6

Figure 16. FT-IR spectra of (a) PASAC7 and (b) OL 37+300 ppm PASAC7+S1

Figure 17. FT-IR spectra of (a) PASAC8 and (b) OL 37+500 ppm PASAC8+S1

Figure 18. FT-IR spectra of (a) PASAC9 and (b) OL 37+800 ppm PASAC9+S1

The FT-Ir spectrum of organic polymer PASAC7 and 300ppm PASAC7+OL37+S1 is show in figure 16a and 16b. This shows the characteristic bands for the adsorbed PASAC 7 on the metal surface. A weak band in the range 3000-3500cm^{-1}, can be assigned to presence of O-H. The presence of C-H, C=O, N-H, C-N, and C-O is indicated by their stretching modes at 2992, 1642, 1443, 1062 and 810 cm^{-1} respectively.

The FT-IR spectrum of organic polymer PASAC8 and of carbon steel immersed in cooling water S1 containing 500ppm PASAC8 is show in figures 17a and 17b. The Ft-Ir spectra of adsorbed protective layer formed on the surface after immersion in S1 containing optimum concentration of inhibitor 500ppm PASAC8 is shown in figure 17b. As can be seen all important peaks in pure compounds appeared in adsorption layer on the metal surface. The band around 3247 cm^{-1} is attributed to O-H stretching, which indicates that the protective film contains H$_2$O. The peak around 2878 cm^{-1} are assigned to C-H stretching vibration, the peaks at 1560 and 1423 cm^{-1} corresponds to the C=O and N-H. The presence of C-N, C-O is indicated by their starching modes at 1078 and 789 cm^{-1}. The bands 3820 cm^{-1} and 3760 cm^{-1} are attributed to are assigned to Fe-O bending. This is already confirmed from the Langmuir adsorption isotherm studies.

The FT-Ir spectrum of pure organic polymer PASAC 9 is depicted in figure 18a and the FT-IR spectrum obtained for the ol 37 immersed in cooling water systems type S1 containing 800ppm PASAC9 inhibitor organic is presented in figure 18b. A broad peak at 3325 cm^{-1} indicates the presence of the C-H bond of the pASAC9 and the presence of C=O, N-H, C-H is indicated by their stretching modes at region 1632, 1581 1315 to 1200 cm^{-1} respectively. The FT-IR spectra obtained for the carbon steel specimen (ol 37) immersed in cooling water systems type S1 containing 800ppm PASAC9 inhibitor organic is presented in figure 18b. A broad band in the range from 3684 cm^{-1} is attributed to C-H, the appearance of the peak in region 1598cm^{-1} is assigned to N-H symmetric stretching vibration. The peaks for C-N stretching modes can be assigned in the region around 1459 cm^{-1}.The bands 1200 cm^{-1}and 1100 cm^{-1}are attributed to C-O and C-N. moreover, these FT-IR measurements indicated at 3800 cm^{-1} the direct bonding between Fe atoms and Pasac 9 molecules via O and N atoms, and the formation Fe-inhibitor complex and this reveal that there is only chemical adsorption occurred on the surface of the metal. This is already confirmed from the Langmuir adsorption isotherm studies.

2.4. EIS – (electrochemical impedance spectroscopy) studies

The corrosion of carbon steel in cooling water system S1and S2 in the absence and presence of PASAC-4, PASAC-5, PASAC-6, PASAC-7, PASAC-8 and PASAC-9 were investigated by EIS. Impedance measurements were performed at open circuit potential on the frequency range between 100 kHz and 40 mHz with an AC wave of ± 10 mV (peak-to-peak) and the impedance data were obtained at a rate of 10 points per decade change in frequency. Nyquist plots for carbon steel obtained at the interface in the presence of inhibitors at optimum concentration are given in figures 19-22. All impedance spectra exhibit one capacitive loop and the diameter of the semicircles increases on increasing the inhibitor concentration suggesting that the formed inhibitive film was strengthened by the addition of inhibitors. However, these diagrams are not perfect semicircles which are attributed to frequency dispersion. The semicircular appearance shows that the corrosion of steel is controlled by charge transfer and the presence of inhibitor does not change the mechanism of dissolution [121-125]. Figures 19-22 also indicates that the diameters of the capacitance loops in the presence of PASAC-4, PA-SAC-5, PASAC-6, PASAC-7, PASAC-8 and PASAC-9 are bigger than that in the absence of organic inhibitors, suggesting that PASAC-4, PASAC-5, PASAC-6, PASAC-7, PASAC-8 and PASAC-9 has good anticorrosion performance on the carbon steel in S1

Bode diagrams presented in figures 23-27- are in accordance with Nyquist diagrams. It can be observed that in absence of organic inhibitor the electrode presents one time constant corresponding to a phase angle of about 25° at medium and low frequencies, this fact indicates an inductive behaviour with low diffusive tendency. On the contrary, in the presence of the organic inhibitor, on the curve-phase angle versus log frequency appears a maximum very well defined corresponding to a phase angle of about 70° which means that in this case the electrode has a strong capacitive behaviour, according with the results obtained by electrochemical polarization and in concordance with the Nyquist diagrams. All the obtained plots show only one semicircle and they were fitted using one time constant equivalent mode with capacitance (C), the charge transfer resistance (R$_{ct}$) and Rs solution resistance. The lower
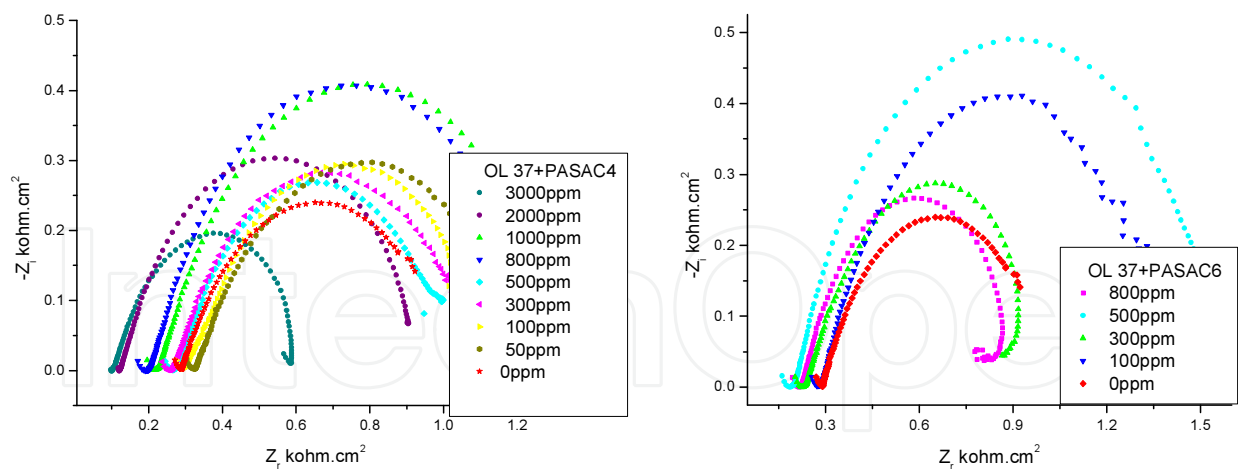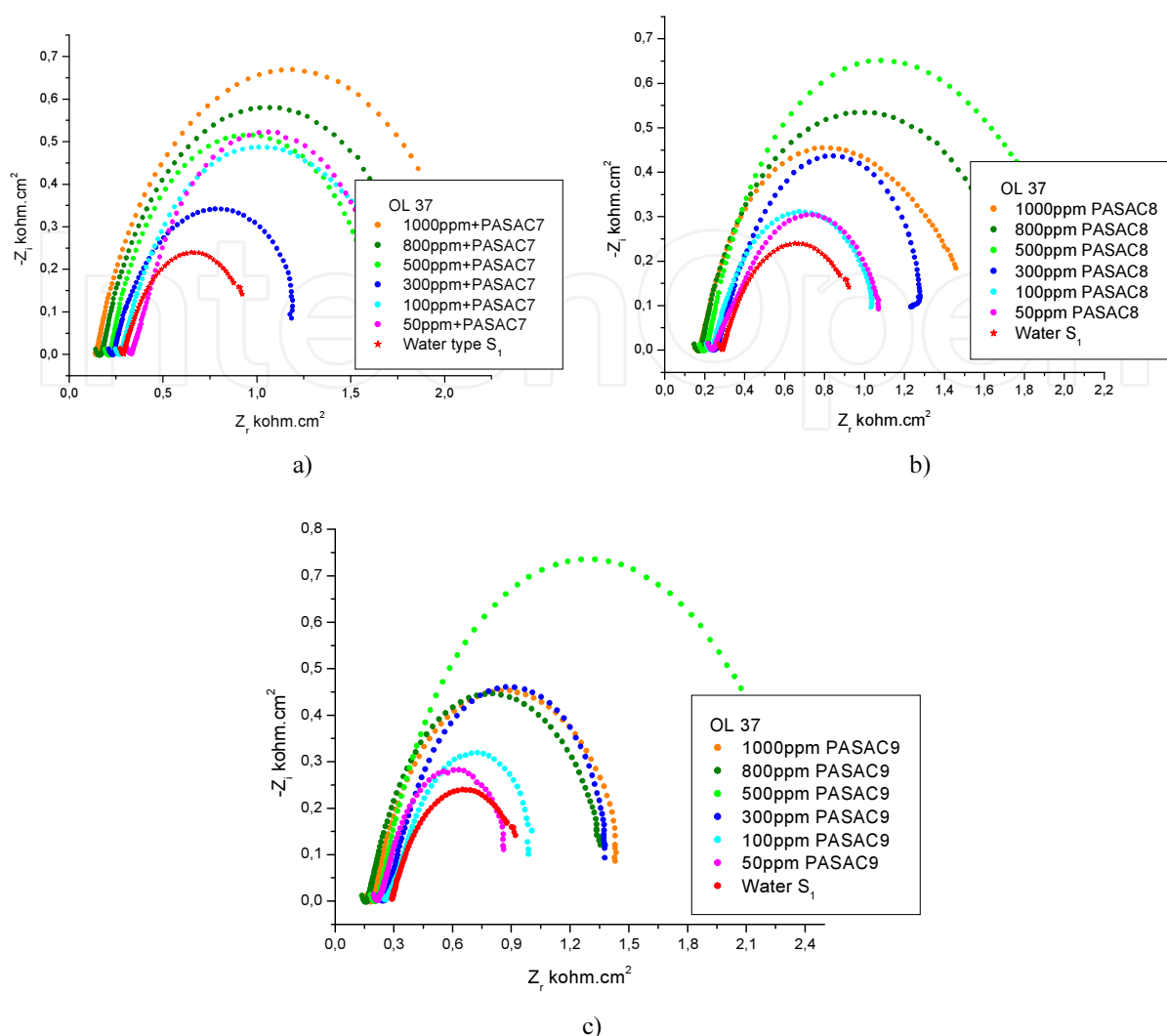
Figure 19. The Nyquist plot for OL 37+ PASAC4 and for OL 37+ PASAC6 in $S_1$with and without organic inhibitor at 25°C
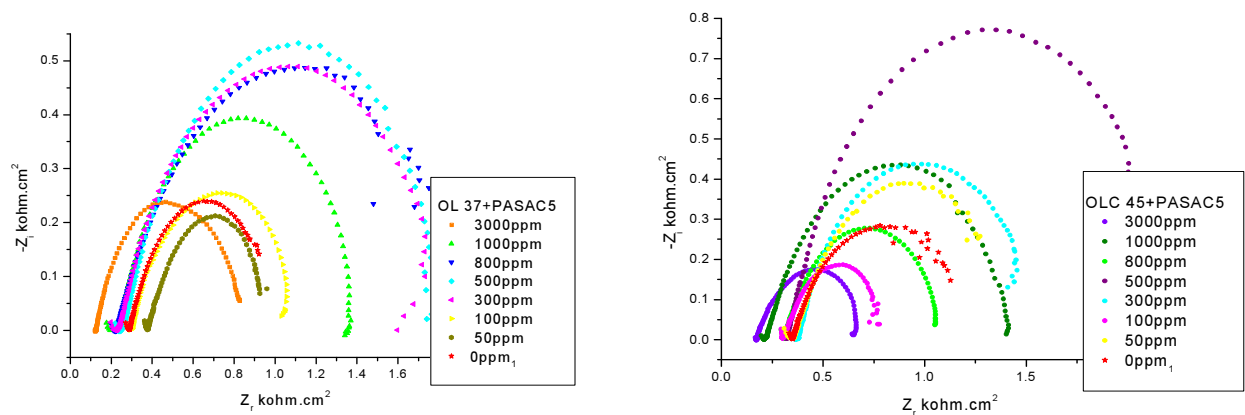
Figure 20. The Nyquist plot for OL 37+ PASAC5 and OLC 45+ PASAC5 in S1with and without organic inhibitor at 25°C
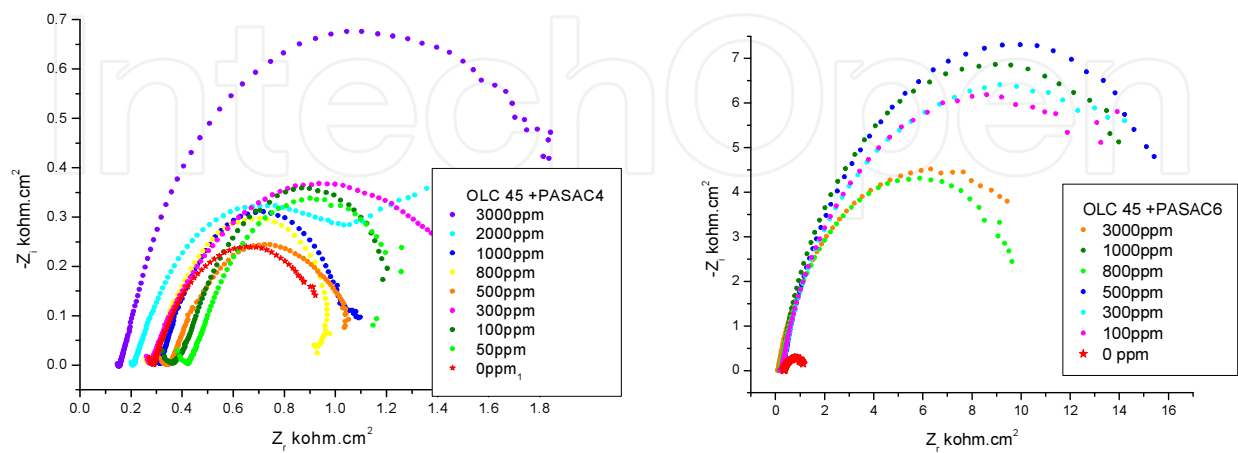
Figure 21. The Nyquist plot for OLC 45+ PASAC4 and OLC 45+ PASAC6 in $S_1$with and without organic inhibitor at 25°C

Figure 22. The Nyquist plot for OL 37 in S1 with and without organic inhibitor at 25°C a) PASAC7, b) PASAC8, c) PA-SAC9

capacitance value for S1+OLC 45 with PASAC 4 and PASAC6 medium indicates the inhomogeneity of surface of the metal roughened due to corrosion. The C_{dl} values decreases on the increasing the inhibitor concentration and reaches very low value for the optimum concentrations of all the studied systems indicating that the reduction of charged accumulated in the double layer due to the formation of adsorbed inhibitor layer.

The Bode plots are shown in figures 23-27 are in accordance with Nyquist diagrams. It can be observed that in absence of organic inhibitor the electrode presents one time constant corresponding to a phase angle of about 20° at medium and low frequencies, this fact indicates an inductive behaviour with low diffusive tendency. On the contrary, in the presence of the organic inhibitor, on the curve-phase angle versus log frequency appears a maximum very well defined corresponding to a phase angle of about 70° which means that in this case the electrode has a strong capacitive behaviour, according with the results obtained by electrochemical polarization and in concordance with the Nyquist diagrams.
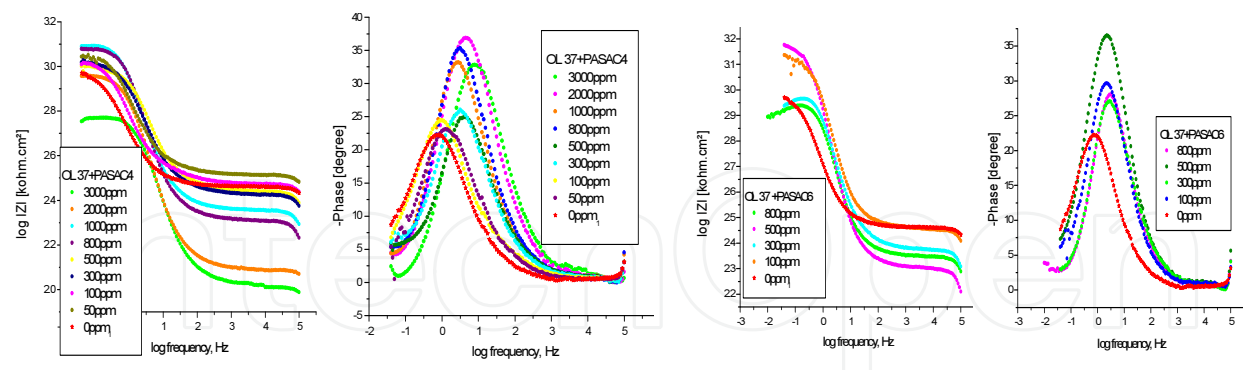
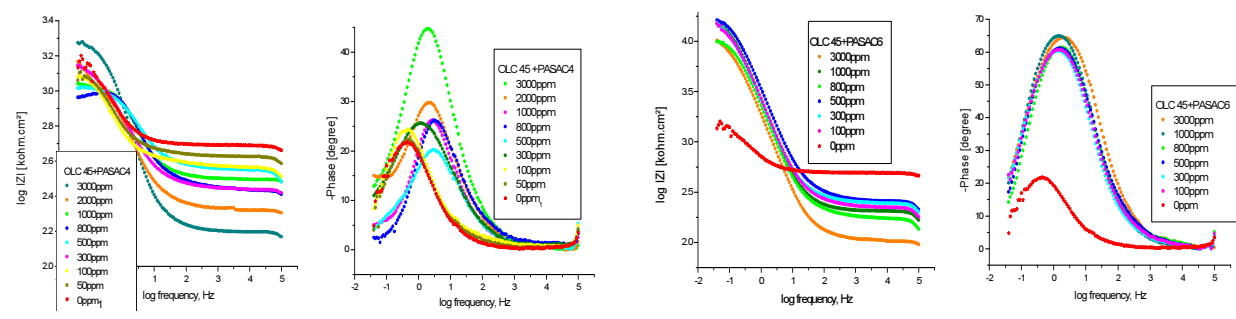**Figure 23.** The Bode plot for OL 37+PASAC 4 and PASAC 6in S_1 at 25°C

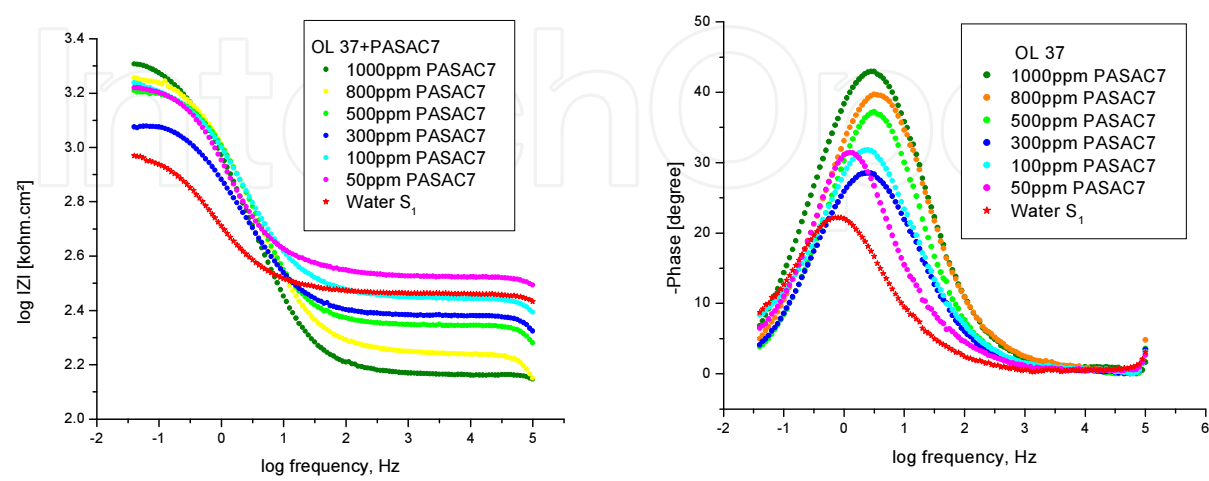**Figure 24.** The Bode plot for OLC 45+PASAC4 and OLC 45+PASAC 6 in S_1 at 25°C
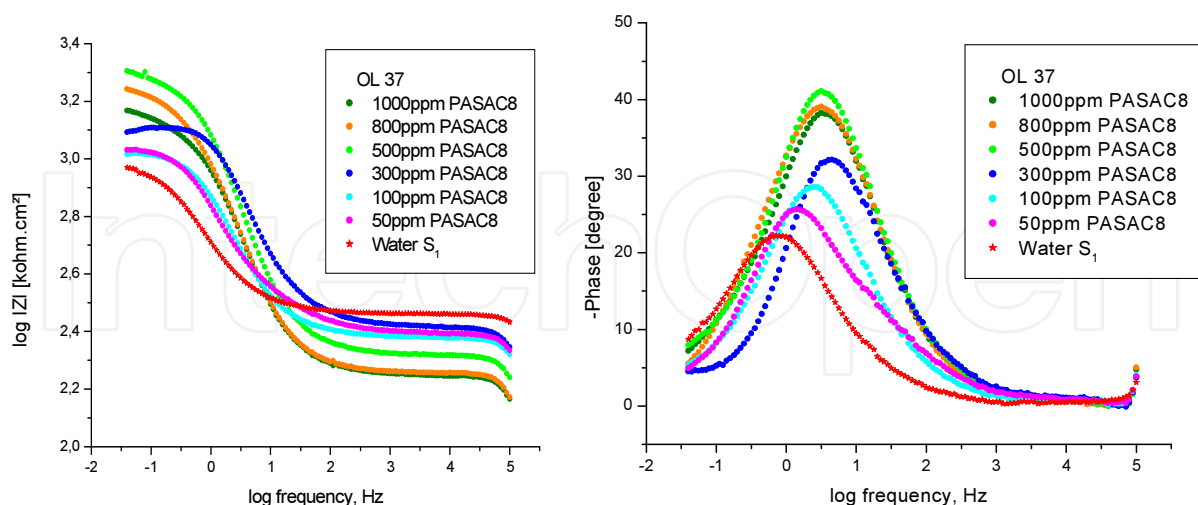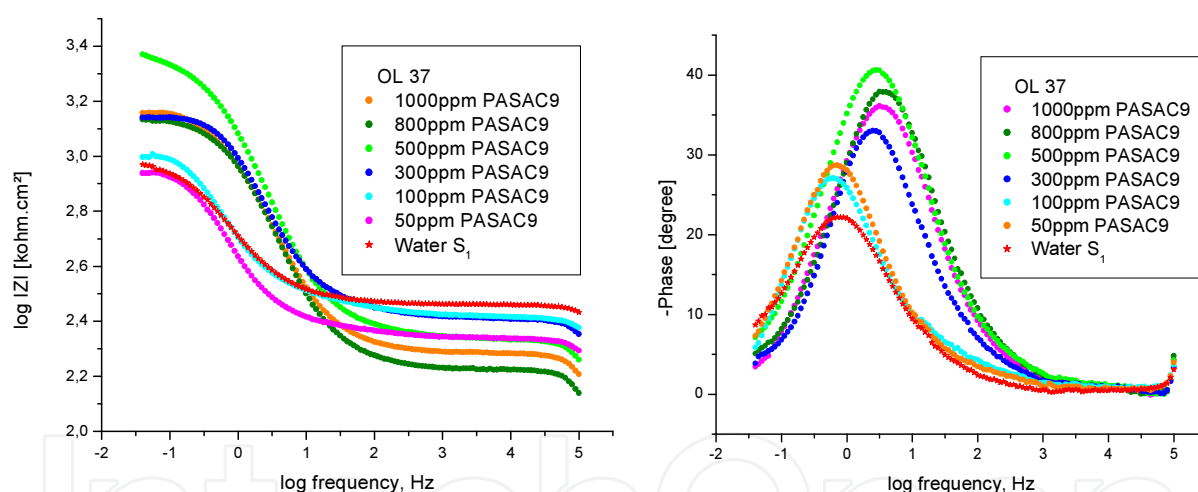
**Figure 25.** The Bode plot for OL 37+ PASAC7 in S_1 at 25°C

Figure 26. The Bode plot for OL 37+ PASAC8 in S_1 at 25ºC

Figure 27. The Bode plot for OL 37+ PASAC9 in S_1 at 25ºC

All the obtained plots show only one semicircle and they were fitted using one time constant equivalent mode (see figure 28) with capacitance (Cdl), values is affected by imperfections on the surface which is simulated via a constant phase element (CPE), the charge transfer resistance (R_2) and R_1 solution resistance. The lower capacitance value for S1+OL37 with PASAC 7 and PASAC8, medium indicates the inhomogeneity of surface of the metal roughened due to corrosion. The Cdl values decreases, the R_2 values increases on the increasing the inhibitor concentration and reaches very low value for the optimum concentrations of all the studied systems indicating that the reduction of charged accumulated in the double layer due to the formation of adsorbed inhibitor layer.
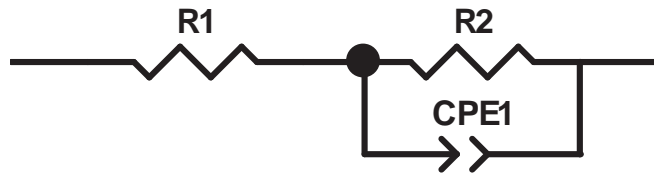
Figure 28. Equivalent circuit
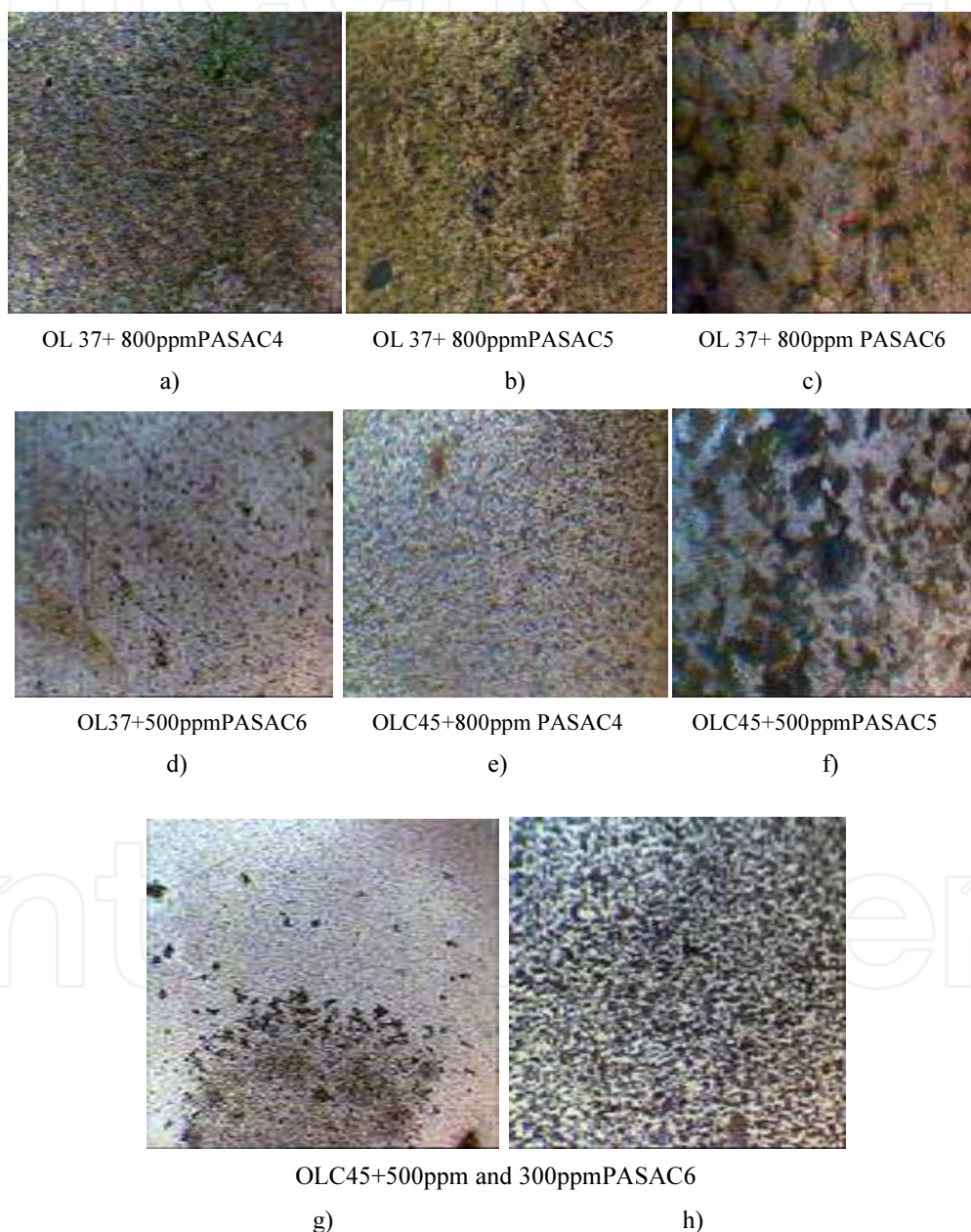
2.5. Microscopic studies of the electrode surfaces

Further, using the metallographic microscope the electrode surfaces were analyzed before and after a certain immersion in cooling water type SC1and SC2. In figure 29-31 are given a few micrographies obtained for the following systems: carbon steel OL 37 and OLC-45 after a certain immersion in cooling water type SC1 and SC2 with and without organic inhibitor. As it can be observed from figures 29-31 the corrosive attack is more accentuated in the cooling water system where the organic inhibitor concentration is lower than in the cases for which the organic inhibitor concentration is higher (see in comparison the micrographies from figure 29-31) [125-127]. Analyzing in comparison the figures 29-31, it can be observed that, on the surface of micrographies there are the adsorbed films of inhibitor and corrosion products and that, these films are thicker if the inhibitor concentration are higher. These films behave like a barrier between corrosive medium and metal surface and as a consequence the corrosion process is inhibited - see in comparison the figures 29-31. Analyzing in comparison the figures
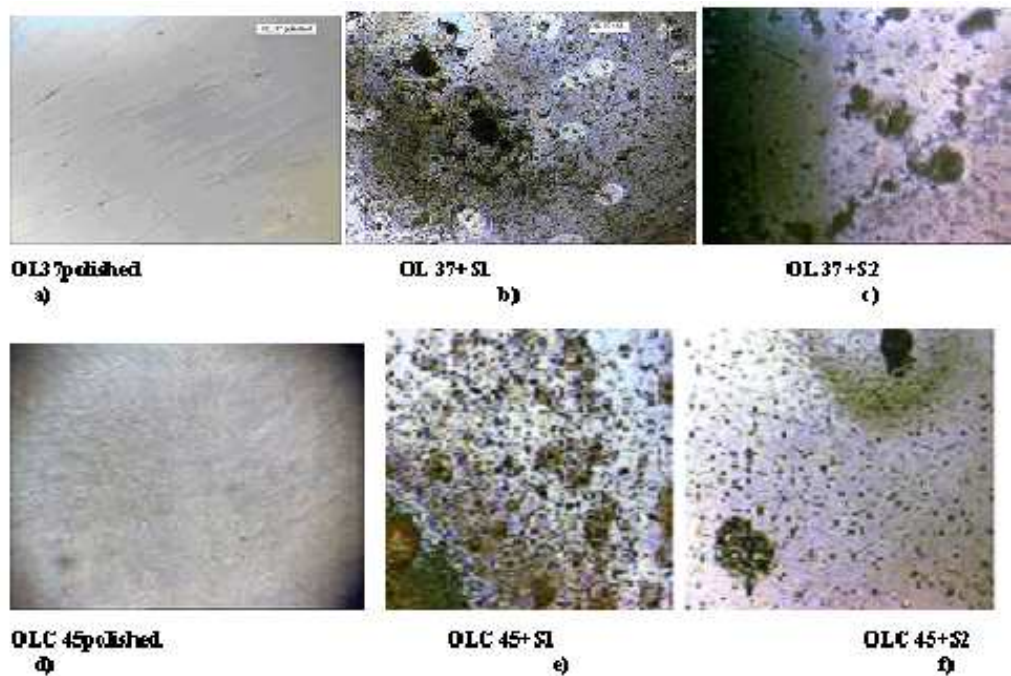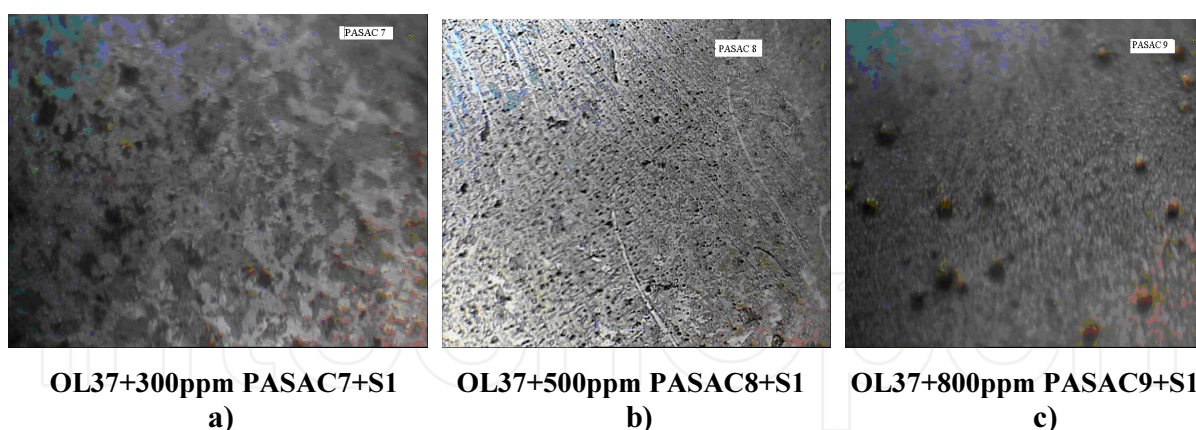

Figure 29. micrographies of the carbon steels in cooling water SC1 and SC2:a) OL 37 polished, b) Ol37+SC1, c) Ol37+SC2, d) OLC 45 polished, e), OlC 45+SC1 and f) OlC 45+SC2

29 a-d and figure 30-31 it can be observed that, the corrosive attack is much more accentuated in the case of OL 37+ water type S1 and OLC 45+ water type S1 system than in the case of OL-37+ water type S1 +800ppm PASAC4, 800ppm PASAC5, 800ppm/500ppm PASAC6, OL37+300ppm PASAC-7, OL37+500ppm PASAC-8 and OL37+800ppm PASAC-9 system. The same behaviour was observed for OLC 45 (see in comparison figures 30 e, f g, and h). This finding is in good concordance with the results obtained by electrochemical method (see tables 4 - 12) and the polarization curves from figures 1-5.

OL 37+ 800ppmPASAC4	OL 37+ 800ppmPASAC5	OL 37+ 800ppm PASAC6
a)	b)	c)
OL37+500ppmPASAC6	OLC45+800ppm PASAC4	OLC45+500ppmPASAC5
d)	e)	f)

OLC45+500ppm and 300ppmPASAC6

g)   h)

Figure 30. Micrographies of the carbon steel in cooling water SC1 with organic inhibitor; a) OL37+800ppm PASAC-4, b)OL37+800ppm PASAC-5, c) OL37+800ppm PASAC-6, d) OL37+500ppm PASAC-6, e) OLC45+800ppm PASAC-4, f) OLC 45+500ppm PASAC-5, g) OLC 45+500ppm PASAC-6 and h) OLC 45+300ppm PASAC-6

OL37+300ppm PASAC7+S1
a)

OL37+500ppm PASAC8+S1
b)

OL37+800ppm PASAC9+S1
c)

Figure 31. micrographies of the carbon steel in cooling water SC1 with organic inhibitor; a) OL37+300ppm PASAC-7 b)OL37+500ppm PASAC-8 and c) OL37+800ppm PASAC-9

3. Conclusions

Investigated corrosion systems at low overvoltages, the corrosion process are under activation control, while at high overvoltages is controlled by diffusion.

- The addition of organic inhibitors led in all cases to the inhibition of the corrosion process.

- The new organic polymer obtained by our team presented a good inhibitory action and a significant efficiency for decreasing of the rate corrosion of the studied carbon steels;

- The organic inhibitors were adsorbed on the carbon steel surface according to a Langmuir isotherm. The values of the adsorption constant determined from the plot of Langmuir isotherm pointed out that, there are both physical and chemical adsorptions.

- FT-IR spectra revealed very clear that the new organic inhibitors: PASAC-4, PASAC-5, PASAC-6, PASAC-7, PASAC-8 and PASAC-9 were adsorbed on the metal surface.

- The adsorption of investigated organic inhibitor follows the Langmuir isotherm and the FT-IR results, also reveals the adsorption of 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 methods.

- PASAC-4, PASAC-6, PASAC-7, PASAC-8 and PASAC-9 inhibit both anodic and cathodic reactions by adsorption on the carbon steel surface and hence behave like mixed type inhibitor. PASAC5 acts preferentially as a cathodic inhibitor.

- In all of the cases, the organic inhibitor type PASAC-4 had a higher efficiency; PASAC-6 had a good efficiency than the organic inhibitor type PASAC-5. The inhibition efficiency follows the order: PASAC4>PASAC6>PASAC5

- In all of the cases, the organic inhibitor type PASAC-8 had a higher efficiency; PASAC-7 had a good efficiency than the organic inhibitor type PASAC-9. The inhibition efficiency follows the order: PASAC8>PASAC7>PASAC9.

The inhibition efficiency follows the order: $E_{PASAC4} > E_{PASAC6} > E_{PASAC5}$ $E_{PASAC8} > E_{PASAC7} > E_{PASAC9}$

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References

[1] H. H. Uhlig and R.W.Revie, "Corrosion and Corrosion Control", Whiley, New York, 3rd edn. 1985.

[2] D. Jones, "Principle and Prevention of Corrosion", MacMillan Publishing Company, New York, 1992.

[3] M.A.Quraishi, H.K.Sharma, *Mater.Chem.Phys*, 2002, 72,18

[4] W.H.Li, Q. He, C.L. Pei, B.R.Hou, Electrochim.Acta 52, 2007, 6386.

[5] L.Tang, X.Li,,G.Mu, G.Liu, *Mat.Chem.Phys*.97, 2006, 301

[6] Florina Branzoi, V. Branzoi, and I. Harabor, *Revue Roumaine de Chimie*, vol. 56 (2), 487-115-128, 2011.

[7] J. L. Rozenfeld, "Corrosion Inhibitors", McGraw-Hill, New York, 1981, p.109.

[8] V. Branzoi, and Florina Branzoi, *Rev Roum Chim.*, 2002, *47*, 1193-1203

[9] V.Branzoi, F. Golgovici, Florina Branzoi, *Materials Chemistry and Physics*, 78, 2002, 122-131

[10] D. P. Schwensberg and V. Ashworth, *Corros. Sci.*, 1988, *28*, 539.

[11] V. Branzoi, Florina Branzoi and L.Pilan, *Materials Chemistry and Physics*, 2009,*118*, 197.

[12] A. Stanca, V. Branzoi, Florina Branzoi, *International Journal of Chemical and Biomolecular Engineering*, vol.1, nr.2, pp.98-103, 2008

[13]   T. Hirai, J. Yamaki, T. Okada and A. Yamagi, *Electrochim. Acta*, 1985, *30*, 61.

[14]   D. G. Leaist, *J. Chem. Soc. Faraday Trans.*, 1990, *86*, 3487.

[15]   E. Kamis, F. Bellucci, R. M. Latonision and E. S. H. El-Ashry, *Corrosion* 1991, *47*, 677.

[16]   M. Beier and J. W. Schultze, *Electrochim. Acta* 1992, *37*, 2299.

[17]   F. Donahue and K. Nobe, *J. Electrochemical. Soc.* 1965, *112*, 886.

[18]   Y. A. Aleksanyan, I. I. Reformatskaya and A. N. Podobaev, *Protection of Metals*, 2007, *43*, 125-128.

[19]   E.M. Sherif and Su-Moon Park, *Electrochimica Acta*, 2006, *51*, 4665-4673.

[20]   V. Branzoi, Florina Branzoi, Luisa Pilan, Florentina Golgovici, *Molecular Crystal &Liquid Crystals*, vol.446, 2006

[21]   M. J Incorvia and S. Contarini, *J.Electrochem.Soc.* 1989, *136*, 2493.

[22]   F. Mansfeld, "Corrosion Mechanism", Marcel Dekker (ed.), New York, 1987, p.119.

[23]   V. Branzoi, F. Branzoi and L. Pilan, *Molec. Crystal &Liquid Crystals*, 2006,*446*, 305.

[24]   G. Banerjee and S. N Malhotra., *Corrosion*, 1992, *48*, 10.

[25]   V. Branzoi, A. Pruna, Florina Branzoi, *Revista de Chimie*, vol.59, nr.5,pp.540-543, 2008

[26]   V. Branzoi, A. Pruna and Florina Branzoi, *Rev Roum Chim.*, 2007, *52*, 587.

[27]   P.Ramesh P, B.Babu, K.Thangavel, Anti-Corros Methods Mater, 2005, 52, 219.

[28]   L Larabi, O Benali, Y Harek, Mater Lett, 2007, 61, 3287

[29]   AS Fouda, HA Mostafa, GY Elewady, Corros Sci, 2005, 47, 1988

[30]   R Yurchenko, L. Pogrebova, L Pilipenko, T Shubina, Russian J. Appl Chem, 2009, 79, 1100

[31]   SA Hossain, AL Almarshad, Corros Eng Sci Technol, 2006, 41, 77.

[32]   S Abd El-Wahaab, G.Gomma, HY El-Barradie, J Chem Technol Biotechnol, 2007, 36, 435

[33]   S Muralidharan, SVK Iyer, Anti-Corros Methods Mater, 1997, 44, 100

[34]   MA Quraishi, MAW Khan, M Ajmal, Anti-Corros Methods Mater, 1996, 43, 5

[35]   F Bentis, M Traisnel, M Lagrenee, J Appl Electrochem, 2001, 31, 41

[36]   M. Sahin, S Bilgic, Anti-Corros Methods Mater, 2003, 50, 34

[37]   M Lebrini, F Bentis, F Bezin, M Lagrenee, Corros Sci, 2006, 48, 1279

[38]   GK Goma, Mater Chem Chem, 1998, 34, 833

[39] L Larabi, Y Harek, m Traisnel, A Mansri, J. Appl Electrochem, 2004, 34, 833

[40] RS Chaudhary RS, H Kumar, Indian J Chem Tech, 2004, 11, 783-786

[41] E.E. Oguzie, Y. Li, F.H. Wang J.Colloid Interface Sci. 310 (2007) 90–98.

[42] P.C. Okafar, Y. Zheng, Corros. Sci. 51 (2009) 850–859.

[43] C. Jeyaprabha, S. Sathiyanarayanan, G. Venkatachari, J.Electroanal. Chem. 583 (2005) 232–240.

[44] S.S. Abdel Rehim, O.A. Hazzazi, M.A. Amin, K.F. Khaled, Corros. Sci. 50 (2008)

[45] 2258–2271.

[46] C. Jeyaprabha, S. Sathiyanarayanan, G. Venkatachari, Electrochim. Acta 51 (2006) 4080–4088.

[47] S.A. Umeron, O. Ogbobe, I.O. Igwe, E.E. Ebenso, Corros. Sci. 50 (2008) 1998–2006.

[48] G.K. Gomma, Mater. Chem. Phys. 55 (1998) 241–246.

[49] A.A. Atia, M.M. Saleh, J. Appl. Electrochem. 33 (2003) 171–177.

[50] M.M. Saleh,, Mat. Chem. Phys. 98 (2006) 83–89.

[51] M.M. Saleh, A.A. Atia, J. Appl. Electrochem.36 (2006) 899–905.

[52] F. Bentiss, M. Lagrenee, M. Traisnel, Corrosion 2000, 56, 733.

[53] P. Bothi Raja, M. G. Sethuraman, Mater. Corros. 2009, 60, 22.

[54] V. S. Sastry, Corrosion Inhibitors: Principles and Applications, John Wiley & Sons, New York, 1998.

[55] S. M. A. Hosseini, A. Azimi, Mater. Corros. 2008, 59, 41.

[56] M. Bouayed, H. Rabaa, A. Srhiri, J. Y. Saillard, A. Ben Bachir, Le Beuzed, Corros. Sci. 1999, 41, 501.

[57] L. B. Tang, X. M. Li, H. C. Liu, G. N. Mu, G. H. Liu, J. Mater.Sci. 2006, 41, 1991.

[58] Sekine, Y. Nakahata, H. Tanabe, Corros. Sci. 1988, 28, 987.

[59] M. G. Fontana, Corrosion Engineering, 3rd edition, McGraw-Hill, Singapore, 1986.

[60] H. Farooqi, A. Hussaiin, M. A. Quaraishi, P. A. Saini,Anti-Corrosion 1999, 46, 328.

[61] Z. Lu, Corros. Prot. 1999, 20, 201.

[62] G. Trabanelli, F. Mansfeld (Ed.), Corrosion Mechanisms, Marcel Dekker, Inc., New York, 1987.

[63] U.S. Congress, Office of Technology Assessment, Biopolymers: Making Materials Nature's Way, 1993.

[64]   W. Hater, B. Mayer, M. Schweinsberg, Power Plant Chem.2000, 12, 721.

[65]   C. S. Sikes, A. P. Wheeler, Chemtech 1988, 18, 620

[66]   M. A. Amin, J. Appl. Electrochem. 2006, 36, 215.

[67]   F. Mansfeld, M. W. Kending, S. Tsai, Corrosion 1982, 38, 570.

[68]   C. B. Breslin, W. M. Carrol, Corros. Sci. 1993, 34, 327.

[69]   M. G. A. Khedr, M. S. Lashien, Corros. Sci. 1992, 33, 137.

[70]   S. S. A. Rehim, H. H. Hassan, M. A. Amin, Mater. Chem. Phys. 2001, 70, 64.

[71]   M. R. Saleh, A. M. Shams El Din, Corros. Sci. 1981, 12, 688.

[72]   K. Maayta, N. A. F. Al-Rawashdeh, Corros. Sci. 2004, 46,

[73]   A. Mohammed, J. Appl. Electrochem. 2006, 36, 215.

[74]   M. Abdallah, E. A. Helal, A. S. Fouda, Corros. Sci. 2006, 48,1639.

[75]   A.Igual Muñoz, J. García Antón, J.L. Guiñón, V. Pérez Herranz, Electrochimica Acta 50(2004), 957

[76]   P. Kern, D. Landolt, Electrochim. Act. 2001, 47, 589.

[77]   P. Kern, D. Landolt, J. Electrochem. Soc. 2001, 148 (6), B228.

[78]   P. Kern, D. Landolt, Electrochim. Act. 2002, 44, 1809.

[79]   L. J. Vracar, D. M. Drazic, Corros. Sci. 2002, 44 1669.

[80]   S. L. Granese, B. M. Rosales, C.Ovideo, J. O. Zerlino, Corros.Sci. 1992, 33, 1439.

[81]   W. Pleith, Electrochim. Acta. 1992, 37, 2115.

[82]   H. Akrout, L. Bousselmi, E. Triki, S. Maximovtch, F. Dalard, J. Mater. Sci. 2004, 39, 7341.

[83]   E.M.Sherif, Su-Moon Park, Electrochimica Acta 51(2006) 6556

[84]   El-Sayed M. Sherif, Applied surface science 252 (2006) 8615

[85]   E.M.Sherif, Su-Moon Park, Corrosion science 48 (2006) 4065

[86]   El-Sayed M.Sherif, A.M.Shamy, Mostafa M.Ramla, Ahmed O.H.El Nazhawy, Materials chemistry and physics 102 (2007) 231

[87]   Gy. Vastag, E. Szöcs, A. Shaban, E. Kálmán, Pure Appl. Chem., 73 (2001) 1861

[88]   F.Zucchi, G.Trabanelli, M.Fonsati, Corrosion science, 38 (1996) 2019

[89]   E.Szõcs, Gy.Vastag, A.Shaban, E.Kálmán, Corrosion Science 47 (2005) 893

[90]   X.R.Ye, X.Q.Xin, J.J.Zhu, Z.L.Xue, Applied Surface Science 135 (1998)307

[91] J.C.Marconato, L.O.Bulhões, M.L.Temperini, Electrochimica Acta 43(1998)771

[92] R.Subramanian, V. Lakshminarayanan, Corrosion Science 44 (2002) 535

[93] S. Ramesh, S.Rajeswari, Corrosion Science 47 (2005) 151

[94] El-Sayed M.Sherif, R.M.Erasmus, J.D.Comins, Journal of colloid and interface science 311 (2007), 144

[95] F. Bentiss, M. Lagrenee, M. Traisnel, Corrosion 56 (2000) 733–742.

[96] M. Bouayed, H. Rabaa, A. Srhiri, J.Y. Saillard, A. Ben Bachir, A. Le Beuze, Corros. Sci. 41 (1998) 501–517.

[97] L. Tang, X. Li, H. Liu, G. Mu, G. Liu, J. Mater. Sci. 41 (2006) 1991–1997.

[98] G. Moretti, G. Quartarone, A. Tassan, A. Zlngales, Electrochim. Acta 41, (1996) 1971–1980.

[99] Yıldırım, M. Cetin, Corros. Sci. 50 (2008) 155–165.

[100] N.M. Hashim, A.A. Rahim, H. Osman, P.B. Raja, Chem. Eng.Commun. 199 (2012) 751–766.

[101] P.B. Raja, M.G. Sethuraman, Mater. Lett. 62 (2008) 1602–1604.

[102] M.A. Amin, S.S. Abd El-Rehim, E.E.F. El-Sherbini, R.S. Bayoumi, I., Electrochim. Acta

[103] 52 (2007) 3588–3600.

[104] D. Kesavan, M. Gopiraman, N. Sulochana, Chem. Sci. Rev. Lett. 1 (2012) 1–8.

[105] A.Y. El-Etre, M. Abdallah, Z.E. El-Tantawy, Corros. Sci. 47 (2005) 385–395.

[106] O.K. Abiola, A.O. James, Corros. Sci. 47 (2010) 661–664.

[107] S. Deng, X. Li, Corros. Sci. 55 (2012) 407–415.

[108] S. Banerjee, V. Shrivatsava, M.M. Singh, Corros. Sci. 59 (2012) 35–41.

[109] S. Garai, S. Garai, P. Jaisankar, J.K. Singh, A. Elango, Corros. Sci. 60 (2012) 193–204.

[110] A.A. Rahim, E. Rocca, J. Steinmetz, M.J. Kassim, Corros. Sci. 50 (2008) 1546–1550.

[111] P.B. Raja, A.A. Rahim, H. Osman, K. Awang, Acta Phys. Chim. Sin. 26 (2010) (2010) 2171–2176.

[112] P.B. Raja, A.A. Rahim, H. Osman, K. Awang,Int. J. Miner. Metall. Mater. 18 (2011) 413–418.

[113] S. Nofrizal, A.A. Rahim, B. Saad, P.B. Raja, A.M. Shah, S. Yahya, Metall. Mater.

[114] K. Aramaki, J.Uehre and H. Nishihare, Proc. of the 11th International Corrosion Congress, Florence, Italy, 1990, 3, 331.

[115] G. B. Hunt and A. K. Holiday, "Organic Chemistry", London, United Kingdom, Buterworth, 1981, p. 229.

[116] R. D Braun, E.E Lopez and D.P. Vollmer, Corros. Sci. 1993, 34, 1251.

[117] Florina Branzoi, V. Branzoi, C. Licu, Materials and Corrosion, 2012, 63, No.9999, DOI10.1002/maco.201206579..

[118] Loupy, Chemistry Today, 2006, 24, 36.

[119] Q. Qu, S.Jiang, W.Bai and L.Li, Electrochim. Acta, 2007, 52,6811

[120] Q. Quing, L.Li, S.Jing and Z.Ding, J. Appl. Electrochem., 2009, 39,569

[121] M. F. L. Granero, P.H.L.S. Matai, I.V.Aoki and I.C.Guedes, J. Appl. Electrochem. 2009, 39, 1199.

[122] D. Gopi, K. M. Govindaraju and L. Kavitha, J. Appl. Electrochem. 2010, 40, 1349.

[123] Prună, V. Branzoi and F. Branzoi, Materials and Technologies, 2007, 23, 233.

[124] V.Branzoi, A. Pruna, Florina Branzoi, Revue Roumaine de Chimie, 52(6), 589-597, 2007

[125] Florina Branzoi, V. Branzoi and A. Stanca, Rev. Chim.,. 2008, 60, 797

[126] I.Harabor, V. Branzoi and Florina Branzoi, Revue Roumaine de Chimie,57 (6), pp. 735-745, 2012.

[127] Florina Branzoi, V. Branzoi, and I. Harabor, Revue Roumaine de Chimie, 55 (8), 487-500, 2010.