Evaluation of Some Corrosion Inhibitors for Industrial Cooling Waters by Electrochemical Methods

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Electrochemical measurements as: corrosion potentials, voltammetry, capacitance measurements, polarization resistance were used to assess the relevant physical properties of new corrosion inhibitors. These new corrosion inhibitors were obtained by radicalic polymerization using the microwaves energy. The inhibition activity analysis of the organic compounds was made by assuming that the mechanism of inhibition by organic molecules is chemisorption and that the energetic of the corrosion process per se is unaffected by the addition of substituents on the parent compound. We presume that, these new organic polymers inhibit corrosion of carbon steel by a protective mechanism, forming insoluble iron complexes and repairing the porous oxide layers. The metallographic micrographies made before and after the potentiodynamic polarizations pointed out the evolution of the corrosion process.The addition of the organic inhibitors led in all the cases to inhibition of the corrosion rate. The corrosion parameters obtained from polarization curves and from EIS spectra are in good concordance and point out the inhibitory action of these new organic polymers. In addition to phosphonate based cooling water inhibitors are stable beyond 100°C, and resistant to oxidation but are sensitive to chlorine.

Keywords: microwaves energy, radicalic polymerization, organic inhibitor, corrosion rate

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 surface contact appear frequent corrosion processes which determine deposition of corrosion products, like scales. Due to these scales formation the exchange heat becomes more difficult, fact that disturbs the normal function of industrial installation. In order to decrease corrosion of pipes, heat exchangers etc. corrosion inhibitors are widely applied. Consequently, an objective is to develop low-toxic, heavy metal and phosphorus free corrosion inhibitors with good biodegradability. For this reason, corrosion inhibiting systems based on different carboxylic acids have been developed. Recent investigations have emphasized the importance of the nature of the metal surface in inhibition performance [1]. 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 [2]. Early studies considered the adsorption of inhibitors on metal surfaces to be primarily physical adsorption and/or chemisorptions [3-6, 9-11]. New investigations have shown that adsorption could also occur through hydrogen bonding [1, 7-8]. In this paper, the inhibition of mild steel corrosion in cooling waters by organic compounds was investigated by potentiodynamic polarizations, EIS measurements and metallography analysis.

This paper 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.

Experimental part

The inhibitory action was studied through tracing the polarization curves obtained using the potentiodynamic method calculation of the kinetic parameters of corrosion in case of solutions with inhibitors, especially the corrosion current densities, and their comparison with the kinetic parameters of the solution without inhibitors. 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 min 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 and also a special type of brass. The chemical compositions of the studied metallic materials are given in the table 1 and 2.

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

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).

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Table 1
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	-	-	-	-	-

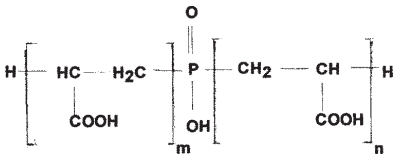
Table 2
CHEMICAL COMPOSITION OF THE WORKING ELECTRODE – BRASS

Electrode	Cu%	Zn%	Pb%	Sn%
Brass	58.79	39.41	1.67	0.13

Table 3
CHEMICAL COMPOSITION OF INDUSTRIAL COOLING WATER TYPE SB

Indicators	UM	Water type SB, values of parameters
PH		7.95
Conductivity	µS/cm	665
Alcalinity	mval/L	4.2
Total Hardness	mval/L	4.18
Calcium Hardness	mval/L	4.16
Cloride, 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

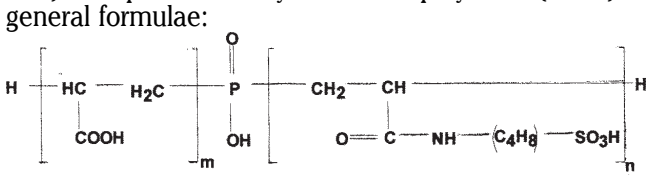
a) Phosphino-carboxylic polyacids (PCA) of general formulae:



(1)

where m + n = 20 – 30

b) Phosphino-carboxylic-sulfonic polyacids (PCSA) of general formulae:



(2)

where m + n = 20 – 30.

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 compounds were: i) *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); (ii) *PMA-M11/O* a mixture with weight ratio 1/1 polymaleic acid and PBTC, which was neutralized and additived with PSO; and (iii) *PCA-M21/T*- a mixture with weight ratio 2/1 PCA/PBTC, which was neutralized and additived with tolyltriazol.

Results and discussions

The polarization behaviour of metallic materials mentionated above was studied in cooling water with chemical composition given in table 3. The corrosion parameters were calculated on the basis of potentiodynamic potential-current characteristics in the Tafel region ($E=E_{corr} \pm 150mV$) and the vicinity of the corrosion potential ($E=E_{corr} \pm 15mV$) according to:

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

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

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:

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

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

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

The corresponding Tafel parameters were obtained from Mansfeld's method, employing polarization date near the corrosion potential. 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. Figures1-6 show a series of potentiodynamic polarization curves for two carbon steels electrodes and brass electrode in a cooling water type SB (with chemical composition given in table 3), in absence and presence of different concentrations of inhibitors.

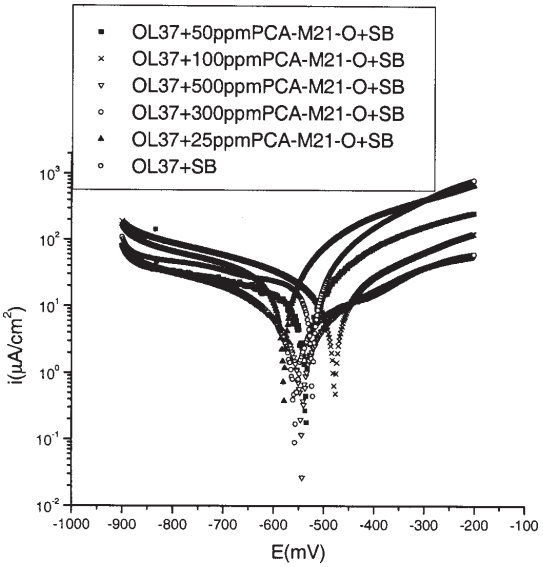


Fig. 1. Polarization curves of OL 37 in cooling water SB +Xppm PCA-M21/O at 25°C

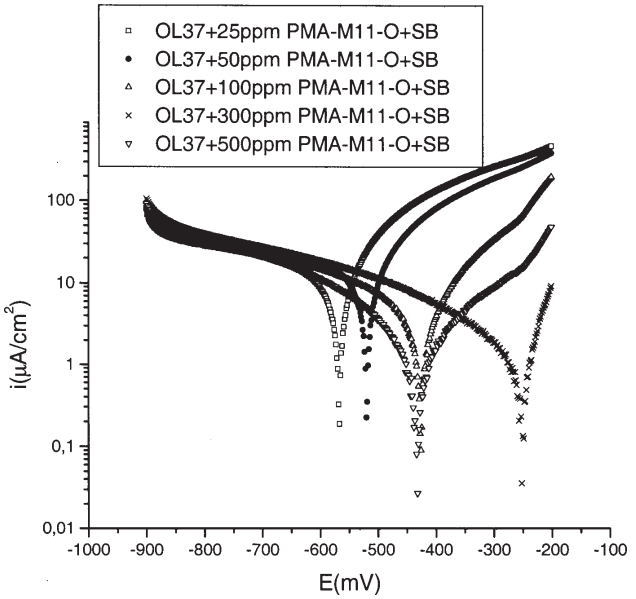


Fig. 2. Polarization curves of OL 37 in cooling water SB +Xppm PMA-M11/O at 25°C

Analysis of the polarization curves from figures 1-6 indicates that at low overvoltages, the Tafel relationship are followed, showing that both anodic and cathodic reactions are activation-controlled. At higher overvoltages

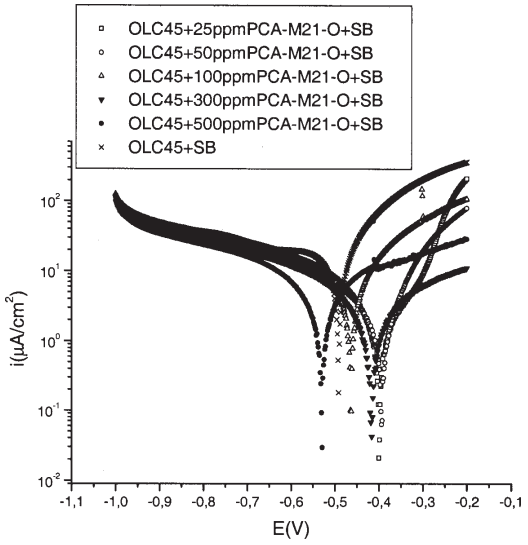


Fig. 3. Polarization curves of OLC 45 in cooling water SB +Xppm PCA-M21/O at 25°C

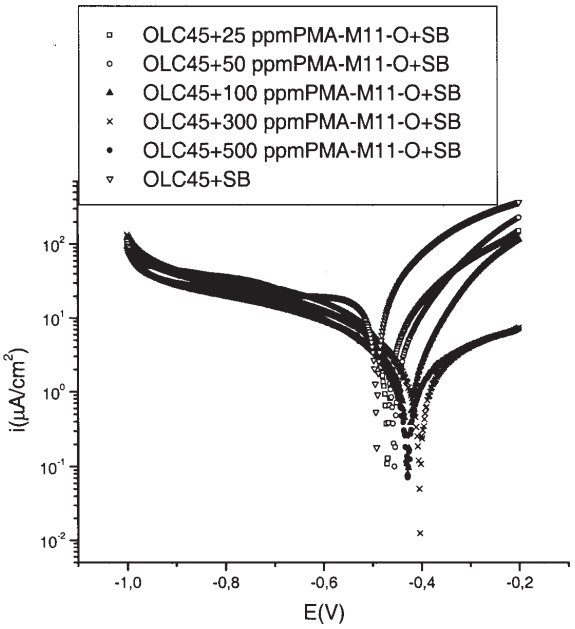


Fig. 4. Polarization curves of OLC 45 in cooling water SB +Xppm PMA-M11/O at 25°C

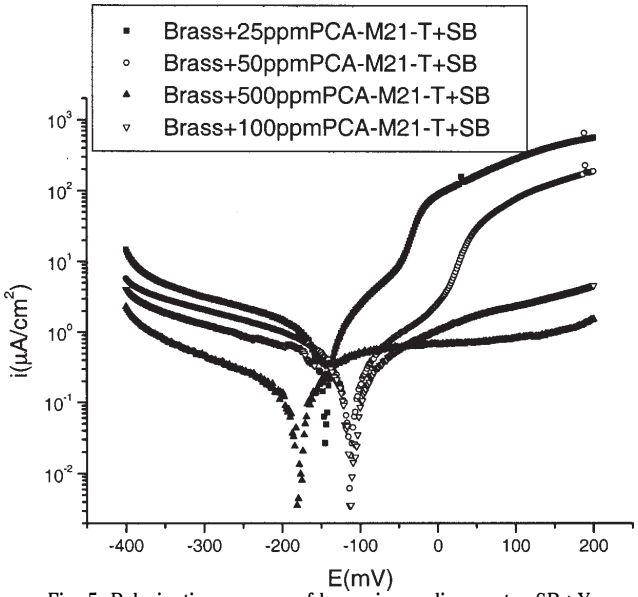


Fig. 5. Polarization curves of brass in cooling water SB+Xppm PCA-M21/T at 25°C

Table 4

KINETIC CORROSION PARAMETERS OF CARBON STEEL OL-37 IN COOLING INDUSTRIAL WATER TYPE SB IN PRESENCE AND ABSENCE OF ORGANIC INHIBITOR TYPE PCA-M21/O at 25°C

Inhibitor (ppm)	i_{corr} ($\mu A/cm^2$)	R_p $K\Omega/cm^2$	R_{mpy}	$P_{mm/year}$	K_g g/m^2h	E (%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	15.17	1.46	7.08	0.17	0.16		-523	102	-369	
25	12.82	1.6	5.98	0.15	0.13	15	-580	97	-187	0.15
50	6.80	3.01	3.17	0.08	0.07	55	-482	123	-138	0.55
100	5.07	3.20	2.36	0.06	0.05	66	-538	81	-122	0.66
300	2.98	7.24	1.39	0.04	0.03	80	-560	156	-125	0.80
500	1.74	9.49	0.81	0.02	0.01	88	-546	104	-99	0.88

Table 5

KINETIC CORROSION PARAMETERS OF CARBON STEEL OL-37 IN COOLING INDUSTRIAL WATER TYPE SB IN PRESENCE AND ABSENCE OF ORGANIC INHIBITOR TYPE PMA-M11/O at 25°C

Inhibitor (ppm)	i_{corr} ($\mu A/cm^2$)	R_p $K\Omega/cm^2$	R_{mpy}	$P_{mm/year}$	K_g g/m^2h	E (%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	15.17	1.46	7.08	0.17	0.16		-523	102	-369	0
25	8.87	2.48	4.13	0.10	0.09	42	-522	105	-250	0.42
50	5.53	2.97	2.58	0.06	0.05	64	-568	73	-146	0.64
100	2.16	7.64	1.01	0.025	0.022	85	-429	84	-126	0.85
300	0.88	17.22	0.41	0.01	0.009	94	-254	50	-149	0.94
500	0.92	21.04	0.43	0.01	0.009	93	-435	113	-112	0.93

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 figure 1, 2, 3 and 4, it can be observed that, on the large range of the potential the carbon steel electrodes and also the brass electrode (fig. 5) 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:

$$\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2HO^- \qquad (7)$$

After this potential range similar to passive range potential the cathodic current increases again and this increasing is due to the hydrogen evolution. The addition of the organic inhibitors to the amounts shown in the tables 4-8 leads in all the cases to the inhibition of the corrosion processes. Analyzing in comparison the figures 1-4 and tables 4-7, it can be observed that, the organic inhibitor type PMA-M11/O has a higher efficiency on the corrosion process of OLC-45 and OL 37 carbon steel in cooling industrial water type SB, than the organic inhibitor type PCA-M21/O. On the other hand, in the some environment, industrial cooling water types, the carbon steel OL-37 has a higher corrosion rate than OLC-45 carbon steel. We can conclude that, in this cooling water system the protection of metallic surfaces from corrosion can be realized by using these new polymers obtained in microwaves field.

Analyzing in comparison the figures 5-6and table 8 with the figures 1-4 and tables 4-7, it can be observed that, in

Table 6

KINETIC CORROSION PARAMETERS OF CARBON STEEL OLC-45 IN COOLING INDUSTRIAL WATER TYPE SB IN PRESENCE AND ABSENCE OF ORGANIC INHIBITOR TYPE PCA-M21/O at 25°C

Inhibitor (ppm)	i_{corr} ($\mu A/cm^2$)	R_p $K\Omega/cm^2$	R_{mpy}	$P_{mm/year}$	K_g g/m^2h	E (%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	10.68	2.06	4.57	0.115	0.103	-	-493	104	-294	
25	3.19	5.37	1.49	0.037	0.034	70	-464	89.8	-129	0.70
50	1.16	18.71	0.54	0.013	0.012	89	-419	134	-121	0.89
100	1.09	15.91	0.50	0.129	0.011	89	-402	113	-97	0.89
300	1.04	14.19	0.48	0.012	0.010	90	-397	67	-105	0.90
500	1.43	9.73	0.66	0.017	0.014	87	-530	86	-90	0.87

Table 7

KINETIC CORROSION PARAMETERS OF CARBON STEEL OLC-45 IN COOLING INDUSTRIAL WATER TYPE SB IN PRESENCE AND ABSENCE OF ORGANIC INHIBITOR TYPE PMA-M11/O at 25°C

Inhibitor (ppm)	i_{corr} ($\mu A/cm^2$)	R_p $K\Omega/cm^2$	R_{mpy}	$P_{mm/year}$	K_g g/m^2h	E (%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	10.68	2.06	4.57	0.115	0.103	-	-493	104	-294	
25	3.38	5.82	1.57	0.04	0.035	68	-472	99	-166	0.68
50	2.62	6.69	0.24	0.006	0.005	75	-458	98	-123	0.75
100	1.07	14.31	0.098	0.0025	0.0022	89	-429	72	-116	0.89
300	0.8	20.56	0.07	0.0018	0.0015	92	-406	126	-104	0.92
500	0.9	23.47	0.083	0.0021	0.0018	91	-430	152	-123	0.91

Table 8

KINETIC CORROSION PARAMETERS OF BRASS IN COOLING INDUSTRIAL WATER TYPE SB IN PRESENCE AND ABSENCE OF ORGANIC INHIBITOR TYPE PCA-M21/ T AT 25°C

Inhibitor (ppm)	i_{corr} ($\mu A/cm^2$)	R_p $K\Omega/cm^2$	R_{mpy}	$P_{mm/year}$	K_g g/m^2h	E (%)	E_{corr} (mV)	b_a (mV)	b_c (mV)	θ
0	1.25	15.96	0.57	0.014	0.013		-104	119	-135	
25	0.81	25.41	0.38	0.009	0.0085	35	-147	92	-211	0.60
50	0.33	73.06	0.15	0.0037	0.0033	74	-115	120	-142	0.98
100	0.2	117.6	0.09	0.0022	0.0020	84	-113	100	-114	0.99
300	0.18	134	0.08	0.0019	0.0018	86	-120	114	-118	1
500	0.14	165	0.069	0.0017	0.0015	89	-181	75	-111	1

the same corrosion environment, the corrosion rate of the brass (with the chemical composition given in the table 2) is much lower than the corrosion rate of the carbon steels type OLC 45 and OL-37. From table 8, it can be observed that, the addition of the organic inhibitor type PCA-M21/T to the amounts shown in this table leads in all cases to the inhibition of the corrosion process. The high efficiency of the brass corrosion inhibition in cooling water type SB points out that, in this cooling water system, can be used for corrosion protection the organic inhibitor type PCA-M21/T that was obtained by us using the polymerization in microwaves field. In all the cases, it can be observed that, the corrosion rate of metallic materials decreases as the inhibitior concentration increases up to a certain value and then, the rate of corrosion increases again if the concentration of the organic inhibitor increases further. We presume that, the higher inhibitor efficiency is a consequence of the 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:

$$\theta/(1-\theta) = Kc \tag{8}$$

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:

$$\theta = (i_{corr} - i_{corr.inhib})/i_{corr} \tag{9}$$

where $i_{corr,inh}$ and i_{corr} are the corrosion rates in industrial cooling water SB 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:

$$c/\theta = c + 1/K \tag{10}$$

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 (fig. 9-10). The adsorption equilibrium constants (K) for our corrosion systems have the following values: for OLC-45+PCA-M21/O and OLC-45+PMA-M11/O the values of K are: 39.062x $10^4 M^{-1}$ and 27.427x $10^4 M^{-1}$, while for OL-37+PCA-M21/O and OL-37+PMA-M11/O the values of K are 3x $10^4 M^{-1}$ and K=11.75x $10^4 M^{-1}$

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 shall try to show what 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:

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

The obtained values ΔG^o_{ads} up to -20Kjmol^{-1} are consistent with 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 co-ordinative type of bond (chemisorptions see table 9).

Further, using the metallographic microscope the electrode surfaces were analyzed before and after electrochemical polarization. In figure 7 are given a few micrographies obtained by us for the following systems:

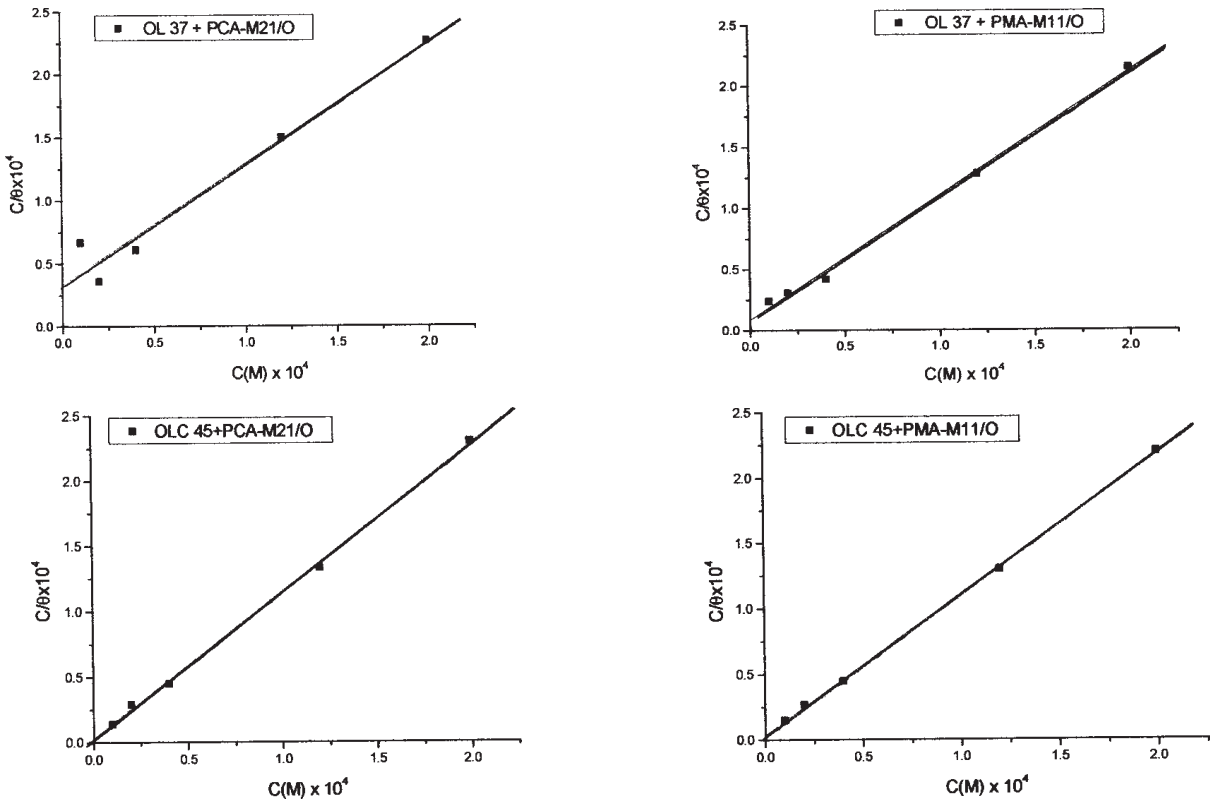


Fig. 6. Langmuir plot for OL-37+PCA-M21/O, OL-37+PMA-M11/O, OLC-45+ PCA-M21/O and OLC-45+PMA-M11/O

Table 9
THE VALUES OF K_{ids} AND ΔG^{o}_{ads} FOR STUDIED SYSTEMS

The system	Type of metallic material	Values of K_{ids}, KJM^{-1}	Values of ΔG°_{ads} KJM^{-1}	Type of adsorption
Cooling water type SB + PCA-M21/O	OL-37	$3x10^4$	-25.529	Physical adsorption and chemisorption
	OLC-45	$39.062x10^4$	-31.885	Chemisorption and physical adsorption
Cooling water type SB + PMA-M11/O	OL-37	$11.75 x10^4$	-28.91	Physical adsorption and chemisorption
	OLC-45	$27.427 x10^4$	-31.009	Chemisorption and physical adsorption
Cooling water type SB + PCA-M21/T	Brass	$1.802 x10^5$	-29.969	Chemisorption and physical adsorption

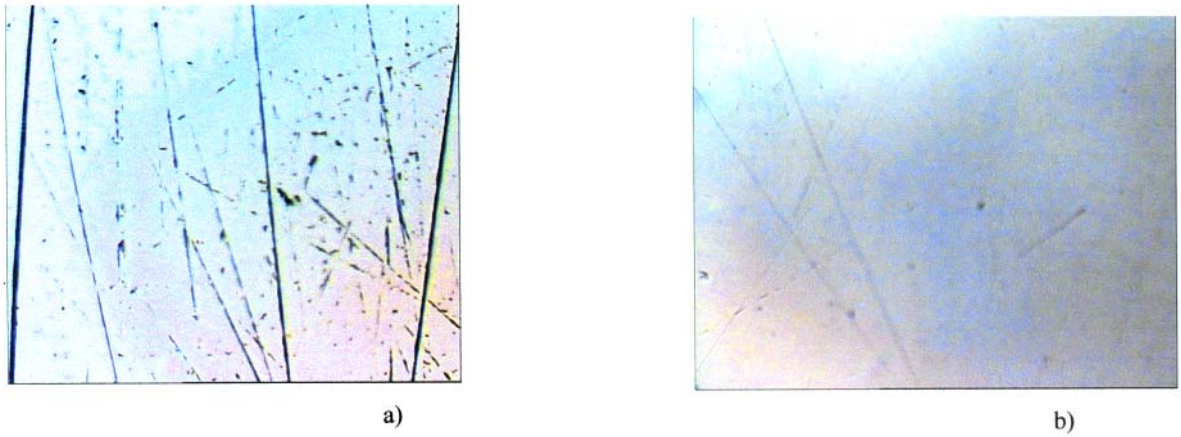


Fig. 7. Micrographies of the carbon steel OL 37 and OLC-45 in cooling water type SB with and without organic inhibitors

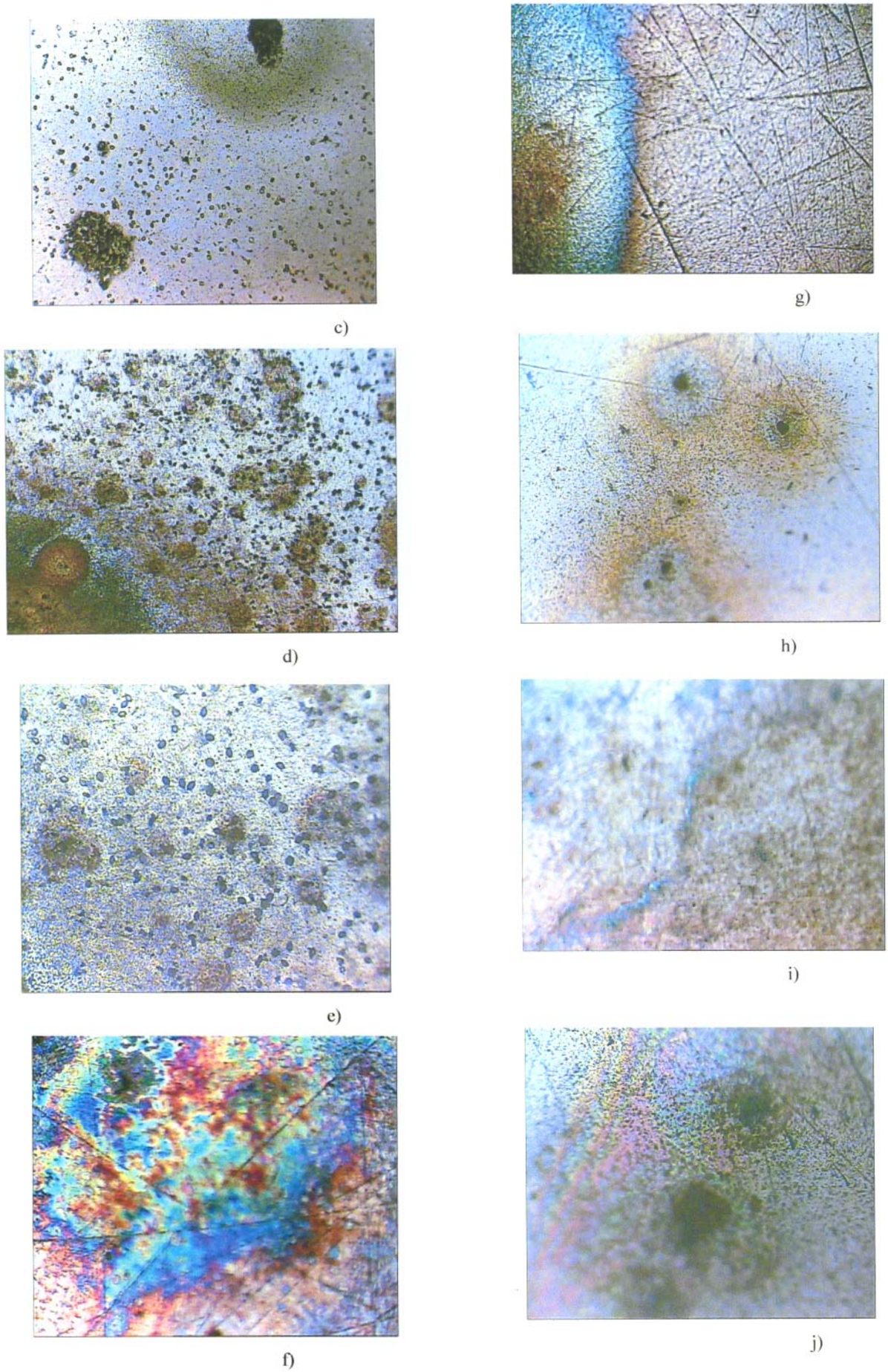


Fig. 7. Micrographies of the carbon steel OL 37 and OLC-45 in cooling water type SB with and without organic inhibitors

carbon steel OL 37 and OLC-45 before polarization and the same carbon steels in cooling water type SB with and without organic inhibitors after electrochemical polarization. As it can be observed from figure 7, 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. 7).

Analyzing in comparison the figures 7e and 7f, it can be observed that, the corrosive attack is much more accentuated in the case of OL 37+ water type SB + 50ppm PMA-M11/O system than in the case of OL-37+ water type SB+300ppm PMA-M11/O system. This finding is in good concordance with the results obtained by electrochemical method (see tables 4 and 5 and the polarization curves from figs. 1 and 2).

From figures 7i and 7j, it can be observed that for the same carbon steel in the same system (industrial cooling water type SB), the corrosive attack is more aggressive in the presence of the organic inhibitor PMA-M11/O than in the case of the organic inhibitor PCA-M21/O type and this finding is also in good concordance with the results obtained by electrochemical method (see tables 6 and 7 and the polarization curves from figures 3 and 4).

Conclusions

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

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

The organic inhibitors were chemisorbed on the carbon steel surface according to a Langmuir isotherm. The values of adsorption constant determined from the plot of Langmuir isotherm pointed out that the adsorption of PCA-M21/O is stronger than the adsorption of PCA-M11/O for the case of carbon steel type OLC- 45, while for the carbon steel type OL-37 the adsorption of PCA-M11/O is stronger than the adsorption of PCA-M21/O.

In the industrial cooling water type SB the corrosion rate of carbon steel type OL- 37 is higher than corrosion rate of carbon steel type OLC- 45.

We can conclude that for the carbon steel type OLC-45 in cooling water SB, the best efficiency has the organic compound PCA-M21/O, while for the system OL-37 in cooling water SB the best efficiency has the organic compound PCA-M11/O.

The micrographies pointed out that the corrosive attack is much stronger in the industrial cooling water type SB without organic inhibitor than in the case of organic inhibitor presence, this fact being in good concordance with the results obtained by electrochemical polarization.

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