

CORROSION PROTECTION OF INDUSTRIAL COOLING WATER SYSTEMS BY USING NEW ORGANIC POLYMERS AS INHIBITORS

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New organic compounds were obtained by radicalic polymerization using the microwave energy. These new polymers were used as scaling and corrosion inhibitors in cooling waters systems. It is well known that, in all the cases of cooling water systems, at the metal/water surface contact appear frequent corrosion processes, which determine deposition of corrosion products, like scales. Due to these scales formation from the decomposition of bicarbonates and in the same time, of the corrosion products on the heat exchange surfaces, the exchange heat becomes more difficult, fact that disturbs the normal function of the industrial installation. The addition of these new organic inhibitors offers protection by forming an adsorption organic barrier film at the metal surface. Electrochemical measurements and metallographic examinations were used to assess the relevant physical properties of the new corrosion inhibitors. The addition of the organic inhibitors led in all the cases to inhibition of the corrosion rate. The organic compounds used are adsorbed on the carbon steel surface according to a Langmuir isotherm.

The inhibition process was attributed to the formation of the adsorbed film on the metal surface that protects the metal against corrosive agents. The EIS measurements have confirmed this protection and pointed out the formation of adsorption layers on the electrode surface.

INTRODUCTION

Metals corrosion in water – conveying system such as cooling water circuits – is of major concern in industrial applications. In order to decrease corrosion of pipes, heat exchangers corrosion inhibitors are widely applied. An inhibitor is a substance that reduces corrosion damage when relatively small amounts of it are present in the aggressive medium. Adsorption inhibitors control electrochemical corrosion by influencing either the anode or cathode reaction, or both. They are usually organic compounds and their mechanism of inhibition is not too well understood. They adsorb on the cathode or anode areas and hinder reaction. The importance of inhibitive protection in different environments is increased by the fact that iron and its alloys, which are more susceptible to be attacked in aggressive media, are the commonly

exposed metals in industrial environments.¹⁻⁵ During the evaluation of new prospective ecologically compatible inhibitors system, several classes of organic compounds have been investigated. The most promising results were obtained using selected carboxylic acids and derivatives thereof. The results clearly showed that the inhibition performance of the carboxylic acids were comparable to that of conventional phosphonate based inhibitor systems. As, it is well known, the corrosion inhibition efficiency of organic compounds is connected with their adsorption properties.³⁻⁷ The effect of the adsorbed inhibitor is to protect the metal from the corrosive medium and/or to modify the electrode reactions that cause dissolution of the metal. It has been observed that, the adsorption depends mainly on certain physico-chemical properties of the inhibitor molecule such as, functional groups, steric factors,

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aromaticity, electron density at the donor and π orbital character of donating electrons and also on the electronic structure of molecules.^{2, 6, 8-11} Our study aim is to investigate the corrosion and the corrosion protection of two carbon steels in industrial cooling water type S2, using two organic

polymers synthesized by radicalic polymerization in microwaves field.

EXPERIMENTAL

The corrosion medium was an industrial cooling water type S₂ with the following chemical composition:

Table 1

Chemical composition of industrial cooling water type S₂

Indicators	UM	Water source 2, values of parameters
PH		7.95
Conductivity	$\mu\text{s}/\text{cm}$	665
Alcalinity	mval/L	4.2
Total Hardness	mval/L	4.18
Calcium Hardness	mval/L	4.16
Chloride, Cl ⁻	mg/L	95.74
Sulfate	mg/L	73.15
Solid matters	mg/L	0.95
Organic matters	mg/L	3.47
Iron	mg/L	0.099
Aluminum	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
Cuprum, Cu ²⁺	mg/L	<0.02
Zinc, Zn ²⁺	mg/L	<0.1

All tests have been performed at 25°C under atmospheric oxygen without agitation. The electrochemical measurements were carried out using a conventional three electrodes system and an automated model VoltaLab 40 potentiostat/galvanostat. A platinum electrode and a saturated calomel electrode (SCE)

were used as counter electrode and reference electrode, respectively.

The working electrode made of carbon steel had a surface of 1 cm². The used carbon steels have the following chemical compositions:

Table 2

The chemical composition of the working electrodes

Electrode	C%	Mn%	Si%	Fe%
Carbon steel type OL 37	0.14	0.38	0.03	99.45
Carbon steel type OLC 45	0.7	0.38	0.03	98.99

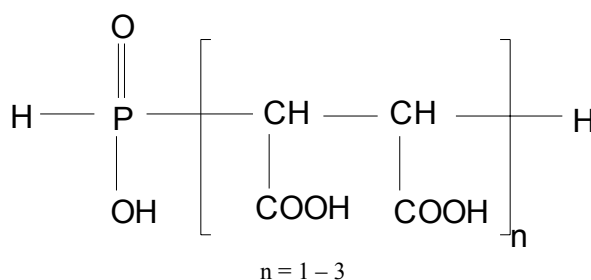
The reference electrode was placed in a separate cell and was connected to the corrosion cell via a salt bridge, which ends as a Luggin capillary in the corrosion cell. This arrangement was used to reduce chloride ion contamination of the corrosion system from the reference electrode and also, to reduce the ohmic resistance of the corrosion system.

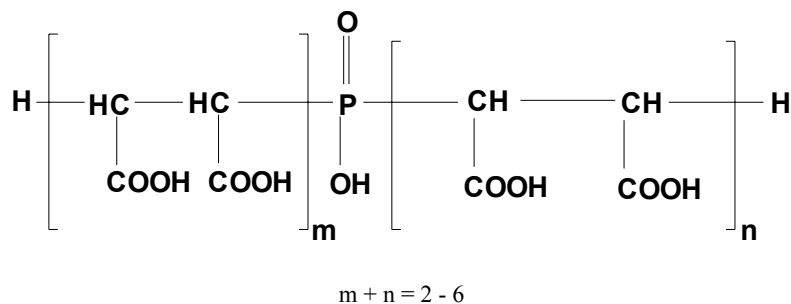
In all experiments the electrochemical polarization was started about 30 minutes after the working electrode was immersed in solution, to allow the stabilization of the stationary potential. Quasi steady-state polarization curves

were obtained by scanning the working electrode potential in anodic and cathodic direction from E_{corr} (the corrosion potential) at the rate of 2mVs⁻¹.

The used organic inhibitors were two polymers, which were obtained by radicalic polymerization in presence of microwave field chain transfer agents, under the action of peroxidic initiators.

The first used organic inhibitor was an oligomer phosphino succinic in the neutralized state which was obtained by mixing two oligomers:





The second inhibitor was obtained by mixing an organophosphonic derivate namely 2-phosphonobutane-1-2-4 tricarboxylic acid with polymaleic acid, a mixture by weight ratio of 1/1. We noted the first inhibitor down with PSO-1 and the second inhibitor with PMA-M1.

RESULTS AND DISCUSSION

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 acting over the anodic or cathodic reaction or 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.

In this paper, have been used as organic inhibitors the following polymers: PSO-1 (an oligomer phosphinosuccinic in neutralized state) and PMA-M1 (mixture by weight ratio 1/1 from 2-phosphonobutane-1-2, 4 tricarboxylic acid with polymaleic acid).

The inhibition activity analysis of these organic compounds was made by assuming that the mechanism of inhibition by organic molecules is chemisorption and that the energetics of the corrosion process per se are unaffected by the addition of substituent on the parent compound.

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) and their comparison with the kinetic parameters from solutions with different concentrations of inhibitors. The corresponding Tafel parameters were obtained by Mansfeld's method, employing polarization data near the corrosion potential. In the present paper, when values of $E - E_{\text{cor}}$ are higher than about 70 mV, slight but significant changes in the anodic and cathodic Tafel slopes were found. Figs. 1-4 show a series of potentiodynamic polarization curves of two-carbon steels electrode in aerated industrial cooling water type S₂ in absence and presence of different concentrations of PSO-1 and PMA-M1.

Table 3

Kinetic corrosion parameters of carbon steel OL-37 in cooling industrial water type S₂ in presence and absence of organic inhibitor type PSO-1 at temperature of 25°C

Inhibitor) (ppm)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	R_p $\text{K}\Omega/\text{cm}^2$	R_{mpy}	$P_{\text{mm/year}}$	K_g $\text{g}/\text{m}^2\text{h}$	$E(\%)$	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	15.17	1.46	7.08	0.17	0.16		-523	102	-369	
5	6.748	2.74	3.14	0.079	0.071	55	-500	103	-138	0.55
10	5.145	3.91	2.35	0.059	0.053	66	-4901	109	-153	0.66
20	4.069	4.03	1.89	0.047	0.042	73	-462	94.7	-117	0.73
50	2.05	8.83	0.94	0.023	0.021	86.5	-333	39.8	-141	0.86
100	1.477	7.75	0.67	0.017	0.015	90.2	-368	49.4	-95.9	0.90
300	0.477	18.64	0.21	0.005	0.0047	97	-305	37.6	-75	0.97

Table 4

Kinetic corrosion parameters of carbon steel OL-37 in cooling industrial water type S₂ in presence and absence of organic inhibitor type PMA-M1 at temperature of 25°C

Inhibitor (ppm)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	R_p ($\text{K}\Omega/\text{cm}^2$)	R_{mpy}	$P_{mm/year}$	K_g ($\text{g}/\text{m}^2\text{h}$)	E(%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	15.17	1.46	7.08	0.17	0.16		-523	102	-369	
5	7.35	2.65	3.43	0.087	0.077	52	-531	99	-173	0.52
10	6.98	2.60	3.25	0.082	0.07	54	-484	95	-137	0.54
20	6.39	2.91	2.98	0.075	0.067	58	-494	99	-150	0.58
50	4.88	2.94	2.27	0.057	0.05	68	-423	63	-134	0.68
100	3.93	4.78	1.83	0.046	0.041	74	-431	90	-159	0.74
300	1.76	9.52	0.82	0.021	0.018	89	-389	88	-118	0.89
500	8.80	2.27	2.77	0.07	0.062	42	-595	110	-163	0.42

Table 5

Kinetic corrosion parameters of carbon steel OLC-45 in cooling industrial water type S₂ in presence and absence of organic inhibitor type PSO-1 at temperature of 25°C

Inhibitor (ppm)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	R_p ($\text{K}\Omega/\text{cm}^2$)	R_{mpy}	$P_{mm/year}$	K_g ($\text{g}/\text{m}^2\text{h}$)	E(%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	10.68	2.06	4.57	0.115	0.103	-	-493	104	-294	
5	1.74	10.49	0.81	0.02	0.018	84.3	-391	110	-122	0.84
10	0.78	15.67	0.36	0.009	0.008	92.6	-384	74	-77	0.92
20	0.63	15.04	0.29	0.007	0.006	94.8	-372	63	-49	0.94
50	0.52	22.89	0.24	0.006	0.005	95	-362	48.5	-66	0.95
100	1.30	10.19	0.60	0.015	0.013	87.8	-392	158	-50	0.87
300	1.60	12.34	0.74	0.018	0.167	85	-417	113	-137	0.85

Table 6

Kinetic corrosion parameters of carbon steel OLC-45 in cooling industrial water type S₂ in presence and absence of organic inhibitor type PMA-M1 at temperature of 25°C

Inhibitor (ppm)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	R_p ($\text{K}\Omega/\text{cm}^2$)	R_{mpy}	$P_{mm/year}$	K_g ($\text{g}/\text{m}^2\text{h}$)	E(%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	10.68	2.06	4.57	0.115	0.103	-	-493	104	-294	
5	3.66	3.44	1.70	0.043	0.038	70.2	-364	54	-114	0.70
10	3.50	4.77	1.63	0.041	0.036	68	-408	70	-167	0.68
20	2.54	5.27	1.18	0.029	0.026	77	-396	73	-95	0.77
50	2.65	6.25	1.23	0.031	0.027	76	-385	84	-153	0.76
100	3.63	7.29	1.69	0.042	0.038	67	-615	89	-112	0.67
300	5.25	3.88	2.45	0.062	0.055	51	-598	115	-151	0.51
500	6.47	2.59	3.01	0.076	0.068	40	-456	85	-138	0.40

It can be observed from Tables 3-6 that, the addition of the organic inhibitor type PSO-1 and PMA-M1 to the amount shown in Tables 3-6 led in all the cases to the inhibition of the corrosion process. It can be observed that, in this case the inhibitor PSO-1 has a higher efficiency for corrosion system OLC-37 in cooling water S₂ than for corrosion system OLC-45 in cooling water S₂. From Figs. 2, 3 and Tables 4, 6, it can be observed that, in the case of the inhibitor PMA-M1, the inhibition efficiency is higher for corrosion system OLC 45 in cooling water S₂. Analyzing in comparison the corrosion rate of carbon steel type OLC 45 in the same conditions (industrial cooling water S₂ without inhibitor), one can see that, the carbon steel OL 37 has a higher corrosion rate than

OLC 45 carbon steel. Also, it can be observed that, the corrosion rate of carbon steel decreases as the inhibitor concentration increases up to a certain value and then, the rate of corrosion increases again if the concentration of the organic inhibitor increases further.

The analysis of the polarization curves from Figs. 1-4 indicate that at low overvoltages, the Tafel relationship is followed, showing that both anodic and cathodic reactions are activation – controlled.¹ At higher overvoltages, a limiting diffusion current appears on the anodic and cathodic polarization curves showing that, at higher current densities, the transport of ions towards the electrode surface becomes the rate-determining step (concentration polarization).

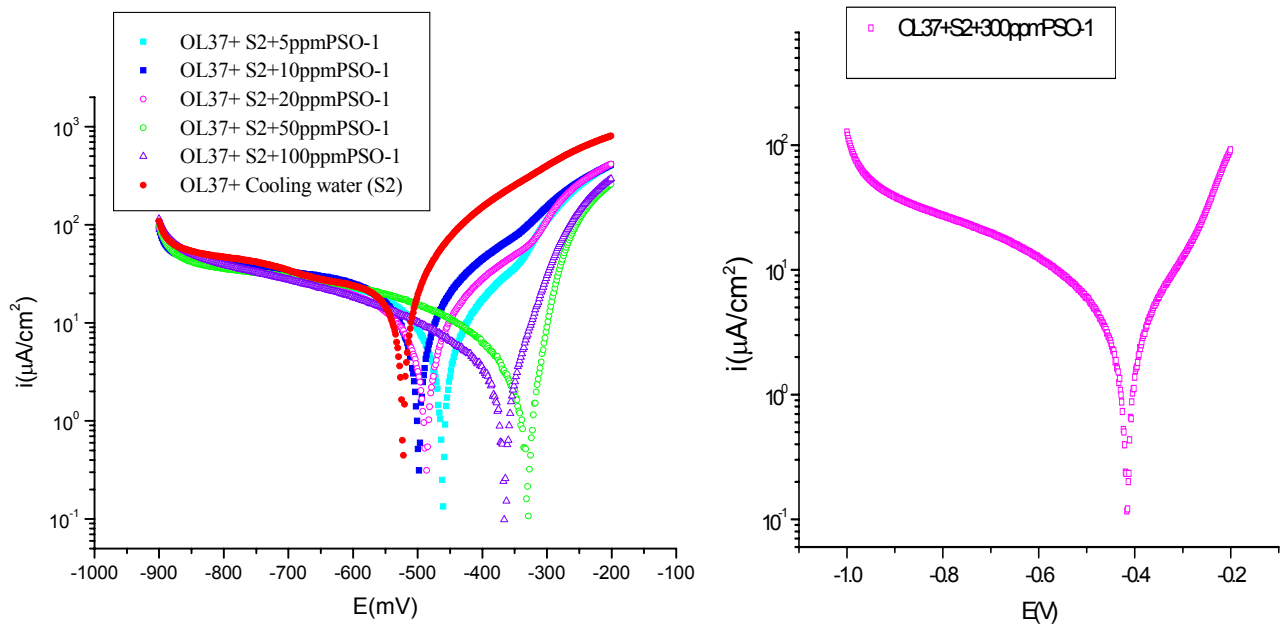


Fig. 1 – Polarization curves of OL 37 in cooling water S_2 +Xppm PSO-1at 25⁰C.

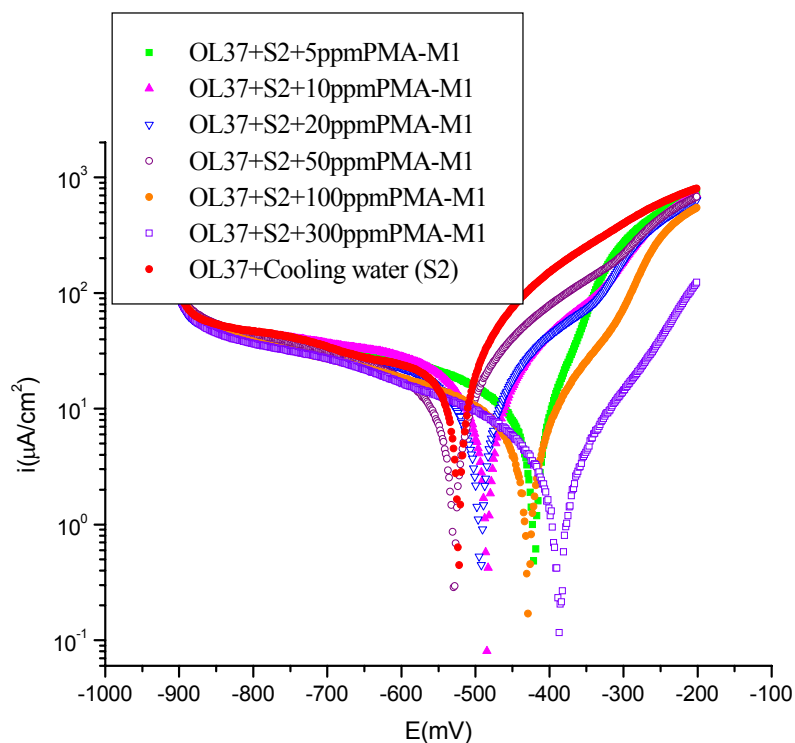
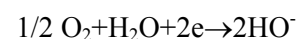


Fig. 2 – Polarization curves of OL 37 in cooling water S_2 +Xppm PMA-M1at 25⁰C.

Analyzing the cathodic polarization curves from figures 1-4 one can see that, on the large range of the potential, the carbon steel electrodes behave very close to a passive behaviour. Practically, one 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:



After this like passive range potential the cathodic current increases again and this increase is due to the hydrogen evolution (see the cathodic curves from figures 1-4). The adsorption of the organic inhibitors at the electrode surface leads to

formation of an adsorbed organic molecules layer, which stabilizes the oxide passive film, and in this way, the anodic and cathodic processes are hindered. As a consequence, the values of the anodic and cathodic Tafel slopes increase, the

corrosion current density and also, the limiting diffusion current density decrease, that means the inhibition of the corrosion process and consequently a higher protection of industrial cooling systems.

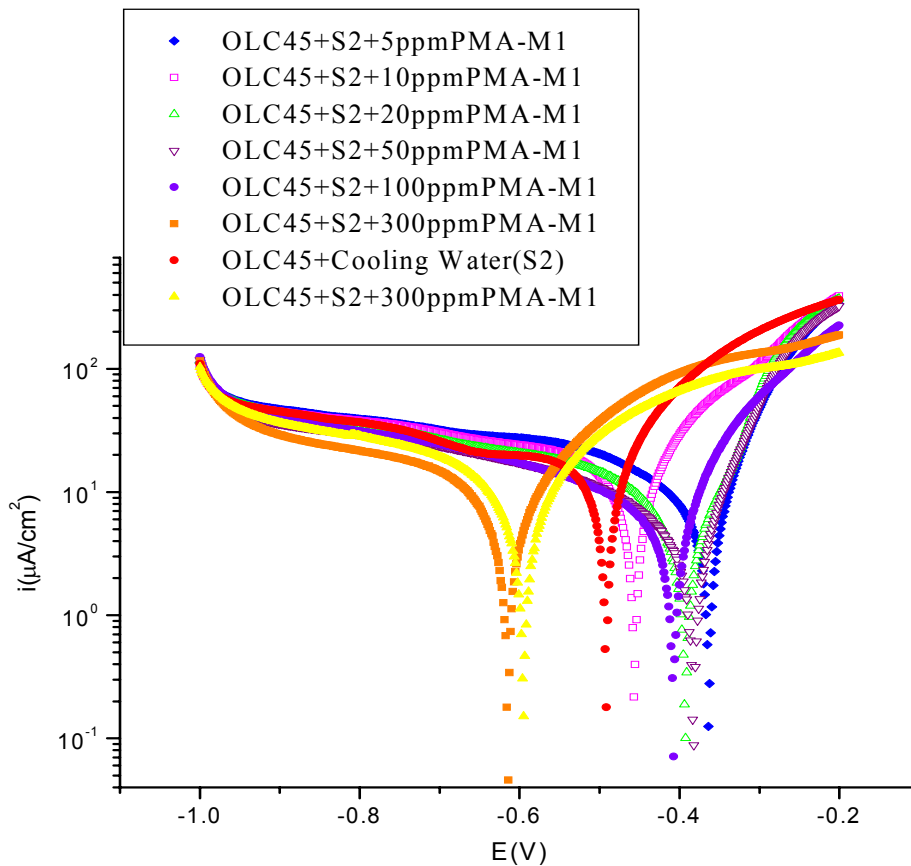


Fig. 3 – Polarization curves of OLC 45 in cooling water $S_2 + X$ ppm PMA-M1 at 25°C .

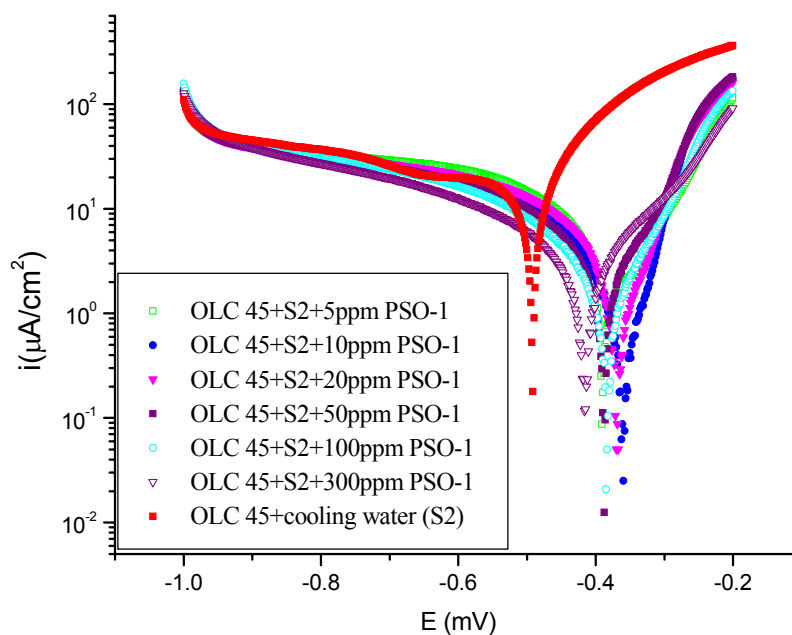


Fig. 4 – Polarization curves of OLC 45 in cooling water $S_2 + X$ ppm PSO-1 at 25°C .

We presume that, the higher inhibitor efficiency, is a consequence of the adsorption process. To quantify the effect of inhibitor concentration on the corrosion rate, it is common to fit the rate data to equilibrium adsorption expressions, such as Langmuir equation: $\theta/(1-\theta) = Kc$, 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: $\theta = (i_{\text{corr}} - i_{\text{corr,inh}})/i_{\text{corr}}$, where $i_{\text{corr,inh}}$ and i_{corr} are the corrosion rates in industrial cooling water S_2 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 $c/\theta = c + 1/K$ and c/θ is plotted against c , when a linear relationship is obtained for each inhibitor and a slope of near unity for each compound indicated approximate Langmuir behaviour (see Fig. 5). The adsorption equilibrium constants (K) for PSO-1 in our two corrosion systems have the following values: for OLC 45+ PSO-1 the value is $4 \times 10^5 \text{M}^{-1}$ and for the system OL 37+ PSO-1 the value is $1.95 \times 10^5 \text{M}^{-1}$ and the adsorption equilibrium constants (K) for PMA-M1 in our two corrosion systems have the following values: for OLC 45+ PMA-M1 the value is $8.4 \times 10^4 \text{M}^{-1}$ and for the system OL 37+ PMA-M1 the value is $6.85 \times 10^4 \text{M}^{-1}$

Further, we shall 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 (ΔG_{ads}^o) by the equation:

$\ln K_{\text{ads}} = -(\Delta G_{\text{ads}}^o / RT)$, where R is the universal gas constant and T the absolute temperature. The obtained values ΔG_{ads}^o characterise the spontaneity of the adsorption process under experimental used conditions. Generally, values of adsorption ΔG_{ads}^o up to -20KJmol^{-1} are consistent with the electrostatic interaction between the charged molecules (in our case, the inhibitor molecules) and the charged metal (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 coordinate type of bond (chemisorption).⁷⁻¹¹

Analyzing the values of ΔG_{ads}^o from Table 7, one can see that, these values are situated between -20KJmol^{-1} and -40KJmol^{-1} , that means a mixture of physical and chemical adsorption of organic inhibitors at the carbon steel surface. This fact proves once again, why the addition of these organic inhibitors leads to the inhibition of the corrosion process in the cooling industrial water.

$$\Delta G_T^o = -RT \ln K = -8.31 \text{J/molK} \times 298 \text{K} \ln 1.95 \times 10^5 = -30164 \text{J/mol OL 37+PSO-1}$$

$$\Delta G_T^o = -RT \ln K = -8.31 \text{J/molK} \times 298 \text{K} \ln 4 \times 10^5 = -31943 \text{J/mol OLC 45+PSO-1}$$

$$\Delta G_T^o = -RT \ln K = -8.31 \text{J/molK} \times 298 \text{K} \ln 6.85 \times 10^4 = -27573 \text{J/mol OL 37+PMA-M1}$$

$$\Delta G_T^o = -RT \ln K = -8.31 \text{J/molK} \times 298 \text{K} \ln 8.4 \times 10^4 = -28079 \text{J/mol OLC 45+PMA-M1}$$

Table 7

The values of ΔG_{ads}^o for studied systems

The system	Type of carbon steel	Values ΔG_{ads}^o KJ/mol	Type of adsorption
Cooling water S_2 +PSO-1	OL-37	-30.164	Chemisorption and physical adsorption
	OLC-45	-31.194	Chemisorption and physical adsorption
Cooling water S_2 +PMA-M1	OL-37	-27.573	Physical adsorption and chemisorptions
	OLC-45	-28.079	Physical adsorption and chemisorptions

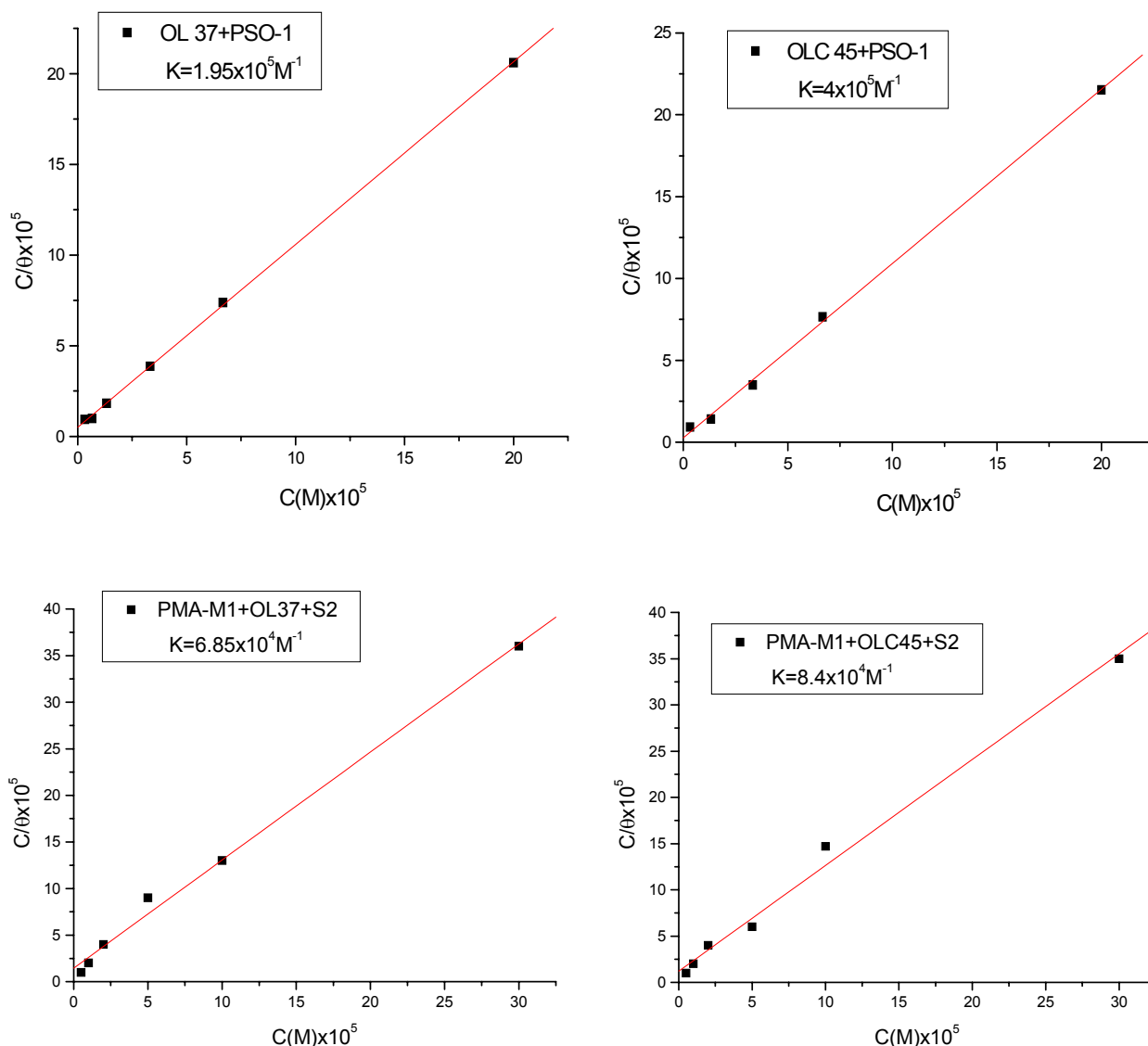


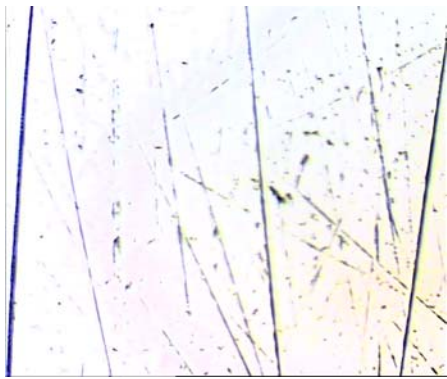
Fig. 5 – Langmuir plot for OL 37+PSO-1, OLC 45+PSO-1, OL 37+PMA-M1 and OLC 45+ PMA-M1.

Further, using the metallographic microscope the electrode surfaces were analyzed before and after electrochemical polarization. In Fig. 6 are given a few micrographies obtained by us for the following systems: carbon steel OL 37 and OLC-45 before polarization and the same carbon steels in cooling water type S_2 with and without organic inhibitors after electrochemical polarization. As it can be observed from Fig. 6, the corrosive attack is more accentuated in the cooling water system without organic inhibitor than in the cases for which the organic inhibitors are used-see in comparison the micrographies from Fig. 6.

Analyzing in comparison the Figs. 6e and 6f, it can be observed that, the corrosive attack is much more accentuated in the case of OL-37+ water type

S_2 +500ppm PMA-M1 system than in the case of OL-37+ water type S_2 +200ppm PMA-M1 system. This finding is in good concordance with the results obtained by electrochemical method – see Table 6 and Fig. 3.

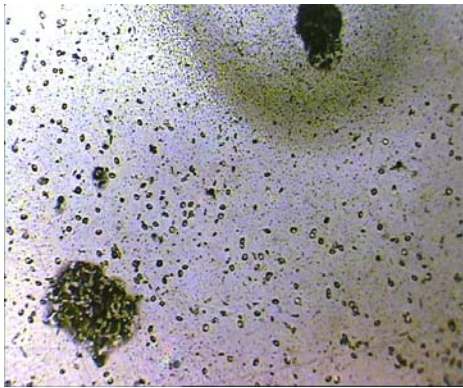
From Figs. 6g and 6h, it can be observed that for the same carbon steel in the same system (industrial cooling water type S_2), the corrosive attack is more aggressive in the presence of the organic inhibitor type PMA-M1 than in the case of the organic inhibitor type PSO-1 and this finding is also in good concordance with the results obtained by electrochemical method – see tables 5, 6 and the polarization curves from Figs. 3 and 4.



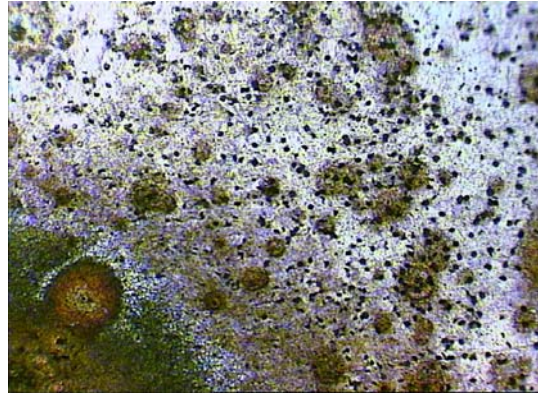
a)

OLC 45 non-corrosive-40x

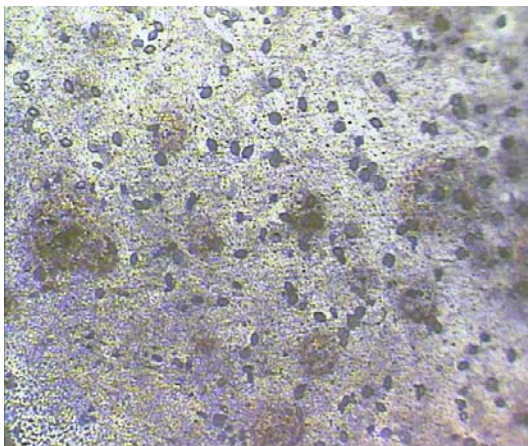
b)

OL37 non-corrosive-100x

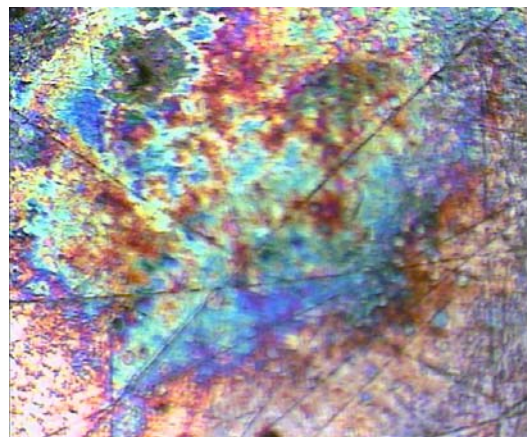
c)

OLC 45 + water type S2-100X

d)

OL 37 + water type S2-100x

e)

OL37+S₂ + 200PMA-M1-200x

f)

OL37+ S₂ + 500PMA-M1-200X

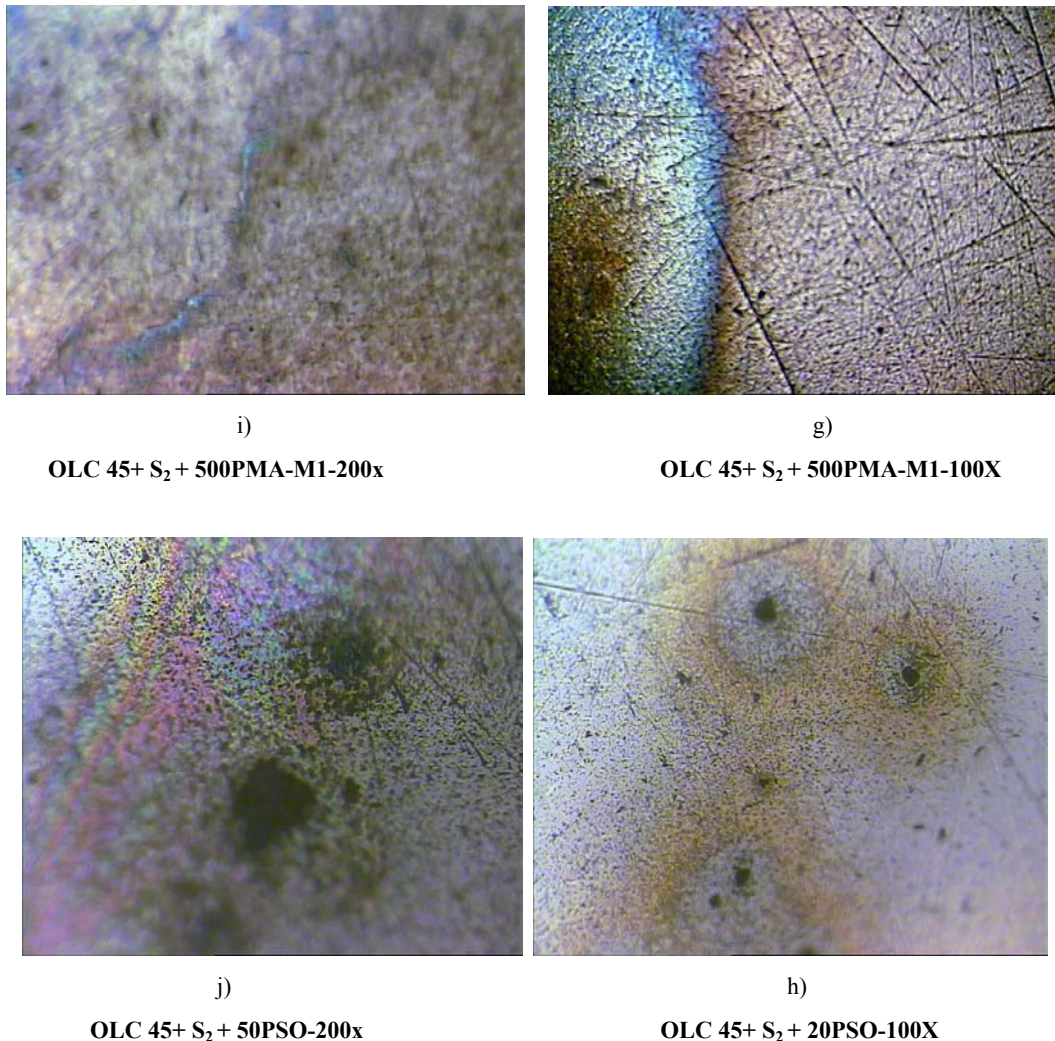


Fig. 6 – Microphotographies of the carbon steel OL 37 and OLC-45 in cooling water type S₂ with and without organic inhibitors.

CONCLUSIONS

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

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

The new organic polymers which were obtained by us have presented a good inhibitory action and a significant efficiency for decreasing of the rate corrosion.

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, in these cases there is a mixture of physical and chemical adsorption of organic inhibitors.

The adsorption of the organic inhibitors at the electrode surface leads to the formation of an adsorbed organic molecules layer, which stabilizes the oxide passive film and in this way, the corrosion process is inhibited.

The inhibitor PSO-1 had a higher efficiency for corrosion system OL-37 in cooling water type S₂ than for corrosion system OLC-45 in the same cooling water S₂.

In the cooling water S₂ without inhibitors, the carbon steel OL-37 had a higher corrosion rate than the carbon steel OLC-45.

The corrosion rate of both carbon steels decreases if the inhibitor concentration increases up to a certain value and then, the corrosion rate increases again if the concentration of the organic inhibitor increases further.

In all of the cases, the organic inhibitor type PSO-1 had a higher efficiency than the organic inhibitor type PMA-M1.

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