NEW FRIENDLY ENVIRONMENT INHIBITORS FOR ANTICORROSIVE PROTECTION OF COOLING WATER SYSTEMS

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Using the microwaves energy, new polymers were synthesized by radicalic polymerization for anticorrosive and antiscaling protection of industrial cooling water systems. Electrochemical polarization techniques and metallurgical research microscopy technique have been carried out using different concentrations and combinations of organic compounds. Various corrosion parameters such as open circuit potential (OCP), current density, Tafel slopes, polarization resistance (Rp), and corrosion rate, etc.were recorded from electrochemical experiments for different metallic materials in cooling water systems. The obtained experimental results pointed out that, these new polymers are corrosion and antiscaling inhibitors and also, the environment friendly compounds. The inhibition activity of these new polymers is due to adsorption (chemisorption—specially) on the metallic surface, which leads to formation of a thin adsorption film, and this film inhibits the corrosion of the metallic material by a protective mechanism, forming insoluble complexes and repairing the porous oxide layers.

INTRODUCTION

Cooling water systems are integral part of most of the industries and their performance is seriously affected by corrosion of materials and scale deposits.

Use of inhibitors in controlling corrosion/scales in cooling water systems is an established technology. A number of inorganic/organic inhibitors have been used in the last sixty years.

Cooling water inhibitors are reviewed, emphasis being on the description of recent environment friendly inhibitors.

It is well known that, carbon steels are used in a wide range of industrial applications. Corrosion of carbon steels and their inhibition in different solutions have attracted the attention of number researchers. Organic compounds containing polar group including nitrogen, sulfur, oxygen, etc. and heterocyclic compounds with polar functional group and conjugated double bonds have been reported to inhibit corrosion.[1-2] The inhibiting action of these organic compounds is usually attributed to their interactions with the metal surface by their adsorption.

Recent investigations have emphasized the importance of the nature of the metal surface in inhibition performance.[3] 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. Generally, it is assumed that strong adsorption of the inhibitors is a prerequisite. The adsorption of inhibitors leads to the formation of a physical barrier that reduces the metal reactivity in the electrochemical reaction of corrosion.[4] Early studies considered the adsorption of inhibitors on metal surfaces to be primarily physical adsorption and/or chemisorptions.[5-8,11-13] New investigations have shown that adsorption could also occur through hydrogen bonding.[3, 9-10] Therefore, a systematic study of the adsorption processes of organic inhibitors, effective in protection enhancement, contributes to a better understanding and ultimately control of corrosion. In this paper,

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several combinations of organic compounds have been investigated which may control corrosion as well as scaling problem in cooling waters systems. The inhibition of two carbon steels corrosion in cooling water by organic compounds was investigated by potentiodynamic polarizations, EIS measurements and metallography analysis.

EXPERIMENTAL

The inhibitory action was studied through tracing the polarization curves obtained using the potentiodynamic method, calculation of the corrosion kinetic parameters in case of solutions with inhibitors, especially the corrosion current

densities, and their comparison with the kinetic parameters of the solution without inhibitors. The polarization curves were obtained by potentiostatic and potentiodynamic methods using a three electrode-cell. In all experiments the electrochemical polarizations were started about 30 minutes after the working electrode was immersed in solution, to allow the stabilization of the stationary potential. The working electrode potential was always measured with reference to the saturated calomel electrode and was plotted against current from external circuit, obtaining the anodic or cathodic curves according to the variation of the working electrode potential. The studied metals were the carbon steels type OL 37 and OLC 45. The chemical compositions of the studied metallic materials are given in the tables 1.

The corrosion medium was industrial cooling water type SCS with the chemical composition given in table 2.

Table 1

The chemical composition of the working electrodes

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	-	-	-	-	-

Table 2

The chemical composition of the cooling water type SCS

Indicators	UM	Water type SCS, 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
Cloride, Cl^-	mg/L	117.01
Sulfate	mg/L	155
Solid matters	mg/L	2.75
Organic matters	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
Cuprum, Cu^{2+}	mg/L	<0.015
Zinc, Zn^{2+}	mg/L	<0.1

All tests have been performed at 25°C under atmospheric oxygen without agitation. The electrochemical measurements were made using an automated model VoltaLab 40 potentiostat/galvanostat.

The used organic inhibitors are a few polymers, which were obtained by radical polymerization of acrylic and/or acrylsulfonate water-soluble monomers, in presence of microwaves field, under the action of peroxidic initiators. As organic inhibitors, two types of polymers were synthesized, namely: a) phosphino-carboxilic polyacids (PCA) and b) phosphino-carboxilic-sulfonic polyacids (PCSA).

Starting from the polymer PCA was obtained other new compounds by mixing with an organophosphonic derivate namely: 2-phosphonobutane-1-2, 4-tricarboxylicacid (PBTC). The new obtained compound used in this paper was: PCA-M21/O - a mixture with weight ratio 2/1 PCA/PBTC which

was neutralized and additived with PSO (an oligomer phosphinosuccinic in neutralized state).

RESULTS AND DISCUSSION

The polarization behaviour of metallic materials mentionated above was studied in cooling water with chemical composition given in table 2. 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.

$$\log i_a = \log i_{corr} + \left(E_i - E_{corr} \right) / b_a \qquad (3)$$

$$\log i_c = \log i_{corr} + \left(E_{corr} - E_i \right) / b_c \qquad (4)$$

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:

$$i_{corr} = b_a b_c / 2.303 \left(b_a + b_c \right) R_p \qquad (5)$$

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

$$R_p = \left(\frac{dE}{di} \right)_{E=E_{corr}} \qquad (6)$$

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

The figures 1-2 show a series of potentiodynamic polarization curves for two carbon steel electrodes in a cooling water type SCS, in absence and presence of different concentrations of inhibitor.

Analysis of the polarization curves from figures 1-2 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 the cathodic polarization curves from figure1-2 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:

$$\frac{1}{2}O_2 \quad H_2O \quad 2e \quad 2HO \qquad (7)$$
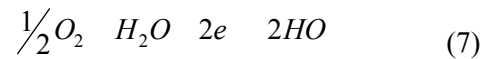
After this like passive range potential the cathodic current increases again and this increasing is due to the hydrogen evolution.

From polarization curves obtained by potentiodynamic method were calculated all kinetic corrosion parameters which are given in tables 3-4.
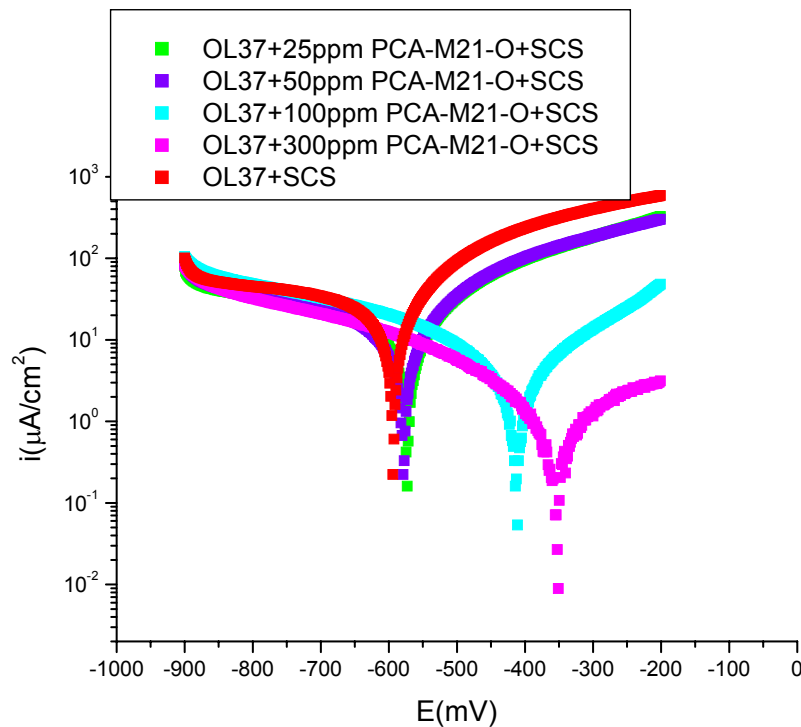

Fig. 1 – Polarization curves of OL 37 in cooling water type SCS+XppmPCA-M21/O at 25°C.
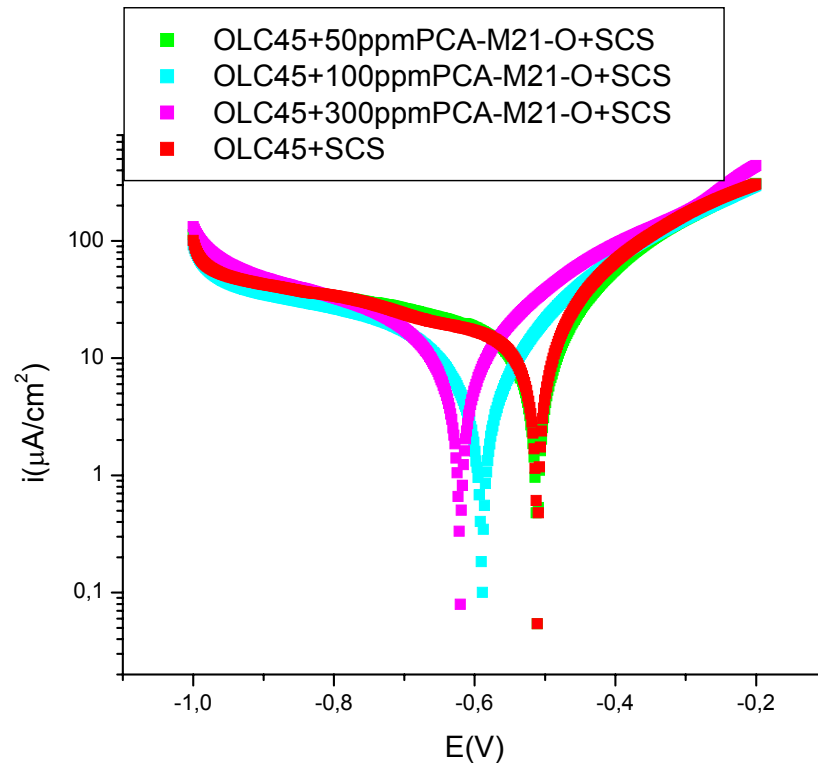
Fig. 2 – Polarization curves of OLC- 45
in cooling water type SCS+Xppm PCA-M21/O at 25°C .

Table 3

Kinetic corrosion parameters of carbon steel type OL-37 in cooling water type SCS + Xppm PCA-M21/O at 25°C
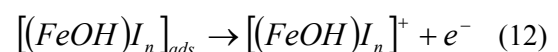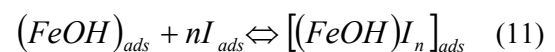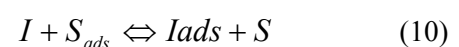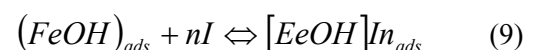
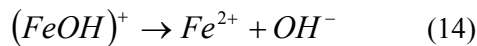| Inhibitor) (ppm)	i_{corr} (μA/cm^2)	R_p KΩ/cm^2	R_{mpy}	$P_{mm/year}$	K_g g/m^{2}h	E(%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	16.86	1.33	7.95	0.201	0.179	-	-554	108	-200	
25	5.83	2.72	2.75	0.0069	0.0062	65	-630	82.6	-123	0.65
50	5.775	3.37	2.72	0.069	0.061	65.5	-626	103	-145	0.655
100	2.167	10.19	1.02	0.025	0.023	87.18	-415	125	-137	0.87
300	0.445	38.5	0.209	0.0053	0.0047	97.3	-357	114	-93	0.97

Table 4

Kinetic corrosion parameters of carbon steel type OLC-45 in Cooling water type SCS+ Xppm PCA-M21/O at 25°C

Inhibitor) (ppm)	i_{corr} (μA/cm^2)	R_p 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	8.75	2.97	4.08	1.03	0.092		-557	85	-425	
25	6.14	3.26	2.86	0.072	0.065	30	-664	99.8	-167	0.3
50	5.50	3.60	2.56	0.065	0.058	37	-594	100	-162	0.37
100	3.20	5.48	1.49	0.038	0.034	64	-690	85	-141	0.64
300	3.09	5.91	1.44	0.036	0.032	65	-592	101	-120	0.65

Analyzing these tables, it can be observed that**,** the addition of the organic inhibitor to the amounts shown in the tables 3-4 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.[14] According to this theory, the corrosion process of carbon steel could takes place thus:

$$Fe + OH^- \Leftrightarrow (FeOH)_{ads} + e^- \qquad (8)$$

$$(FeOH)_{ads} + nI \Leftrightarrow [EeOH]In_{ads} \qquad (9)$$

$$I + S_{ads} \Leftrightarrow Iads + S \qquad (10)$$

$$(FeOH)_{ads} + nI_{ads} \Leftrightarrow [(FeOH)I_n]_{ads} \qquad (11)$$

$$[(FeOH)I_n]_{ads} \rightarrow [(FeOH)I_n]^+ + e^- \qquad (12)$$

$$(FeOH)_{ads} \rightarrow (FeOH)^+ + e^- \qquad (13)$$

$$(FeOH)^+ \rightarrow Fe^{2+} + OH^- \qquad (14)$$

$$[(FeOH)I_n]^+ \rightarrow [FeIn]^{2+} + OH^- \qquad (15)$$

The symbol 'S' denotes the solvent or any specifically adsorbed ions and the symbol 'I' denotes the organic inhibitor. The step (10) would be the mode of inhibition, which has been designated as "blocking"or adsorption, while the steps (9) and (11) are the surface chelate modes. If the process described by (11) were 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 (13), the chelation process, i.e., step (11), 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 (11) and that the equilibrium of (8) and (10) are shifted toward the right as adsorption sites are generated by dissolution, then importance of chelate ought to increase with increasing immersion time.[14] The extent to which the steps (8) and (10) are shifted to the right relative to each other and the stoichiometry of (11), 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 (8), (10) and (11), 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 (9) 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 (11). We presume that both adsorption and surface chelate function in a more or less concerted manner to achieve inhibition (see tables 3-6 and figures1-2)

Further, it was studied the influence of the immersion time and inhibitor concentration on the polarization behaviour of these two carbon steels in cooling water type SCS. Because in the tables 3-6 are given synthetically all kinetic corrosion parameters, in figures 3-4 are presented only a few characteristic polarization curves for exemplification.

The variation curves of the corrosion current density function of the inhibitor concentration at different immersion times are presented in figures 5-6. 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.
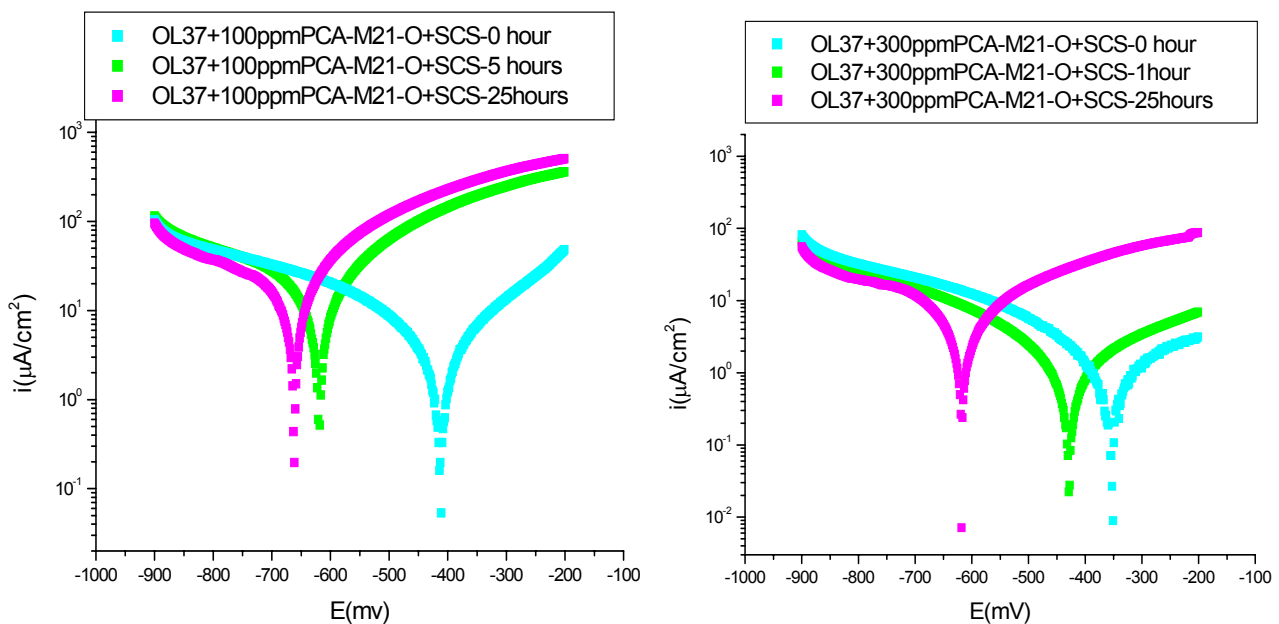

Fig. 3 – The polarization curves of OL-37 carbon steel in cooling water type SCS in presence of PCA-M21/O organic inhibitor at 25°C and different immersion times.
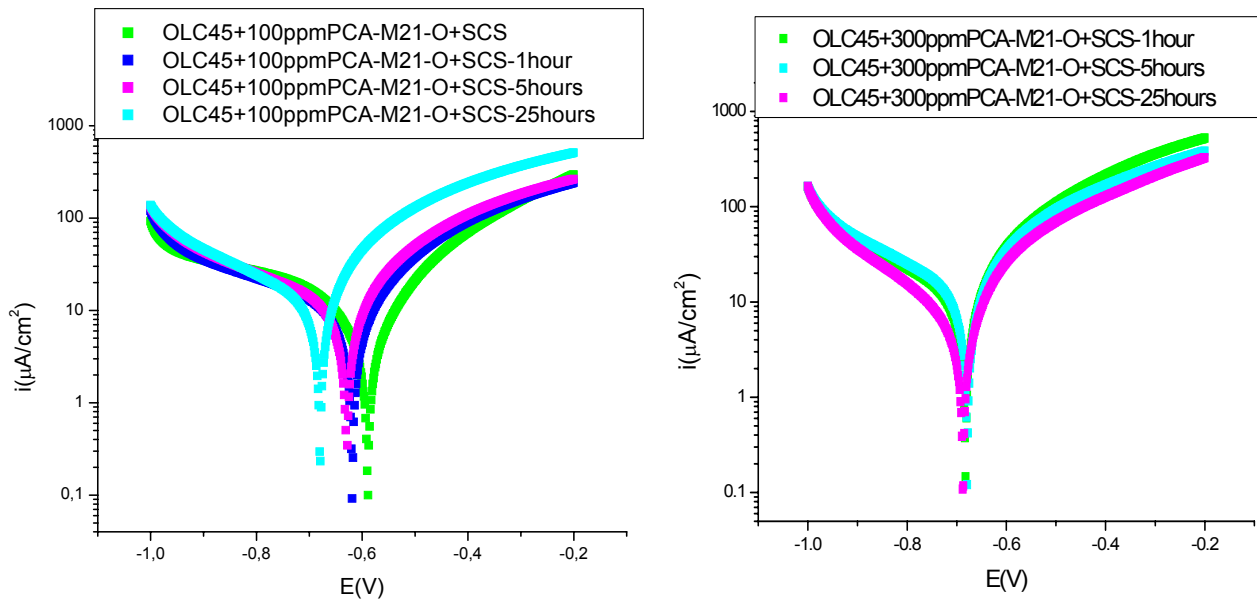
Fig. 4 – The polarization curves of OLC-45 carbon steel in cooling water type SCS in presence of PCA-M21/O organic inhibitor at 25°C and different immersion times.

Table 5

Kinetic corrosion parameters of carbon steel OL-37 +X ppm PCA-M21/O +SCS at 25°C and different immersion times

Inhibitor (ppm)	Immersion times (h)	i_{corr} ($\mu A/cm^2$)	R_p 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	0	16.86	1.33	7.95	0.201	0.179	-	-554	108	-200	
25	0	5.83	2.72	2.75	0.0069	0.0062	65	-630	82.6	-123	0.65
50	0	5.775	3.37	2.72	0.069	0.061	65.5	-626	103	-145	0.655
100	0	2.167	10.19	1.02	0.025	0.023	87.18	-415	125	-137	0.87
300	0	0.445	38.5	0.209	0.0053	0.0047	97.3	-357	114	-93	0.97
25	1	7.078	2.93	3.06	0.077	0.069	58	-576	106.8	-171	0.58
50	1	6.349	3.19	2.95	0.075	0.066	63	-581	101.9	-171	0.63
100	1	3.80	8.14	1.77	0.045	0.040	77.5	-610	118	-132	0.775
300	1	0.65	33.76	0.306	0.0078	0.0069	96	-431	146	-132	0.96
25	5	8.891	2.17	4.19	0.106	0.094	47	-672	103	-155	0.47
50	5	7.705	2.56	3.63	0.092	0.082	54	-661	108	-155	0.54
100	5	7.305	2.43	3.44	0.087	0.077	57	-622	103	-123	0.57
300	5	1.42	12.80	0.67	0.017	0.015	92	-461	147	-130	0.92
25	25	10.08	2.08	4.75	0.12	0.107	41	-705	109	-217	0.41
50	25	9.72	2.04	4.58	0.116	0.103	42	-703	100	-228	0.42
100	25	8.52	2.01	4.02	0.102	0.091	50	-682	118	-132	0.50
300	25	3.18	8.89	1.5	0.038	0.034	82	-621	149	-137	0.82

Analyzing in comparison the tables 3-6, it can be observed that, the increase of inhibitor concentration led in all the cases to the decrease of the corrosion rate and once with the increase of the immersion time takes place a weakly decreasing of the inhibition efficiency and this fact can be explained on the basis of foregoing presented mechanism. We presume that, once with increasing the immersion time takes place an increasing of activity of steps namely (13) -(15) and the inhibitor efficiency decreases slowly (see tables 5-6). On the other hand, in the same conditions, in our case, in the cooling water type SCS at 25⁰C carbon steel OL-37 has a higher corrosion rate than carbon steel type OLC-45 (see in comparison the figures 1-2 and the tables 3-4). This fact means that in the cooling water type SCS the stability of the carbon steel type OLC-45 is higher than stability of carbon steel type OL-37. Analyzing the polarization behaviour of these two carbon steels in the same cooling water namely SCS, it can be observed, from figures 5-6 and tables 3-6, that at the same concentration of the organic inhibitor type PCA-M21/O, the inhibition of corrosion process is much

higher in the case of OL-37 carbon steel than in the case of OLC-45 carbon steel. This fact means that the steps (9)-(11) are much more activated for the carbon steel type OL 37 than for OLC-45 in the same cooling water and in the same conditions.

Table 6

Kinetic corrosion parameters of carbon steel OLC-45+ X ppm PCA-M/21+SCS at 25°C and different immersion times

| Inhibitor) (ppm)	Immersion times (h)	i_{corr} (μA/cm²)	R_p KΩ/cm²	R_{mpy}	$P_{mm/year}$	K_g g/m²h	E(%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	0	8.75	2.97	4.08	1.03	0.092		-557	85	-425	
25	0	6.14	3.26	2.86	0.072	0.065	30	-664	99.8	-167	0.30
50	0	5.50	3.60	2.56	0.065	0.058	37	-594	100	-162	0.37
100	0	3.20	5.48	1.49	0.038	0.034	64	-690	85	-141	0.64
300	0	3.09	5.91	1.44	0.036	0.032	65	-592	101	-120	0.65
25	1	6.40	3.09	2.98	0.076	0.067	27	-664	101	-167	0.27
50	1	6.16	3.31	2.87	0.073	0.065	30	-498	104	-158	0.30
100	1	4.01	4.58	1.87	0.047	0.042	54	-622	92	-141	0.54
300	1	3.91	3.90	1.82	0.046	0.041	56	-623	95	-109	0.56
25	5	7.05	2.56	3.33	0.084	0.075	20	-514	104	-158	0.20
50	5	6.20	3.09	2.89	0.073	0.065	30	-498	100	-172	0.30
100	5	4.66	3.71	2.17	0.055	0.048	47	-632	94	-134	0.47
300	5	4.88	3.18	2.27	0.057	0.051	45	-685	84	-134	0.45
25	25	7.51	2.59	3.50	0.088	0.079	15	-518	105	-188	0.15
50	25	7.07	2.79	3.29	0.083	0.074	20	-558	109	-162	0.20
100	25	6.97	2.63	3.25	0.082	0.073	21	-683	99.5	-191	0.21
300	25	5.64	3.17	2.63	0.066	0.059	36	-682	91	-150	0.36
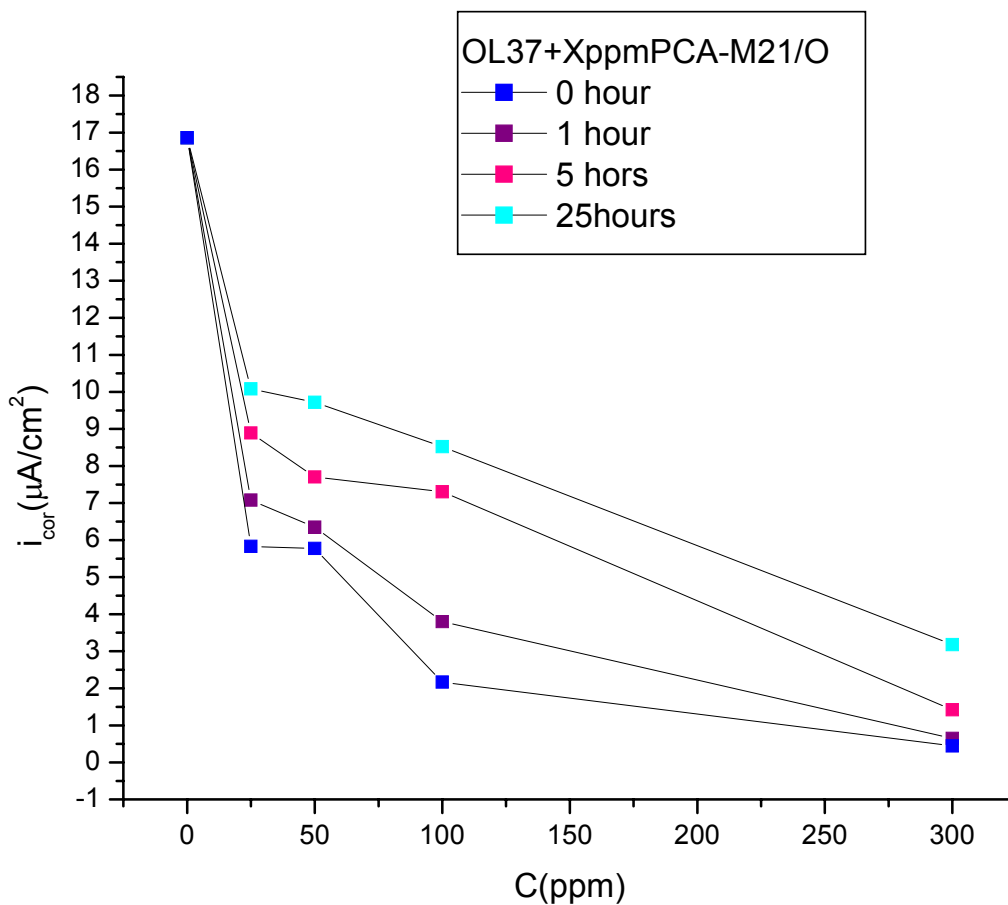
Fig. 5 –The influence of the inhibitor PCA-M21/O concentration on the corrosion rate of carbon steel OL-37 in cooling water type SCS at 25⁰C and different immersion times.
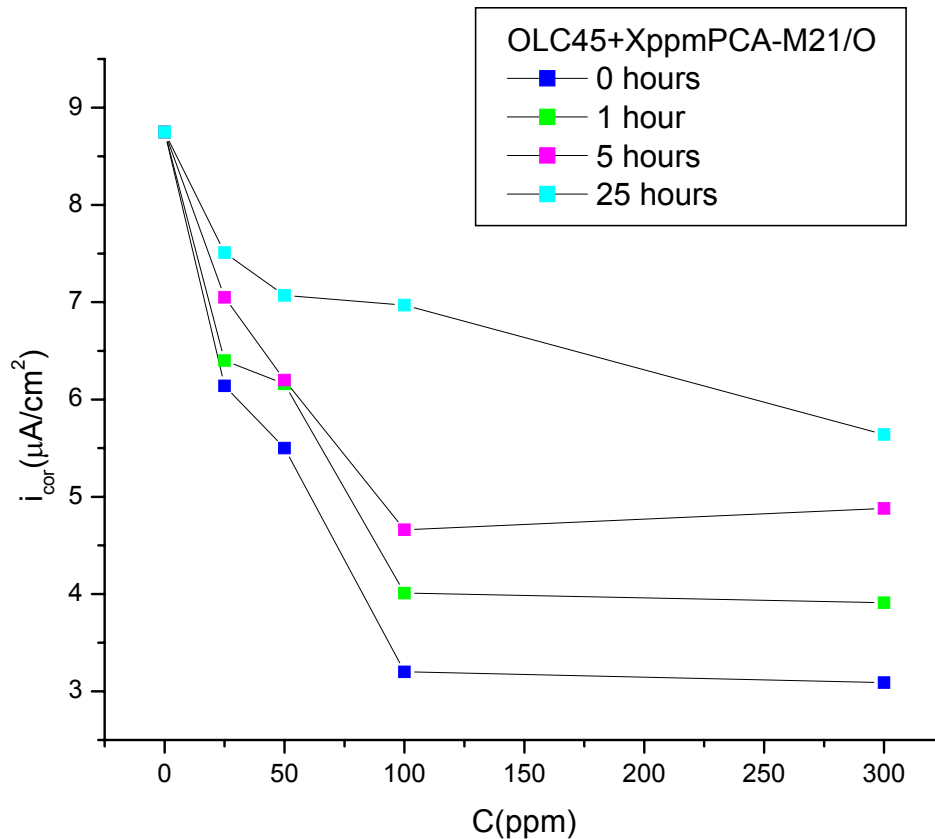
Fig. 6 – The influence of the inhibitor PCA-M21/O concentration
on the corrosion rate of carbon steel OLC-45 in cooling water type SCS at 25^0C and different immersion times.

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:

$$\theta / (1 - \theta) = Kc \qquad (16)$$

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:

$$\theta = \left(i_{corr} - i_{corr.inhib}\right) / i_{corr} \qquad (17)$$

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

$$c/\theta = c + 1/K \qquad (18)$$

and 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 (see for exemplification figure 7) The adsorption equilibrium constants (K) for our corrosion systems are given in table 7

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:

$$\ln K_{ads} = -\left(\Delta G_T^\circ / RT\right) \qquad (11)$$

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 7).

Table7

The values of K_{ads} and ΔG_{ads}° for studied systems

| The system	Type of metallic material	Values of K_{ads}, M^{-1}	Values of ΔG_{ads}° KJM^{-1}	Type of adsorption
Cooling water type SCS + PCA-M21/O	OL-37	1.68918×10^5	-29,808	Physical adsorption and chemisorption
	OLC-45	0.645×10^5	- 27.425	Physical adsorption and chemisorption
Cooling water type SCS + PCA-M21/O and immersion time of 1 hour	OL-37	1.0911×10^5	-28.726	Physical adsorption and chemisorption
Cooling water type SCS + PCA-M21/O and immersion time of 5 hours	OL-37	0.6161×10^5	-27.311	Physical adsorption and chemisorption
Cooling water type SCS + PCA-M21/O and immersion time of 25 hours	OL-37	0.478×10^5	-26.685	Physical adsorption and chemisorption
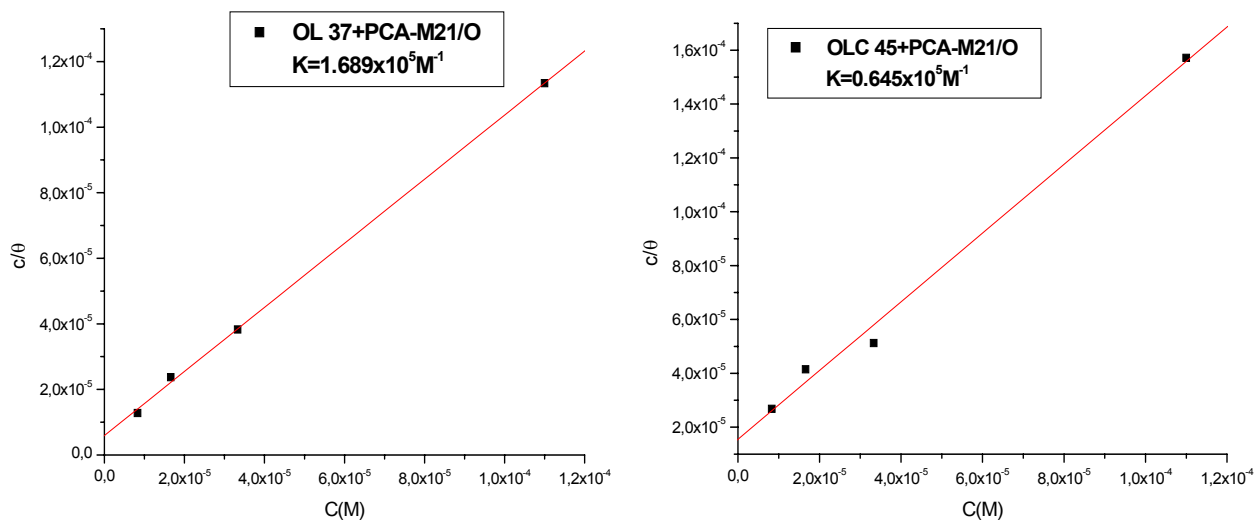
Fig. 7 – Langmuir plot for OL-37+PCA-M21/O and OLC-45+ PCA-M21/O at different inhibitor concentrations.

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.

Table 8

Electrochemical parameters of OL37+X ppm PCA-M21-O + SCS

Sample OL37	Time of Exposure time (h)	R_{el}, $k\Omega/cm^2$	R_p, $k\Omega/cm^2$	C_{dl}, $\mu F/cm^2$
0ppm	0	0.288	0.749	675
25ppm	0	0.482	1.399	159
	1	0.497	1.366	175
	5	0.453	1.159	187
	25	0.448	1.148	193
50ppm	0	0.445	1.529	146
	1	0.460	1.505	176
	5	0.438	1.412	188
	25	0.419	1.296	197
100ppm	0	0.451	1.824	87
	1	0.394	1.269	140
	5	0.390	1.241	163
	25	0.377	1.233	198

300ppm	0	0.421	3.219	90.4
	1	0.416	3.807	69.2
	5	0.394	4.232	58.3
	25	0.388	5.052	51.4

Table 9

Electrochemical parameters of OLC 45+X ppm PCA-M21-O + SCS

Sample OLC45	Time of Exposure time (h)	R_{el}, kΩ/cm^2	R_p, kΩ/cm^2	C_{dl}, μF/cm^2
0ppm	0	0.559	0.957	570
25ppm	0	0.486	1.308	437
	1	0.549	1.437	390
	5	0.585	1.663	304
	25	0.446	0.163	520
50ppm	0	0.440	2.085	105
	1	0.424	1.994	164
	5	0.385	1.535	170
	25	0.281	0.998	234
100ppm	0	0.594	1.514	121
	1	0.580	2.349	94
	5	0.535	2.07	105
	25	0.508	1.374	142
300ppm	0	0.387	1.455	153
	1	0.310	1.564	138
	5	0.371	1.634	129
	25	0.344	1.820	114

All tests have been performed in SCS with the chemical composition given in Table 2, at 25°C under atmospheric oxygen conditions without agitation. In Figure 8a are presented the Nyquist diagrams for the carbon steel OL-37 with 50 ppm organic inhibitor and different immersion times . In case of coolig water without organic inhibitor, a well defined capacitive loop can be observed while for the case when the inhibitor is present it can be observed a capacitive loop much bigger than in the foregoing case , which corresponds to a much higher polarisation resistance (see table.8-9). This fact points out very clear that the presence of organic inhibitor hinders the corrosion process and leads to the increase of the polarisation resistance which means that the rate of the charge transfer reaction becomes much lower (see table 8-9) Bode diagrams presented in figure 8c- 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 to proposed corrosion mechanism and with the results obtained by electrochemical polarization and in concordance with the Nyquist diagrams.

In figures 9a and 9b are presented the Nyquist and Bode diagrams for carbon steel type OLC-45 in cooling water SCS in presence and absence of organic inhibitor and at different immersion times.It can be observed a behaviour very close to the foregoing system, but in this case the capacitive loops are lower than in the case of OL-37 and the phase angle from Bode diagrams are much lower.This fact means that, in this case the adsorbtion of organic inhibitor is much lower than in the case of carbon steel OL-37. This fact is in good concordance with the results obtained by electrochemical polarisation and with the metallographic analysis .

The electrochemical parameters obtained by circular regression from Nyquist diagrams are presented in table 8 and are in accordance with data obtained at the potentiodynamic polarization curves, confirming once again the proposed corrosion mechanism.
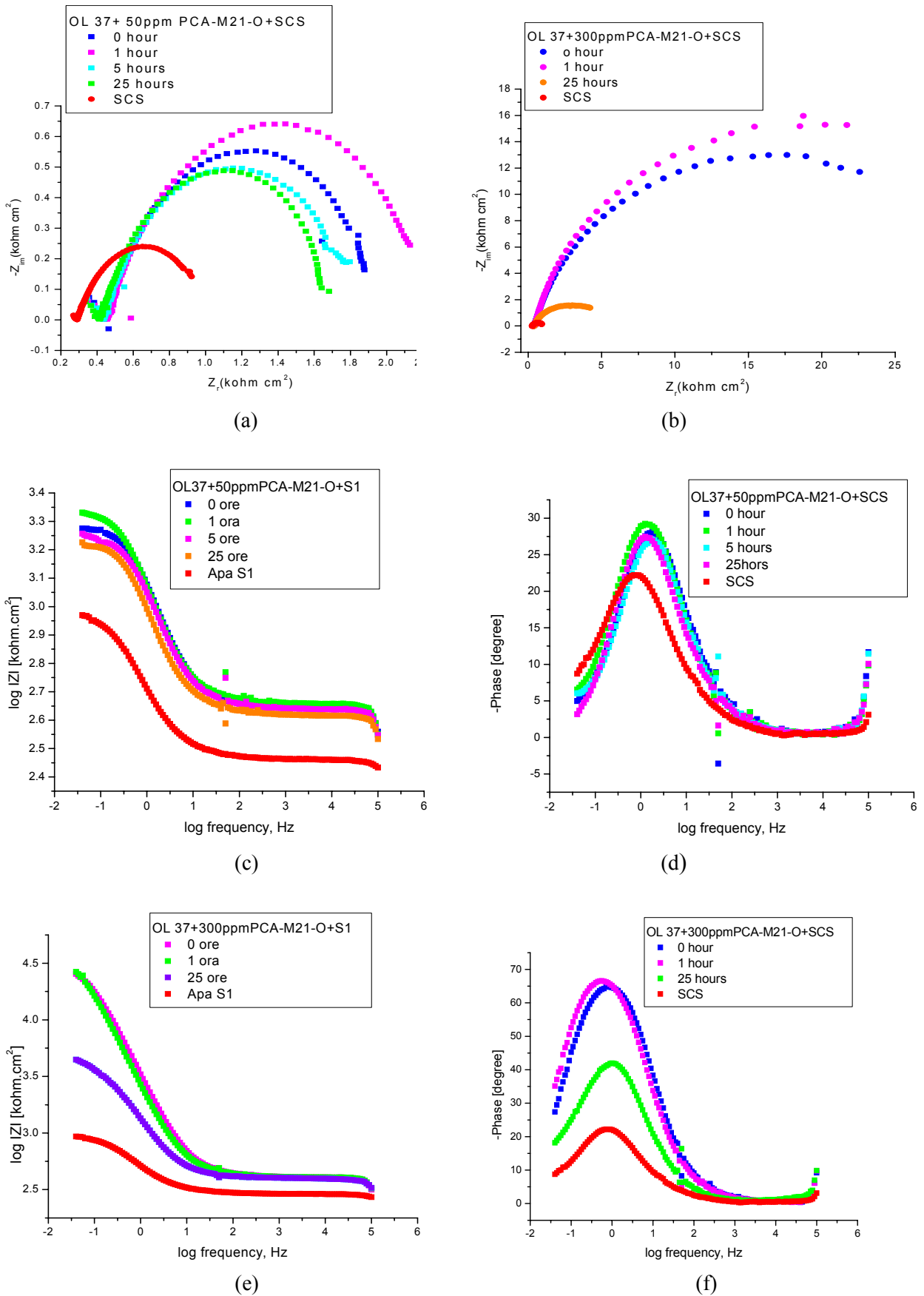
(a)

(b)

(c)

(d)

(e)

(f)

Fig. 8 – The Nyquist plot and the Bode plot for OL37 in SCS with and without organic inhibitor and at different immersion times.
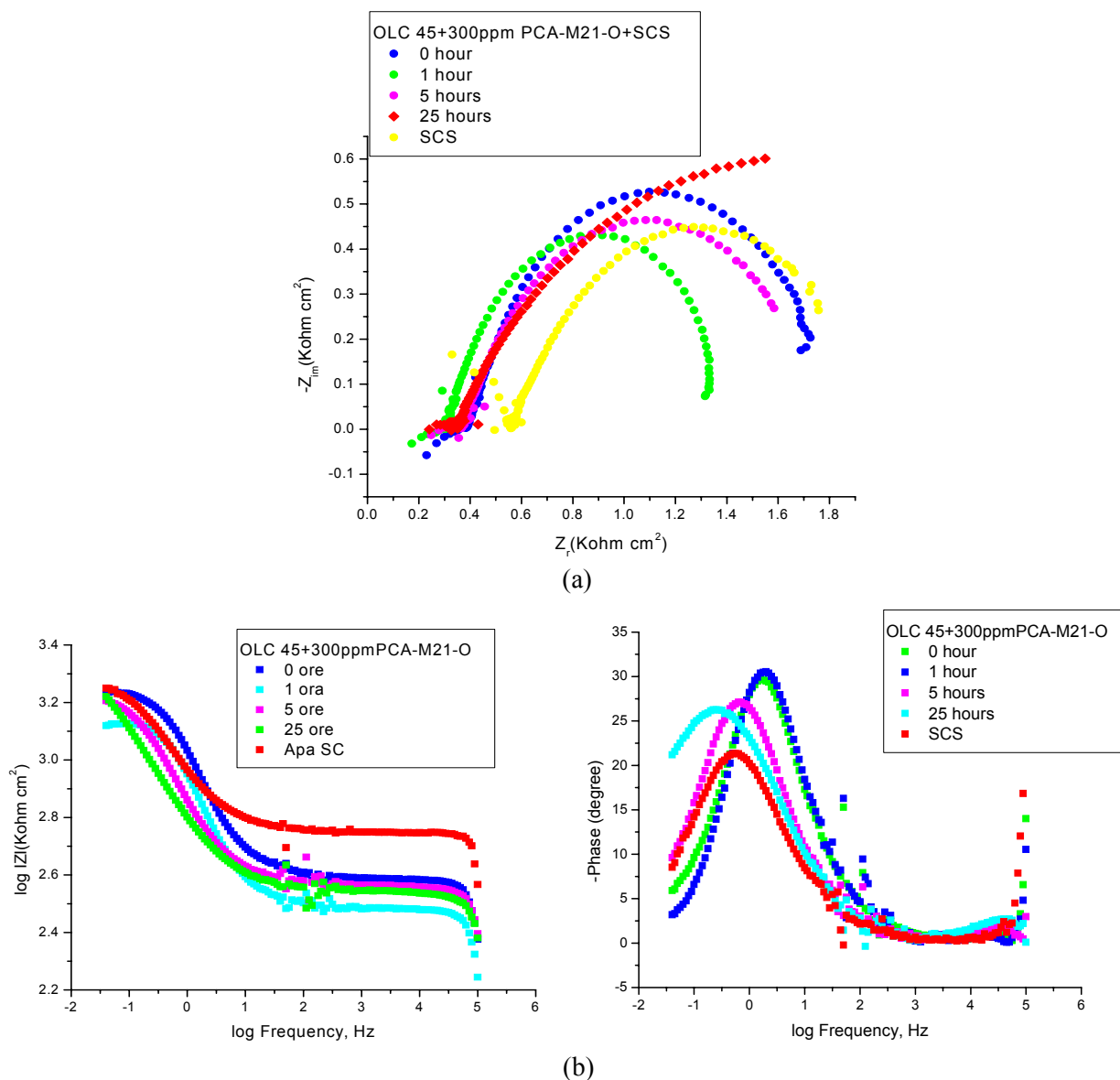
(a)

(b)

Fig. 9 – The Nyquist plot and the Bode plot for OLC 45 in SCS with and without organic inhibitor and at different immersion times.

Further, using the metallographic microscope the electrode surfaces were analyzed before and after a certain immersion time. In figure 10 are given a few micrographies obtained by us for the following systems: carbon steel OL 37 and OLC-45 before and after a certain immersion time in cooling water type SCS with and without organic inhibitor. As it can be observed from figures 10 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 10).

Analyzing in comparison the figures 10b, 10c, 10f and 10g, 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 immersion time and 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 10.

Analyzing in comparison the figures 10b and 10f, it can be observed that, the corrosive attack is much more accentuated in the case of OL 37+ water type SCS system than in the case of OL-37+ water type SCS +300ppm PCA-M21/O system. The same behaviour was observed for OLC 45(see in comparison figures 10i and 10m). This finding is in good concordance with the results obtained by electrochemical method – see tables 4 and 5 and the polarization curves from figures 1 and 2.
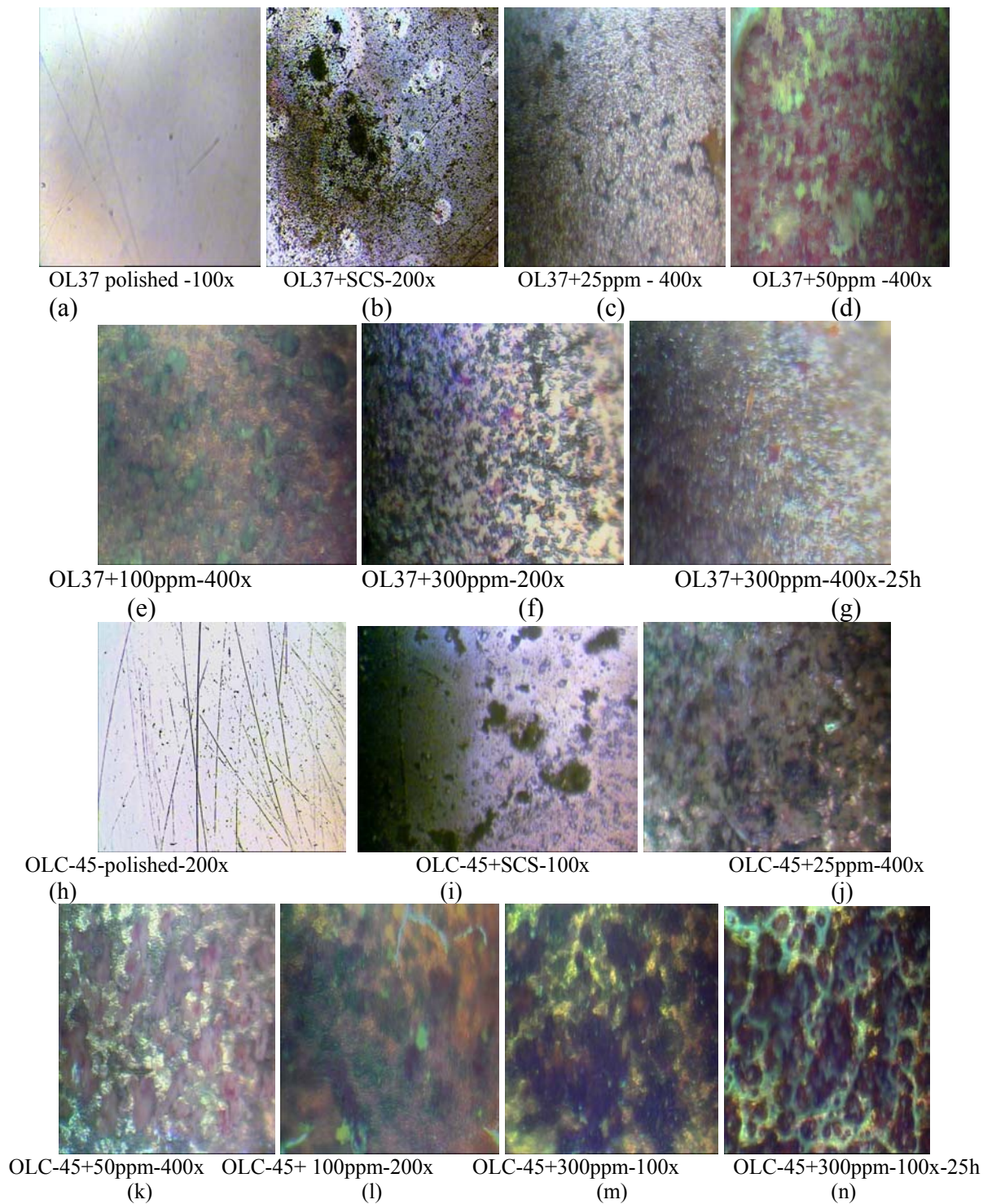
OL37 polished -100x

(a)

OL37+SCS-200x

(b)

OL37+25ppm - 400x

(c)

OL37+50ppm -400x

(d)

OL37+100ppm-400x

(e)

OL37+300ppm-200x

(f)

OL37+300ppm-400x-25h

(g)

OLC-45-polished-200x

(h)

OLC-45+SCS-100x

(i)

OLC-45+25ppm-400x

(j)

OLC-45+50ppm-400x   OLC-45+ 100ppm-200x

(k)   (l)

OLC-45+300ppm-100x

(m)

OLC-45+300ppm-100x-25h

(n)

Fig. 10 – Micrographies of the carbon steel OL 37 and OLC-45 in cooling water type SCS
with and without organic inhibitor PCA-M21/O.

CONCLUSIONS

In the studied corrosion systems at low overvoltages the corrosion process is under activation control, while at high voltages is controlled by diffusion.

A corrosion mechanism was proposed in concordance with Donahue's theory.

The corrosion rate of carbon steel OL-37 in cooling water type SCS without organic inhibitor is higher than for carbon steel OLC-45 in the same conditions.

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

The inhibition efficiency of organic inhibitor type PCA-M21/O is higher for OL-37+cooling water SCS system than for OLC-45 +cooling water SCS system.

The inhibition activity increases with immersion time and with inhibitor concentration. After a certain immersion time, the inhibition activity of PCA-M21/O starts to decrease weakly in according to the proposed corrosion mechanism.

The organic inhibitors were chemisorbed on the carbon steel surface according to a Langmuir isotherm. The values of adsorption constants determined from the plot of Langmuir isotherm pointed out that the adsorption of PCA-M21/O is stronger on the carbon steel OL37 than on the carbon steel OLC45.

The EIS measurements have confirmed the results obtained by potentiodynamic polarization and pointed out the importance of organic inhibitor concentration and immersion time.

The results obtained by EIS method are in according to with proposed corrosion mechanism.

Metallurgical micrographies pointed out the adsorption of organic inhibitor on the surface of carbon steel and the start of the corrosive attack.

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