



*Dedicated to Professor Victor-Emanuel Sahini
on the occasion of his 85th anniversary*

EFFECT OF NEW ORGANIC POLYMERS AS GREEN INHIBITORS ON THE CORROSION BEHAVIOUR OF CARBON STEELS IN COOLING WATER SYSTEMS

Iulia HĂRĂBOR,^a Viorel BRÂNZOI^a and Florina BRÂNZOI^{b,*}

^a University Politehnica of Bucharest, 132 Calea Griviței, Bucharest - 010737, Roumania

^b Institute of Physical Chemistry, 202 Splaiul Independenței, Bucharest - 060021, Roumania

Received March 21, 2012

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 new organic synthesis inhibitors obtained in microwaves field. Using the microwaves energy new organic polymers were synthesised by radicalic polymerization. These new organic compounds have anticorrosive and antiscale properties and for this reason, were used for cooling water systems protection. The inhibition activity analysis of these new organic polymers 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 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 methods employed were potentiodynamic polarization, electrochemical impedance spectroscopy and metallurgical microscopy techniques. The inhibition efficiency was high in all the studies cases. 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. The adsorptions of the organic compounds on the carbon steels surface obeyed Langmuir's isotherm. Using Fourier transform infrared spectroscopy (FT-IR) it was proved the adsorption of organic inhibitors and the formation of corrosion products on the carbon steels surface. 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. The addition of the organic inhibitors led in all the cases to inhibition of the corrosion rate.

INTRODUCTION

Carbon steel is a common constructional material for many industrial units because of its cost and excellent mechanical properties. However, it suffers severe attack in service, in cooling water systems, in oil and gas production and in various aggressive environments. There has been a substantial change in cooling water chemistry over the past decade. Use of high-performance antiscalants, corrosion inhibitors, polymers for better dispersion, total prevention of microbial deposits by using powerful biocides and

biodispersants, pH boosters, and advanced hardness stabilizers is current practice for the treatment of cooling water. The use of organic inhibitor leads to decrease the rate of corrosion processes of carbon steels in different environments.¹⁻⁵ Corrosion is a major problem in cooling water industrial systems, in oil and gas production systems. 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

* Corresponding author: fbrinzoi@chimfiz.icf.ro

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.²⁻¹¹ Many problems such as high cost of operation, compatibility with other chemicals, difficulty in understanding the cooling water systems, mechanism of inhibition, dosage of inhibitor required, arise in cooling water systems.¹⁰⁻¹⁴

In the present work, the inhibition of carbon steel corrosion in cooling waters by organic compounds was investigated by potentiodynamic polarizations, EIS, FT-IR measurements and metallography analysis 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.¹⁵⁻²²

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 electrochemical impedance spectra were obtained in a frequency range from 100 kHz to 40 mHz. Disturbance amplitude of 10mV was applied relative to open circuit potential and ten measurements were performed for each frequency decade. The studied metals were the carbon steel type OL 37. The chemical compositions of the studied metallic materials are given in Table 1.

Table 1

The chemical composition of the working electrodes

Electrode	C%	Si%	Mn%	Fe%	P%	S%	Al%	Ni%	Cr%	Cu%	Sn%	As%
OL 37	0.15	0.09	0.4	99.293	0.023	0.02	0.022	-	-	-	-	-

The corrosion medium was industrial cooling water type S1 with the chemical composition given in Table 2.

Table 2

The chemical composition of the cooling water type S1

Indicators	UM	Water type SC1 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 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 were three polymers, which were obtained by radicalic polymerization in presence of microwave field: PASAC-7 (polyaspartic acid and phosphoric acid molar ratio 1:0.06 in ammonium salt at t=200°C), PASAC-8 (polyaspartic acid and H₃PO₄ 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).

RESULTS AND DISCUSSION

Fig. 1 depicts the anodic and cathodic polarization curves recorded on carbon steel OL-37 in cooling

water system S1 with and without inhibitors at 25°C. Both anodic and cathodic curves were polarized in comparison with that obtained in the absence of inhibitor, thus inhibiting both the anodic dissolution of carbon steel and the

reduction of hydrogen ions on the metal surface. This confirms that these inhibitors behave as a mixed inhibitor. The electrochemical parameters derived from the polarization curves at different concentrations are given in Tables 3-5.

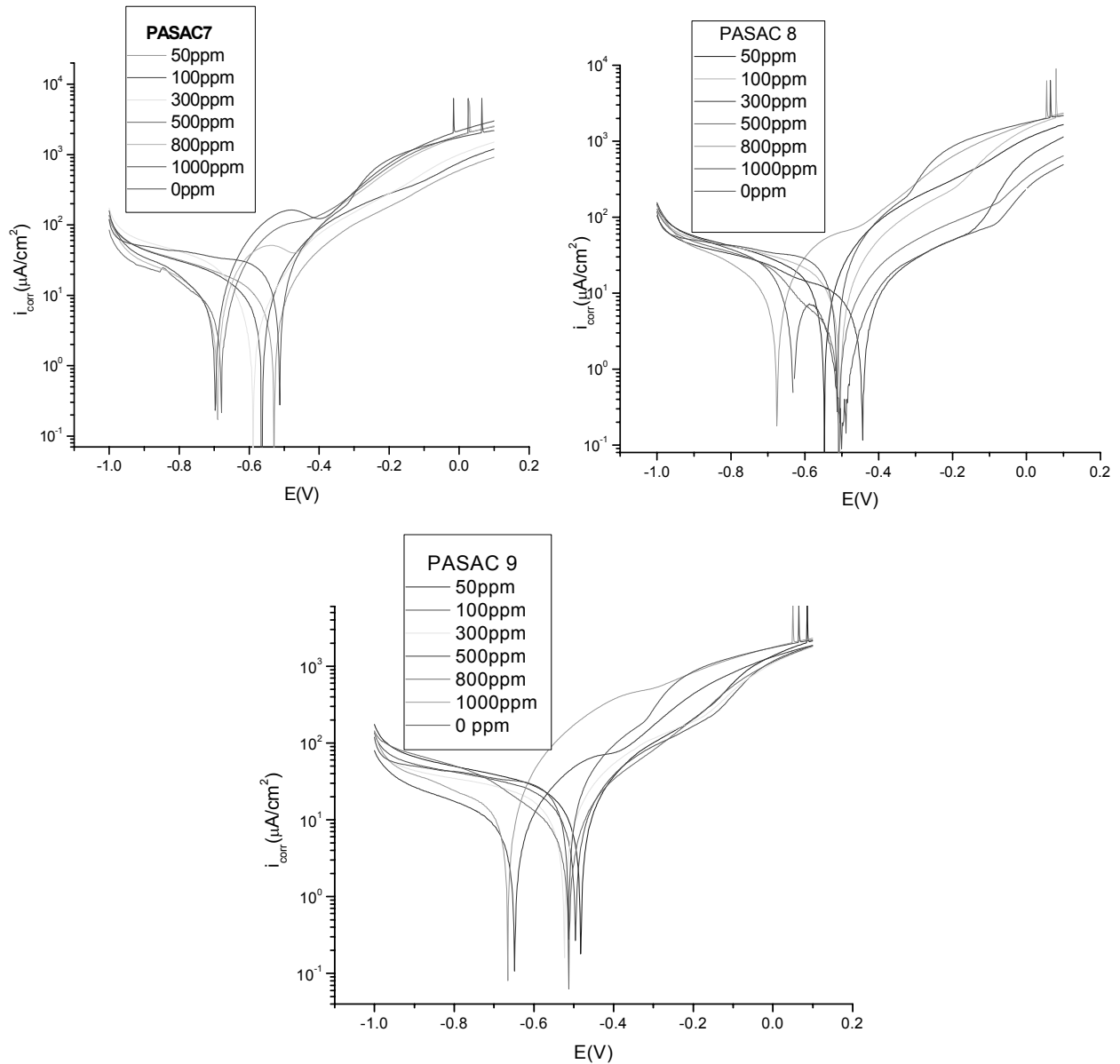


Fig. 1 – The polarization curves of OL 37 carbon steel in cooling water type S1 in presence of PASAC7, PASAC8 and PASAC9 at 25°C.

Table 3

Kinetic corrosion parameters of OL 37+ X ppm PASAC 7+S1 at 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	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 4

Kinetic corrosion parameters of OL 37+ X ppm PASAC 8+S1 at 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	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 5

Kinetic corrosion parameters of OL 37+ X ppm PASAC 9+S1 at 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	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	0.5111
100	6.27	3.29	2.661	0.0675	0.0600	56.16	-520	107	-167	0.5616
300	5.703	3.24	2.926	0.0742	0.0660	51.80	-495	101	-137	0.5180
500	3.683	5.11	1.718	0.0436	0.0387	71.69	-640	96	-143	0.7169
800	3.55	5.12	1.656	0.0420	0.0373	72.71	-512	90	-133	0.7271

Analyzing these tables, it can be observed that, the addition of the organic inhibitor to the amounts shown in Tables 3-5 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.¹² It can be observed from Tables 3-5 that the inhibitor PASAC8 has a higher efficiency for corrosion system OL37+S1 than for PASAC9 in same condition. Analyzing in comparison the corrosion rate of organic inhibitors, in the same condition, one can see that the PSAC-8 had a higher efficiency for corrosion system OL 37 in S1, PASAC7 had a good efficiency for corrosion system OL 37 in S1 than PASAC-9. 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 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.

The variation curves of the corrosion current density and efficiency function of the inhibitor concentration are presented in Fig. 2. From it, one can see much better the influence of these parameters on the polarization behaviour of the carbon steel OL 37 in cooling water system.

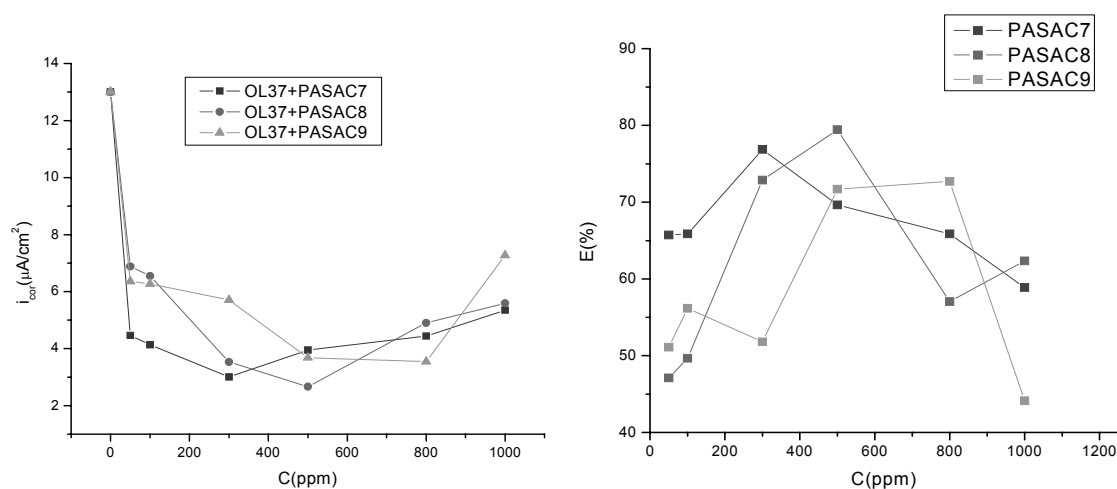


Fig. 2 – The influence of the inhibitor PASAC7, PASAC8 and PASAC9 concentration on the corrosion rate and efficiency of carbon steel OL-37 in cooling water type S₁ at 25°. The inhibition efficiency follows the order: $E_{\text{PASAC8}} > E_{\text{PASAC7}} > E_{\text{PASAC9}}$.

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: $\theta = (i_{\text{corr}} - i_{\text{inh}})/i_{\text{corr}}$, where i_{inh} and i_{corr} are the corrosion rates in industrial cooling water S1 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 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. 3). 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 ($\Delta G_{\text{ads}}^{\circ}$) by the equation:

$$\ln K_{\text{ads}} = -(\Delta G_{\text{ads}}^{\circ} / RT)$$

The obtained values $\Delta G_{\text{ads}}^{\circ}$ 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 6).²³⁻²⁵

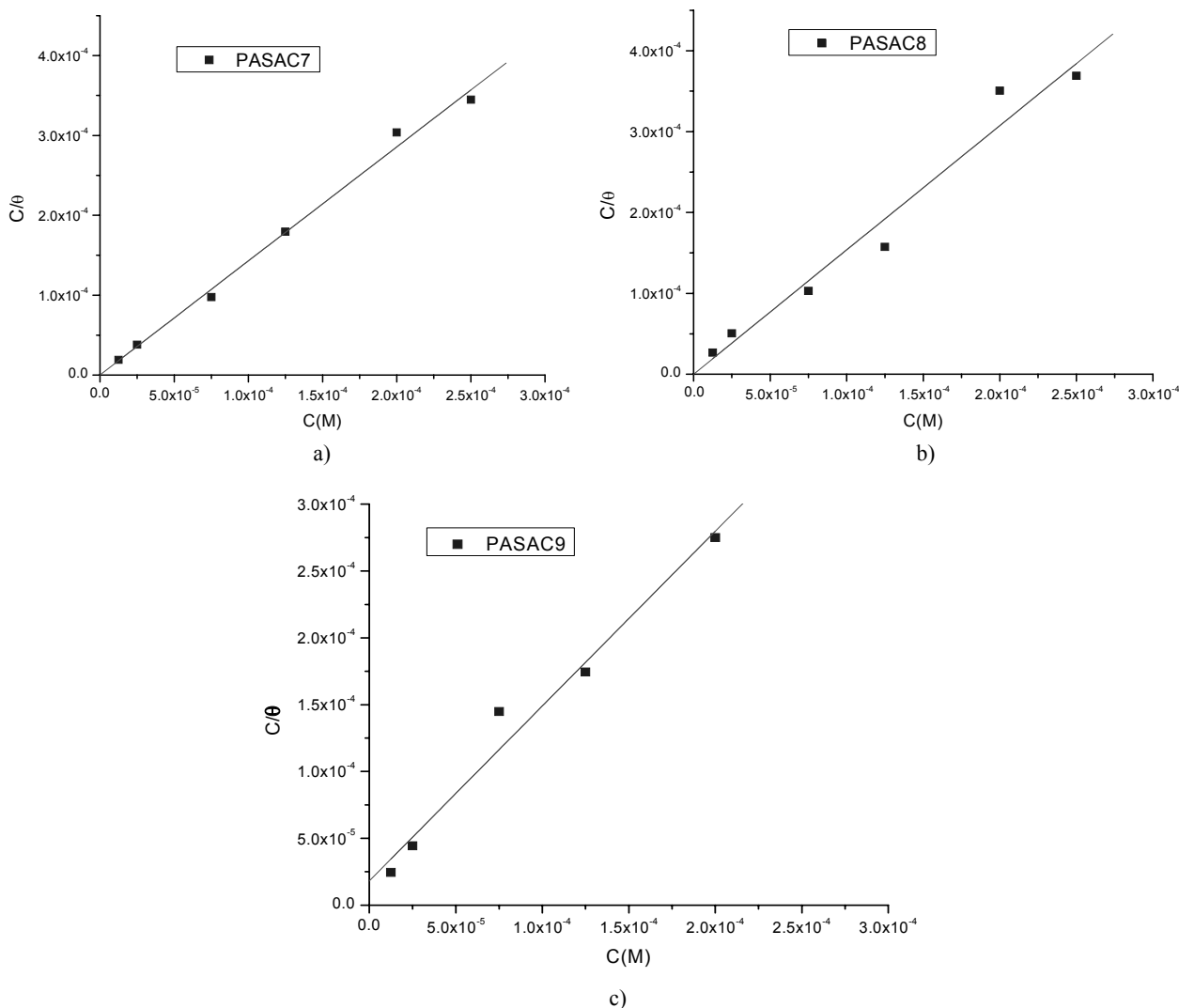


Fig. 3 – Langmuir plot for a) PASAC 7, b) PASAC 8 and c) PASAC 9 on OL 37 in S1 at different inhibitor concentrations.

The corrosion of carbon steel in cooling water system in the absence and presence of PASAC7, PASAC8, and PASAC9 were investigated by EIS at the open circuit potential condition 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. The Nyquist diagrams (Fig. 4) show only one semicircle and the diameter of the semicircle

increases on increasing the inhibitor concentration suggesting that the formed inhibitive film was strengthened by the addition of inhibitors. Fig. 4 also indicates that the diameters of the capacitance loops in the presence of PASAC 7, PASAC8 and PASAC 9 are bigger than that in the absence of organic inhibitors, suggesting that these inhibitors has good anticorrosion performance on the carbon steel in S_1 .

Table 6
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 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

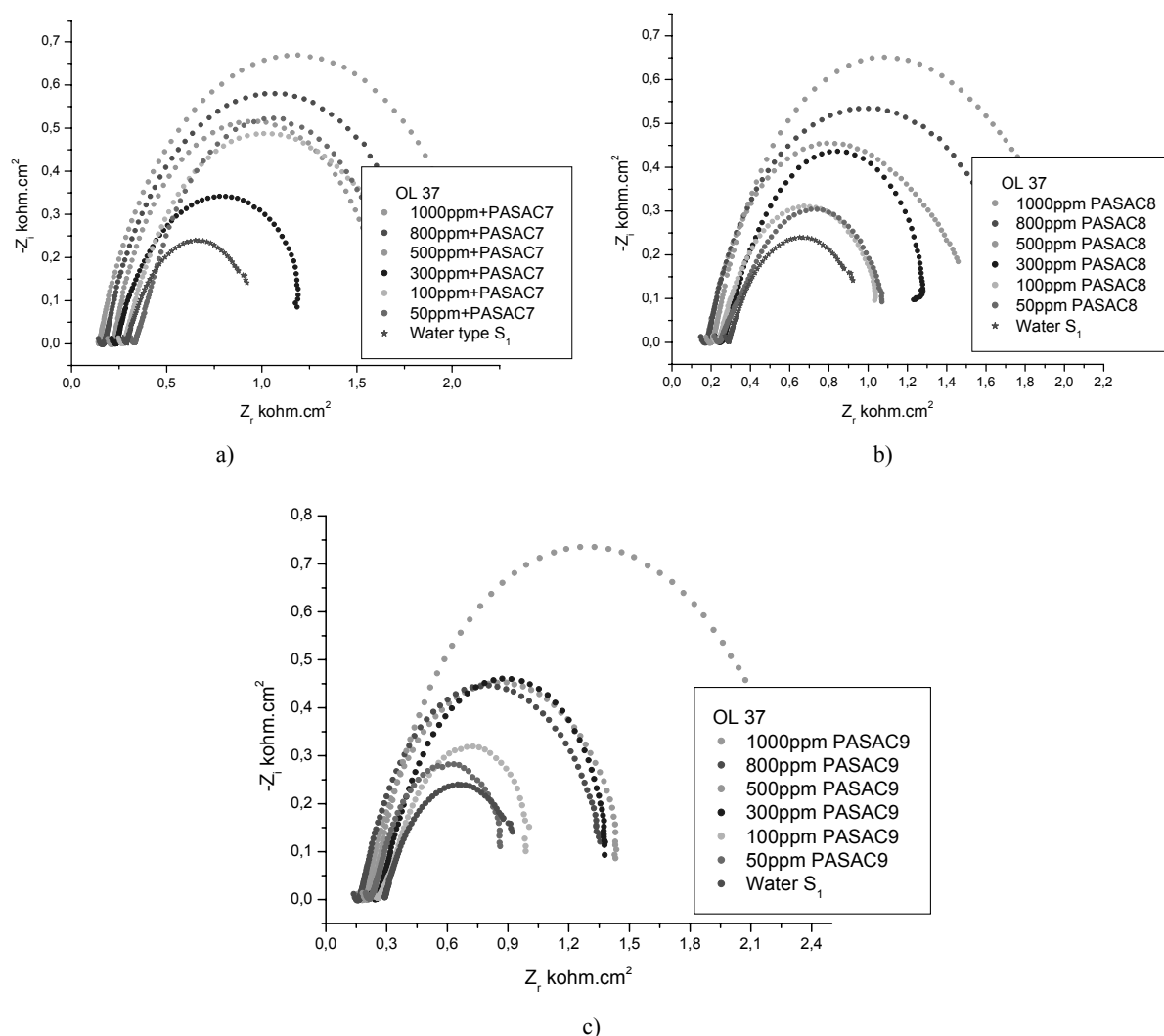


Fig. 4 – The Nyquist plot for OL 37 in S_1 with and without organic inhibitor at 25°C a) PASAC7, b) PASAC8, c) PASAC9.

The Bode plots are shown in Figs. 5-7 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 60° 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.

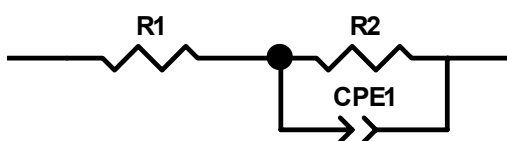


Fig. 5 – Equivalent circuit.

All the obtained plots show only one semicircle and they were fitted using one time constant equivalent mode (see Fig. 5) 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.

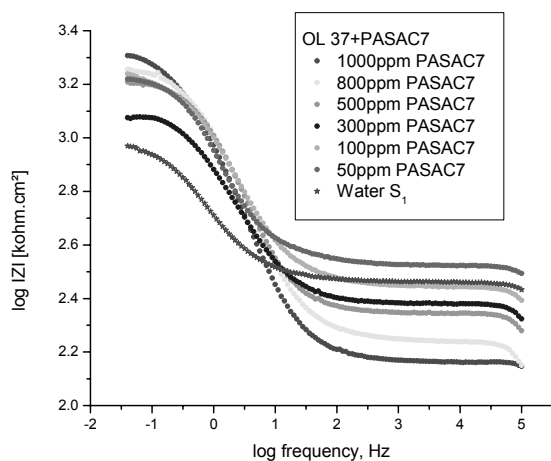
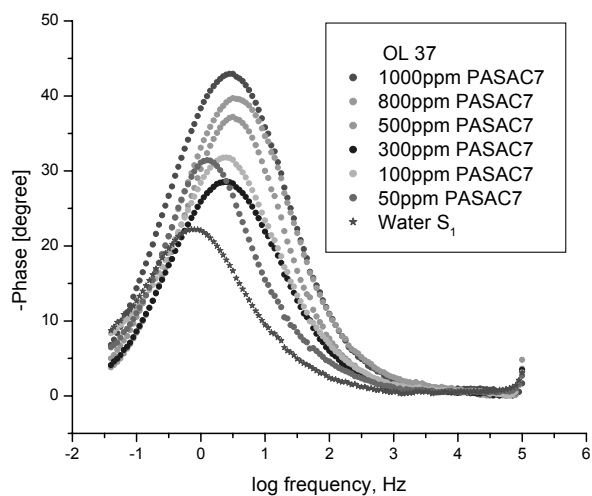


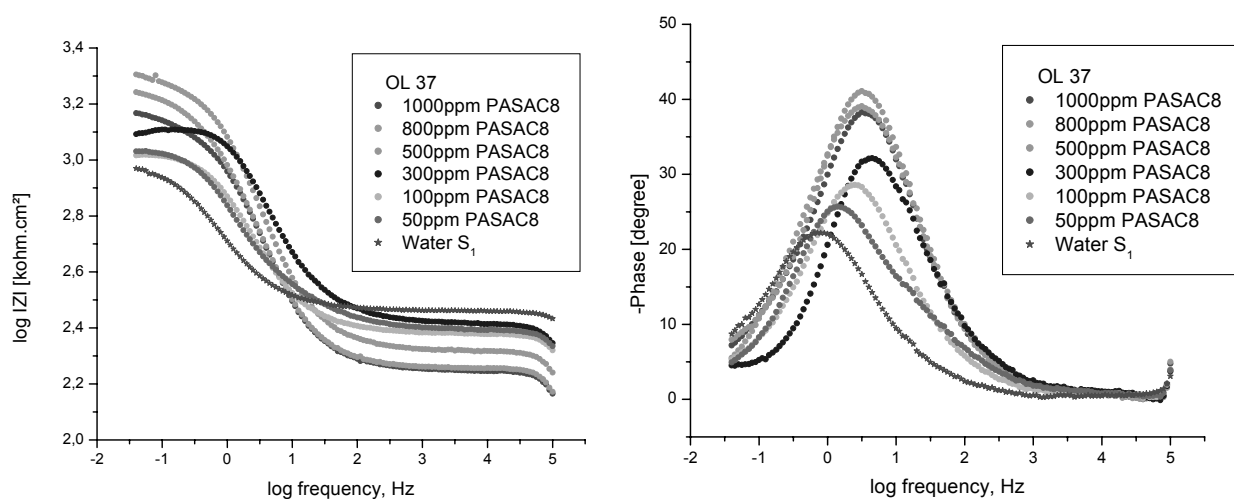
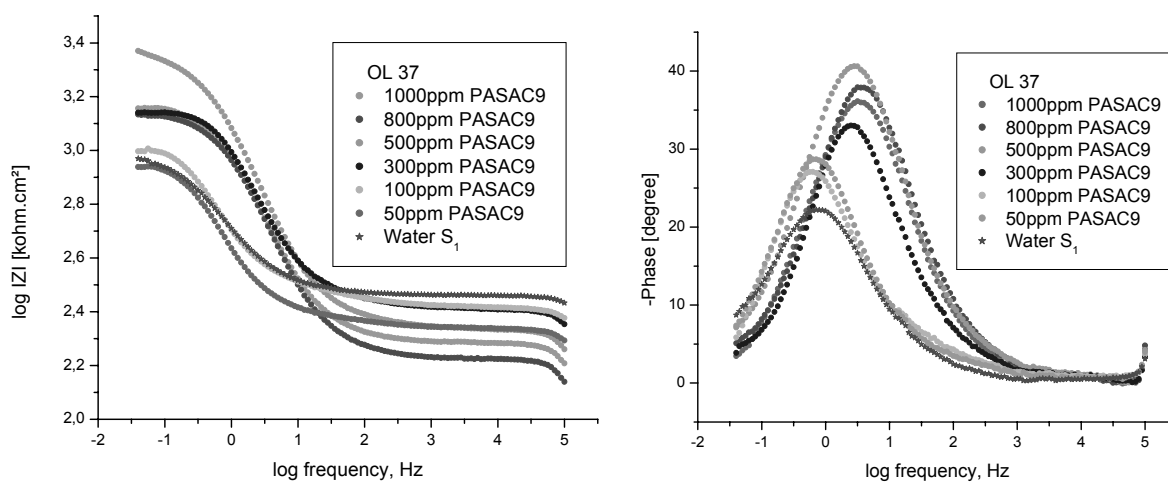
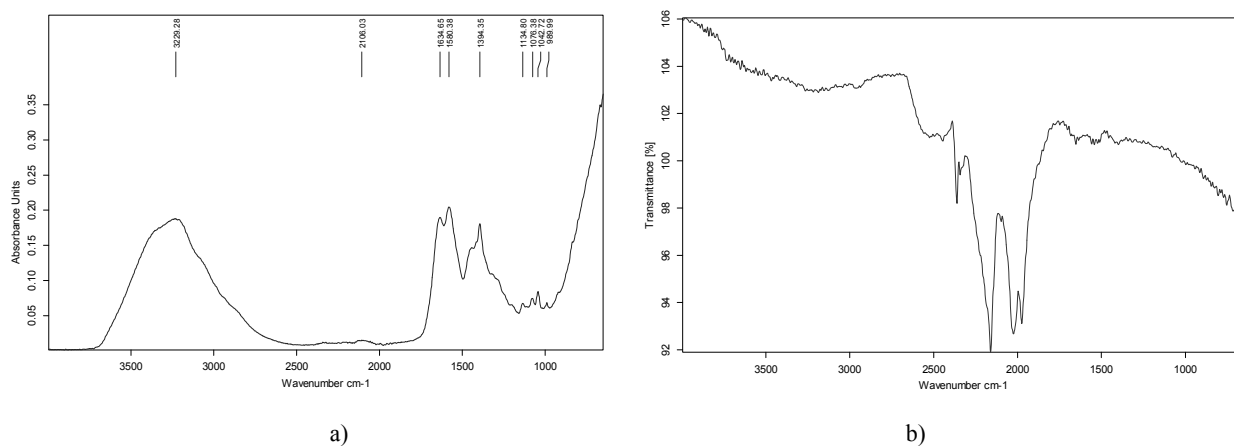
Fig. 6 – The Bode plot for OL 37+ PASAC7 in S₁ at 25°C.

In this paper, FT-IR spectrometry was used to identify whether there was adsorption and to provide new bonding informations on the steel surface after immersion in the cooling water system containing organic inhibitors.²⁶⁻³⁰ All spectra in these experiments were obtained at a resolution 4cm^{-1} in the region $4000\text{-}650\text{ cm}^{-1}$. The FT-IR spectrum of organic polymer PASAC7 and 300ppm PASAC7+OL37+S1 is shown in Fig. 9a and 9b. This shows the characteristic bands for the adsorbed PASAC 7 on the metal surface. A weak band in the range $3000\text{-}3500\text{cm}^{-1}$, 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 shown in Fig. 10a and 10b. 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 Fig. 10b. 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_2O . 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 stretching modes at 1078 and 789 cm^{-1} . The bands 3820 cm^{-1} and 3760 cm^{-1} are attributed to Fe-O bending. This is already confirmed from the Langmuir adsorption isotherm studies.



Fig. 7 – The Bode plot for OL 37+ PASAC8 in S₁ at 25°C.Fig. 8 – The Bode plot for OL 37+ PASAC9 in S₁ at 25°C.Fig. 9 – FT-IR spectra of (a) PASAC7 and (b) OL 37+300 ppm PASAC7+S₁.

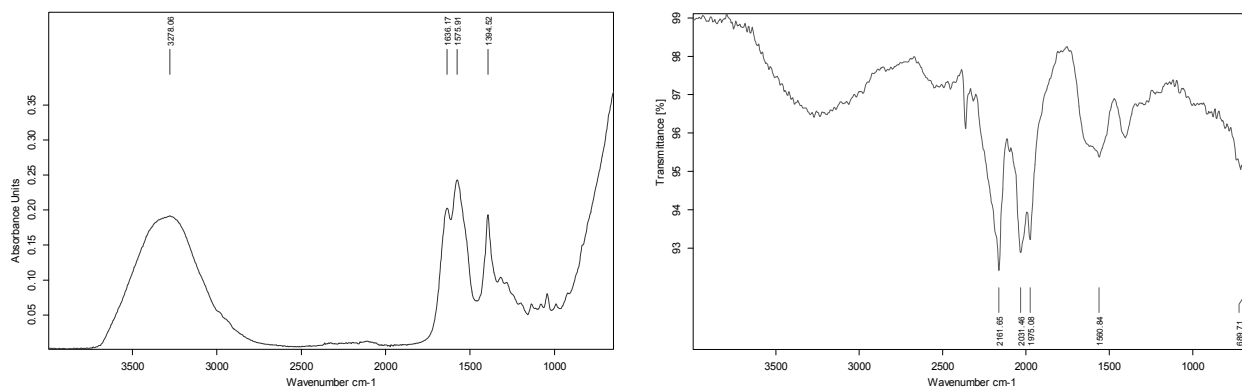


Fig. 10 – FT-IR spectra of (a) PASAC8 and (b) OL 37+500 ppm PASAC8+S1.

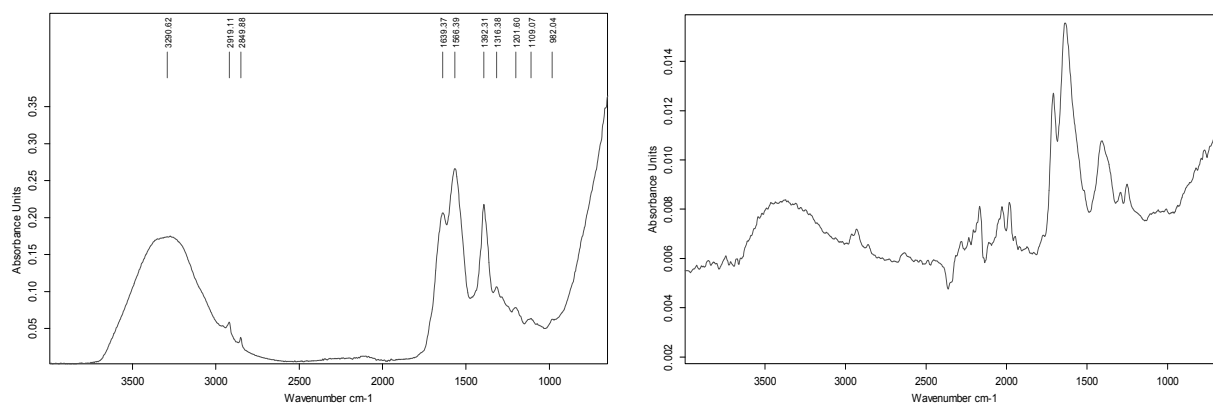


Fig. 11 – FT-IR spectra of (a) PASAC9 and (b) OL 37+800 ppm PASAC9+S1.

The FT-IR spectrum of pure organic polymer PASAC 9 is depicted in Fig. 11a 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 Fig. 11b. 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 Fig. 11b. A broad band in the range from 3684 cm^{-1} is attributed to C-H, the appearance of the peak in region 1598 cm^{-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.

In Fig. 12 are given a few micrographies obtained by us for the following systems: carbon steel OL37 before and after a certain immersion in cooling water type S1 with and without organic inhibitor. Analyzing in comparison the Fig. 12b, 12c, 12d and 12e, 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 Fig. 12 (a, b, c, d and e).³⁰

Analyzing in comparison Fig. 12(b-e), it can be observed that the corrosive attack is much more accentuated in the case of OL 37+ water type S1 system than in the case of OL-37+ water type S1 +Xppm inhibitor system. This finding is in good concordance with the results obtained by electrochemical method – see Tables 3-5 and the polarization curves from Fig. 1.

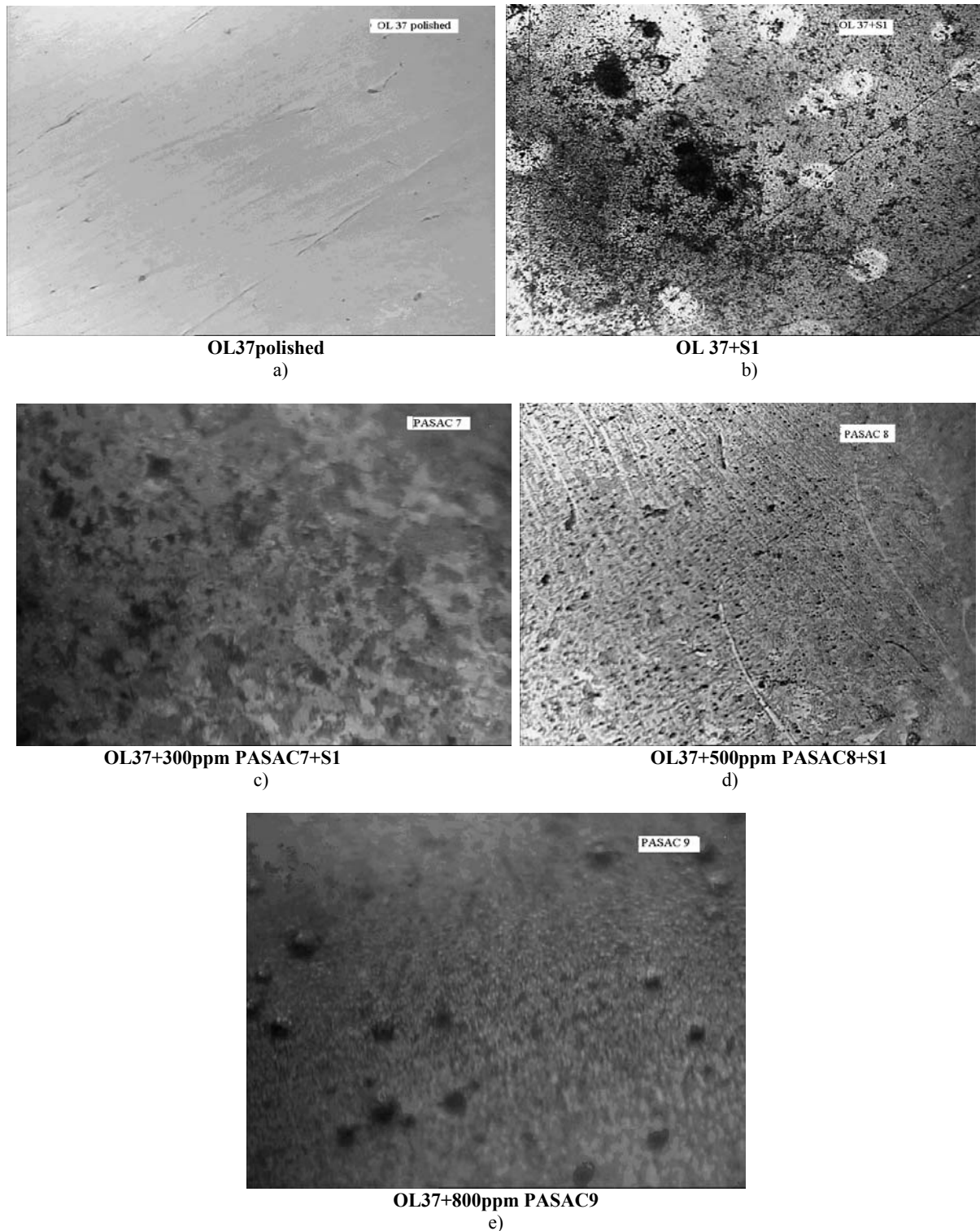


Fig. 12 – Micrographies of the carbon steel OL 37 in cooling water type S1 with and without organic inhibitor PASAC-7, PASAC-8 and PASAC-9.

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 all organic inhibitors investigated follows the Langmuir isotherm and the FT-IR, results also revealing the adsorption of inhibitor molecule on the metal surface and blocking the active sites.

PASAC7, PASAC8 and PASAC9 inhibit both anodic and cathodic reactions by adsorption on the carbon steel surface and hence behave like mixed type inhibitor.

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.

REFERENCES

1. D. Jones, "Principle and Prevention of Corrosion", MacMillan Publishing Company, New York, 1992.
2. V. Branzoi and F. Branzoi, *Rev. Roum. Chim.*, **2002**, *47*, 1193.
3. V. Branzoi, F. Branzoi and L. Pilan, *Materials Chemistry and Physics*, **2009**, *118*, 197.
4. H. H. Uhlig and R. W. Revie, "Corrosion and Corrosion Control", Wiley, New York, 3rd edition, 1985.
5. K. C. Pillai and R. Narayan, *J. Electrochem. Soc.*, **1978**, *125*, 1393.
6. J. L. Rozenfeld, "Corrosion Inhibitors", McGraw-Hill, New York, 1981, p. 109.
7. D. P. Schwensberg and V. Ashworth, *Corros. Sci.*, **1988**, *28*, 539.
8. T. Hirai, J. Yamaki, T. Okada and A. Yamagi, *Electrochim. Acta*, **1985**, *30*, 61.
9. D. G. Leaist, *J. Chem. Soc. Faraday Trans.*, **1990**, *86*, 3487.
10. E. Kamis, F. Bellucci, R. M. Latonision and E. S. H. El-Ashry, *Corrosion* **1991**, *47*, 677.
11. M. Beier and J. W. Schultze, *Electrochim. Acta*, **1992**, *37*, 2299.
12. F. Donahue and K. Nobe, *J. Electrochemical. Soc.*, **1965**, *112*, 886.
13. Y. A. Aleksanyan, I. I. Rformatskaya and A. N. Podobaev, *Protection of Metals*, **2007**, *43*, 125.
14. E. M. Sherif and Su-Moon Park, *Electrochimica Acta*, **2006**, *51*, 4665-4673.
15. M. J. Incurvia and S. Contarini, *J. Electrochem. Soc.*, **1989**, *136*, 2493.
16. F. Mansfeld, "Corrosion Mechanism", Marcel Dekker (Ed.), New York, 1987, p. 119.
17. V. Branzoi, F. Branzoi and L. Pilan, *Molec. Crystal & Liquid Crystals*, **2006**, *446*, 305.
18. G. Banerjee and S. N. Malhotra., *Corrosion*, **1992**, *48*, 10.
19. V. Branzoi, A. Pruna and F. Branzoi, *Rev Roum de Chim.*, **2007**, *52*, 587.
20. K. Aramaki, J. Uehre and H. Nishihara, *Proc. of the 11th International Corrosion Congress*, Florence, Italy, **1990**, *3*, 331.
21. G. B. Hunt and A. K. Holiday, *Organic Chemistry* **1981**, *14*, 229.
22. Braun R. D., E. E. Lopez and D. P. Vollmer, *Corros. Sci.* **1993**, *34*, 1251.
23. D. Gopi, K. M. Govindaraju and L. Kavitha, *J. Appl. Electrochem.*, **2010**, *40*, 1349.
24. A. Prună, V. Branzoi and F. Branzoi, *Materials and Technologies*, **2007**, *23*, 233-239.
25. V. Branzoi, F. Branzoi and I. Harabor, *Rev. Roum. Chim.*, **2010**, *55*, 487-500.
26. H. W. Shen and Z. S. Smialowsky., *Corrosion Sci.*, **1989**, *45*, 720.
27. Loupy A., *Chemistry Today*, **2006**, *24*, 36.
28. Q. Qu, S. Jiang, W. Bai and L. Li, *Electrochim. Acta*, **2007**, *52*, 6811.
29. Q. Quing, L. Li, S. Jing and Z. Ding, *J. Appl. Electrochem.*, **2009**, *39*, 569.
30. M. F. L. Granero, P. H. L. S. Matai, I. V. Aoki and I. C. Guedes, *J. Appl. Electrochem.*, **2009**, *39*, 1199.

