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# INVESTIGATION OF SOME ORGANIC POLYMERS AS CORROSION INHIBITORS ON CARBON STEEL IN COOLING WATER SYSTEMS

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*The inhibition activity analysis of various combinations of these organic polymers of PASAC3, PASAC 11 and PASAC13 on the corrosion behavior of carbon steel in cooling water was studied by potentiodynamic polarization, EIS, FT-IR spectroscopy and metallurgical microscopy techniques. The addition of the organic inhibitors led in all the cases to inhibition of the corrosion process. Results show that these organic inhibitors exert a good inhibiting effect on OL37 corrosion and act as a mixed-type inhibitor. The inhibition efficiency of these combinations of organic polymers may be caused by adsorption of inhibitor molecules building a protective film on the electrode surface. Characterization using FT-IR demonstrates the adsorption of organic inhibitors on carbon steel surface. EIS results confirm its corrosion inhibition ability.*

**Keywords:** organic inhibitor, carbon steel, cooling water, electrochemical techniques, EIS and FT-IR

## 1. Introduction

Carbon steel is one of the most widely used materials of construction. Corrosion of carbon steel in various aggressive environments is of practical importance. The main problem in using carbon steel in aggressive environments is that of uniform corrosion. A possible solution to protect carbon steel in aggressive environments is the application of corrosion inhibitors or coatings. Adding of an inhibitor to the electrolyte is known as one method of inhibiting corrosion. Many studies on the addition of inhibitors have been done in the field of carbon steel corrosion inhibition in the different environments. In general organic compounds containing polar groups including nitrogen, sulfur and oxygen and heterocyclic

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compounds with polar functional groups and/or conjugated double bond. Some researches have reported the inhibiting effects of alkyl amines, phenyl-alkyl amines, imines derivatives and polymer inhibitors [1-5]. The most important inhibitors are the organic ones, also called adsorption inhibitors. They control the corrosion action either on cathodic or anodic response, or on both of them. When they are present in a relatively high concentration, they usually affect the whole metal surface and, therefore, they cannot be called anodic or cathodic inhibitors. Therefore, the interaction of polymer and metal surface can be proved by adsorption isotherm and, in general, inhibitors can function either by physical adsorption, or chemisorption on the metal [5-9].

Metals corrosion in water–conveying systems 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 [9-15]. It is well known that, in all the cases of cooling water systems, frequent corrosion processes appear at the metal/water interface, which determines deposition of corrosion products, like scales. Due to the scales formation, the heat exchange becomes more difficult, and disturbs the normal function of industrial installation [10-18]. The use of inhibitors is one method to reduce corrosion and protect metals and alloys in the aggressive medium. Recently, research in corrosion prevention is oriented to the development of green compounds with good inhibition efficiency, non-toxicity, but low risk of environmental pollution. Therefore, the ability of an inhibitor to provide corrosion protection widely depends upon the interaction between inhibitor and metal surface under corrosion conditions. It is generally assumed that strong adsorption of the inhibitors is a prerequisite [15-18].

The corrosion inhibition of carbon steel in industrial cooling waters system of several combinations inhibitors has been examined by electrochemical methods, electrochemical impedance spectroscopy, FT-IR and metallographic analysis. Electrochemical impedance spectroscopy (EIS) measurements are used to evaluate the anticorrosive properties of these new inhibitors. This work is a continuation of previous work on the evaluation of some organic polymers that have been synthesized by radical polymerization, using the microwaves energy.

## 2. Experimental

The aggressive environment used was cooling water system type S1 and chemical composition is given in table 1. The studied metals were the carbon steels type OL 37 with composition: C% 0.15; Si% 0.09; Mn% 0.4; Fe% 99.293; P% 0.023; S% 0.02; Al% 0.022; Ni% 0.001; Cr% 0.001.

The investigated inhibitors have been various combinations of organic polymers, which were obtained by radical polymerization in presence of a microwave field: PASAC3 (urea and maleic anhydride at molar rapport 1:1 at temperature of $120^0$C, the reaction in the solid state), PASAC 11 (polyaspartic acid and $H_3PO_4$ molar ratio 1**:**0.05 at temperature of $170^0$C), PASAC13 (polyaspartic acid 0.07M and $H_3PO_4$, gravimetric ratio 1/1.5 with trisodium citrate at temperature of $200^0$C) was selected.

*Table 1*

**Chemical composition of $S_1$**

| Indicators | UM | Water type $S_1$, values of parameters |
|---|---|---|
| PH | | 8.42 |
| Conductivity | µs/cm | 1061 |
| Alcalinity p | mval/L | 0.1 |
| Alcalinity m | mval/L | 3.3 |
| Total Hardness | mval/L | 8.3 |
| Calcium Hardness | mval/L | 3.0 |
| Chloride, $Cl^-$ | mg/L | 117.01 |
| Sulfate | mg/L | 155 |
| Solid substances | mg/L | 2.75 |
| Organic compounds | mg/L | 11.37 |
| Iron | mg/L | 0.073 |
| Aluminum, | mg/L | 0.0175 |
| Nitrite, $NO_2^-$ | mg/L | <0.1 |
| Nitrate, $NO_3^-$ | mg/L | 10 |
| Phosphate, $PO_4^{3-}$ | mg/L | 0.046 |
| Copper, $Cu^{2+}$ | mg/L | <0.015 |
| Zinc, $Zn^{2+}$ | mg/L | <0.1 |

Experiments were carried out in absence and presence of inhibitors at their 20/80, 40/60, 50/50, 40/60, 80/20, 100 ppm concentrations at $25^0$C. The working electrode for electrochemistry measurements was prepared from a cylindrical carbon steel rod with area 0.5 $cm^2$. This shape is preferred, because it assures a greater surface and a reduce number of edges. The working electrode was mechanically polished on wet silicon carbide (SiC) papers (1200, 2500, 4000 grid) rinsed with bidistilled water, degreased with acetone and ethanol and dried at room temperature.

Polarization behavior of carbon steel in cooling water S1 in presence and absence of organic inhibitors has been examined by potentiostatic and potentiodynamic methods. The inhibitory action was evaluated through tracing the polarization curves obtained using potentiodynamic method. The kinetic parameters of corrosion in case of solutions with inhibitors, especially the corrosion current densities, have been calculated, and they were compared with those of the solution without inhibitors. Potentiostatic, potentiodynamic and EIS measurements were carried out by using the conventional three electrodes set up; the cell was connected to the automated model VoltaLab 40 potentiostat/galvanostat. A platinum sheet served as counter electrode (CE), a saturated calomel electrode (SCE) as reference electrode and a working electrode was made of carbon steel type OL37. All potential values (E) given in this study were measured on this electrode at a temperature of $25^0$C. Fourier transform infrared spectroscopy (FT-IR) used to identify whether there was adsorption of organic inhibitor on the metal surface was performed with Bruker Optics. A metallografic/metallurgical microscopy technique was obtained with Hund H600 microscope.

## 3. Results and Discussion

The corrosion inhibition is the result of the organic compound adsorption on the metal surface, forming an invisible film of a few molecular diameters thickness. The inhibition activity analysis of the organic compound was made by assuming that the mechanism of inhibition by organic molecules is chemisorption. The effect of various combinations of organic polymers (PASAC3, PASAC11 and PASAC13) was investigated as corrosion inhibition for carbon steel in cooling water system S1. Electrochemical corrosion kinetics parameters (corrosion rate, inhibition efficiency, corrosion current density ($i_{corr}$), corrosion potential ($E_{corr}$), cathodic ($b_c$) and anodic ($b_a$) Tafel slopes of different combinations of organic polymers as corrosion inhibitors was determined by potentiodynamic polarization technique.

The polarization behaviour of the carbon steel mentioned above was studied through the plotting of the polarization curves obtained using the potentiodynamic method. The kinetic parameters of corrosion from solutions without inhibitors were found, and they were compared to the kinetic parameters from solutions with different concentrations of inhibitor. The corresponding Tafel parameters were obtained by Mansfeld's method, employing polarization data near the corrosion potential. When values of $E$-$E_{cor}$ are higher than about 70 mV, slight but significant changes in the anodic and cathodic Tafel slopes were found. Figures 1-3 show a series of potentiodynamic polarization curves of carbon steel electrode (it was not aerated) in absence and presence of different concentrations of various combinations of organic inhibitors PASAC3/PASAC11 and PASAC3/PASAC13. Both anodic and cathodic polarization curves for carbon steel S1 at different concentrations of various combinations of organic inhibitor are shown in figures 1-3.

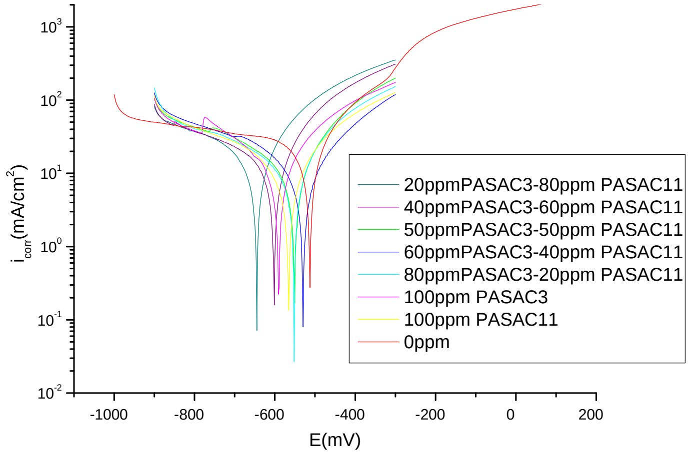


Fig. 1 Polarization curves of OL 37 in S1 +Xppm PASAC3/PASAC11 at temperature of $25^0$C

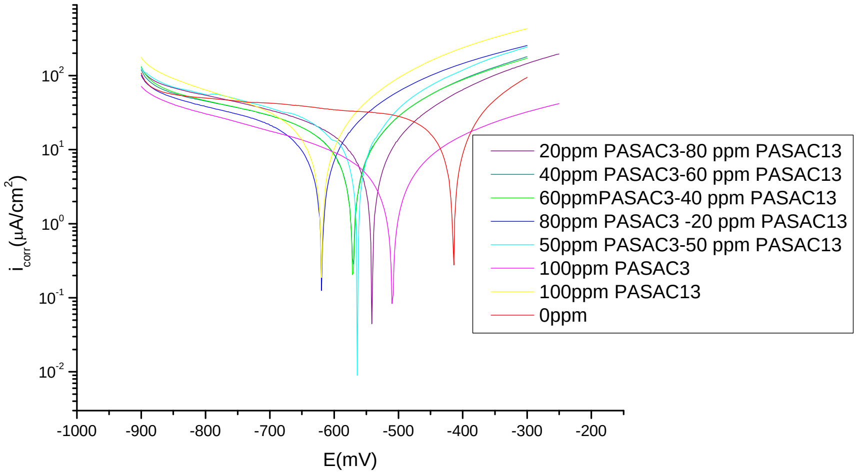


Fig. 2 Polarization curves of OL 37 in S1 +Xppm PASAC3/PASAC13 at temperature of $25^0$C

It is clear that the presence inhibitors cause a markedly decrease in the corrosion rate, i.e. it shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials; it decreases the cathodic current density, and the reduction of hydrogen ion is limited. This can be assigned to adsorption of inhibitor over the carbon steel surface. Both cathodic and anodic reactions of carbon steel electrode were inhibited with the increase of organic inhibitor concentration in cooling water system. The addition of various combinations of organic inhibitor PASAC 13, PASAC 11 and PASAC 3 significantly decreases the corrosion current density values ($i_{corr}$) for all the studied concentrations, because of the electrode blocked fraction increase by adsorption. This confirms that these inhibitors behave as a mixed inhibitor. The combination of PASAC3/PASAC13 can be considered as an inhibitor with predominant cathodic effect to protect carbon steel in S1.

*Table 2*

**Kinetic corrosion parameters of OL 37 in S1 in presence and absence of various amounts of organic inhibitors PASAC3/PASAC11 at 25°C**

| Concentration PASAC3/PASAC13 (ppm) | $i_{corr}$ (mAcm$^{-2}$) | $R_p$ Ωcm$^{-2}$ | $R_{mpy}$ | P mm/year | $K_g$ g/m$^2$h | E (%) | $-E_{corr}$ (mV) | $b_a$ (mVdec$^{-1}$) | $-b_c$ (mVdec$^{-1}$) | θ |
|---|---|---|---|---|---|---|---|---|---|---|
| 00/00 | 13.01 | 1.78 | 6.07 | 0.015 | 0.137 | - | 513 | 110 | 215 | - |
| 20/80 | 4.413 | 3.86 | 2.132 | 0.0541 | 0.0484 | 66 | 530 | 97 | 159 | 0.66 |
| 40/60 | 4.42 | 3.84 | 2.13 | 0.054 | 0.048 | 66 | 568 | 94 | 121 | 0.66 |
| 50/50 | 6.07 | 3.22 | 2.93 | 0.074 | 0.066 | 53 | 551 | 97 | 159 | 0.53 |
| 60/40 | 6.78 | 2.41 | 3.26 | 0.082 | 0.073 | 48 | 649 | 88 | 125 | 0.48 |
| 80/20 | 6.01 | 2.64 | 2.90 | 0.073 | 0.015 | 54 | 602 | 80 | 127 | 0.54 |
| 100/PASAC3 | 5.52 | 3.32 | 2.63 | 0.067 | 0.060 | 58 | 552 | 104 | 179 | 0.58 |
| 100/PASAC11 | 7.13 | 2.83 | 3.44 | 0.087 | 0.078 | 45 | 591 | 115 | 150 | 0.45 |

*Table 3*

**Kinetic corrosion parameters of OL 37 in S1 in presence and absence of various combinations of organic inhibitor type PASAC3/PASAC13 at temperature of 25°C**

| Concentration PASAC3/PASAC11 (ppm) | $i_{corr}$ (mAcm$^{-2}$) | $R_p$ Ωcm$^{-2}$ | $R_{mpy}$ | $P_{mm/year}$ | $K_g$ g/m$^2$h |
|---|---|---|---|---|---|
| 0 | 13.01 | 1.78 | 6.07 | 0.015 | 0.137 |
| 20/80 | 4.55 | 3.33 | 2.41 | 0.055 | 0.049 |
| 40/60 | 4.72 | 3.07 | 2.28 | 0.057 | 0.051 |
| 50/50 | 5.29 | 2.07 | 2.55 | 0.064 | 0.057 |
| 60/40 | 5.31 | 3.15 | 2.56 | 0.065 | 0.058 |
| 80/20 | 5.92 | 2.93 | 2.86 | 0.072 | 0.065 |
| 100/PASAC3 | 5.52 | 3.32 | 2.63 | 0.067 | 0.060 |
| 100/PASAC13 | 2.62 | 7.98 | 1.26 | 0.032 | 0.028 |

| Concentration PASAC3/PASAC11 (ppm) | E (%) | $-E_{corr}$ (mV) | $b_a$ (mVdec$^{-1}$) | $-b_c$ (mVdec$^{-1}$) | θ |
|---|---|---|---|---|---|
| 0 | - | 513 | 110 | 215 | - |
| 20/80 | 65 | 543 | 87.5 | 112 | 0.65 |
| 40/60 | 64 | 571 | 88 | 106 | 0.64 |
| 50/50 | 60 | 564 | 79 | 119 | 0.60 |
| 60/40 | 59 | 572 | 92 | 123 | 0.59 |
| 80/20 | 54 | 619 | 93 | 128 | 0.54 |
| 100/PASAC3 | 57 | 552 | 104 | 179 | 0.57 |
| 100/PASAC13 | 80 | 510 | 120 | 150 | 0.80 |

The electrochemical parameters derived from the polarization curves obtained for different combinations of inhibitors PASAC3/PASAC11 and **PASAC3/PASAC13** are given in Tables 2-3. Analyzing these tables, it can be observed that**,** the addition of various combinations of organic inhibitor (PASAC11, PASAC13 and PASAC3) showed good inhibition properties for the corrosion of carbon steel in cooling water system type S1. By examining in comparison the inhibition efficiency and the corrosion rate ($R_{mpy}$, in mil per year; P, in mm per year and Kg, in gm$^{-2}$h$^{-1}$) of all inhibitors, one can observe as, the combination PASAC3/PASAC13 have a very good efficiency for anticorrosion protection of OL37 in S1 and PASAC3/PASAC11 had good inhibition efficiency. The maximum efficiency is obtained at the inhibitor concentration for PASAC 13 is 100ppm, for PASAC3/PASAC13 is 20/80ppm and 40/60ppm and for PASAC3/PASAC11 is 20/80ppm. These dates demonstrate as these polymers can be classified as mixed type corrosion inhibitors. The inhibition efficiency of these combinations of organic polymers may be caused by adsorption of inhibitor molecules building a protective film on the electrode surface.

Fig. 3 showed a typical set of Nyquist plots for carbon steel in cooling water system in absence and presence of various combinations of organic inhibitors. The impedance response of OL 37 in cooling water system showed significant changes after addition of the inhibitors. The impedance spectra of OL 37 electrode display one capacitive loop. In all cases, it is found that the diameter of the capacitive loop increases in presence of different concentrations and combinations of the inhibitors PASAC3, PASAC11, PASAC13. It results that the formed protective film has been accomplished by the addition of organic inhibitors. However, these capacitive loops are not perfect semicircles and this fact is attributed to frequency dispersion, largely given to roughness and inhomogeneities of the solid surface.

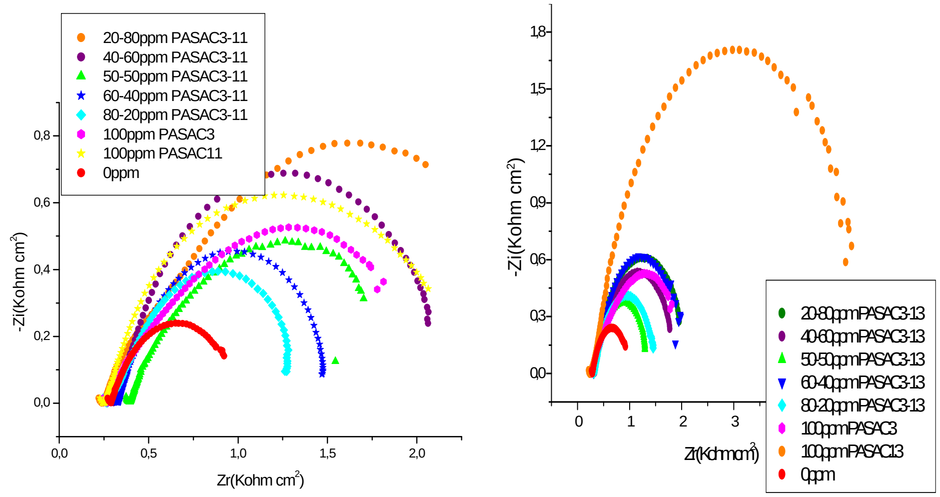


Fig. 3 The Nyquist plot for OL 37 in S1 in presence and absence of various combinations of organic inhibitor type PASAC3/PASAC11 and PASAC3/PASAC13

The maximum efficiency is obtained at the combination of the inhibitors: 20/80ppm PASAC3/PASAC13, 40/60ppm PASAC3/PASAC13 and for 20/80ppm PASAC3/PASAC11 and 40/60ppm PASAC3/PASAC11.

Fig. 3 shows as well that the diameters of these semicircles in the presence of 20/80ppm PASAC3/PASAC13, 100ppm PASAC13, and 40/60ppm PASAC3/PASAC13 and for 20/80ppm PASAC3/PASAC11, and 40/60ppm PASAC3/PASAC11 are much higher than those in the absence of organic compounds, resulting a good anticorrosion protection on the carbon steel in S1.

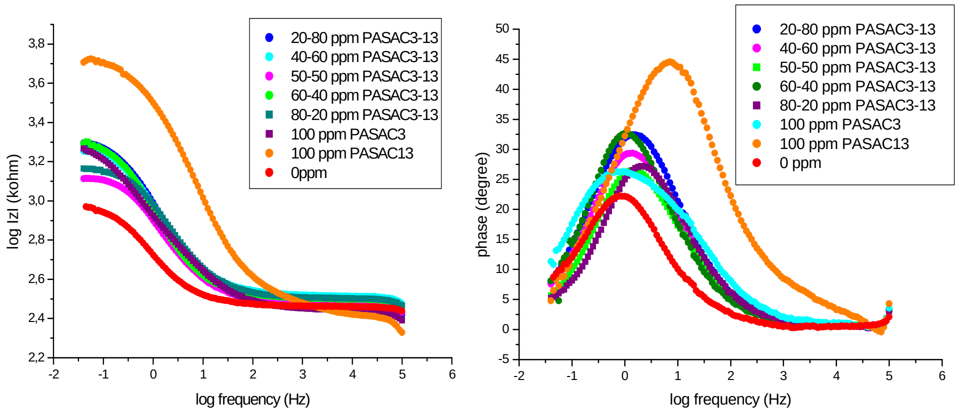


Fig. 4 The Bode plot for OL 37 in S1 in presence and absence of various combinations of organic inhibitor type PASAC3/PASAC13

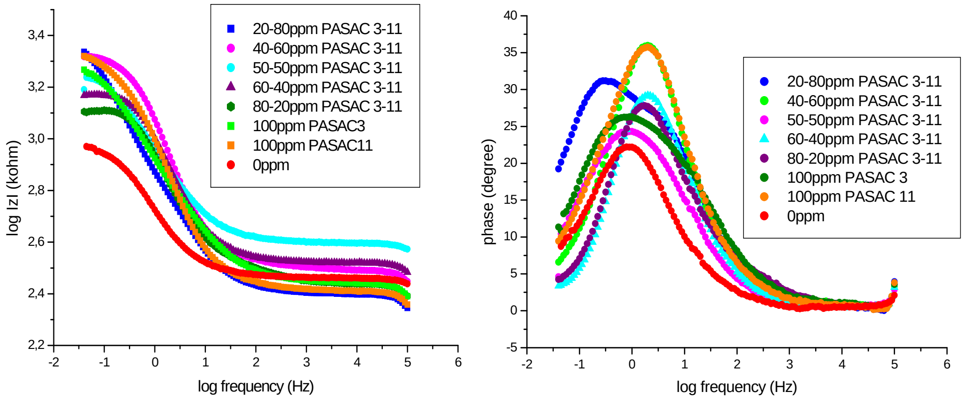


Fig. 5. The Bode plot for OL 37 in S1 in presence and absence of various combinations of organic inhibitor type PASAC3/PASAC11

Bode diagrams presented in FIGS. 4-5 are in accordance with Nyquist diagrams. It could be observed that, in the absence of inhibitor, the carbon steel has only one time constant for $25^0$ phase angle at medium and low frequencies, presenting an inductive behaviour with low diffusive predisposition.

From Figs. 4-5, it can see that in presence of different combinations of the inhibitors to seem a top corresponding to a phase angle of 45-50º. This means that the electrode has a capacitive behaviour, in according with the results obtained by electrochemical polarization and in concordance with the Nyquist diagrams.

The electrochemical impedance spectra are characterized by one semicircle for all combinations of organic inhibitors. They were fitted using one time constant equivalent model with capacitance CPE1, the charge transfer resistance $R_2$ and R1 solution resistance were obtained using the Nyquist diagrams [18-23].

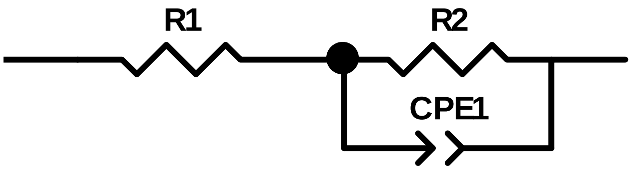


Fig. 6 Equivalent circuit

The equivalent circuit that describes the investigated metal/electrolyte interface is shown in Fig. 6, where the standard Randle's circuit is used for the analysis of the impedance spectra containing a single capacitive semicircle. The equivalent circuit is composed of R1 refer to solution resistance, R2 charge transfer resistance and CPE constant phase element of the double layer to replace a pure double layer capacitance [19-24]. The resistor R1 is in series with R2, while R2 is in parallel with the double layer capacitance."

Several researchers have confirmed that Fourier transform infrared spectroscopy (FT-IR) is a powerful tool that can be used to determine the type of bonding for organic inhibitors adsorbed on the metal surface [25-29]. In this study, FT-IR spectra revealed that the various combinations of new organic inhibitors were adsorbed on the carbon steel surface and to provide new bonding information's of adsorption process. All spectra in this paper were obtained at a resolution 4cm$^{-1}$ in the range 4000-500 cm$^{-1}$. In order to evaluate the protective layer formed on the metal surface in presence of various combinations of organic inhibitors on the carbon steel surface was analyzed by FT-IR spectra.

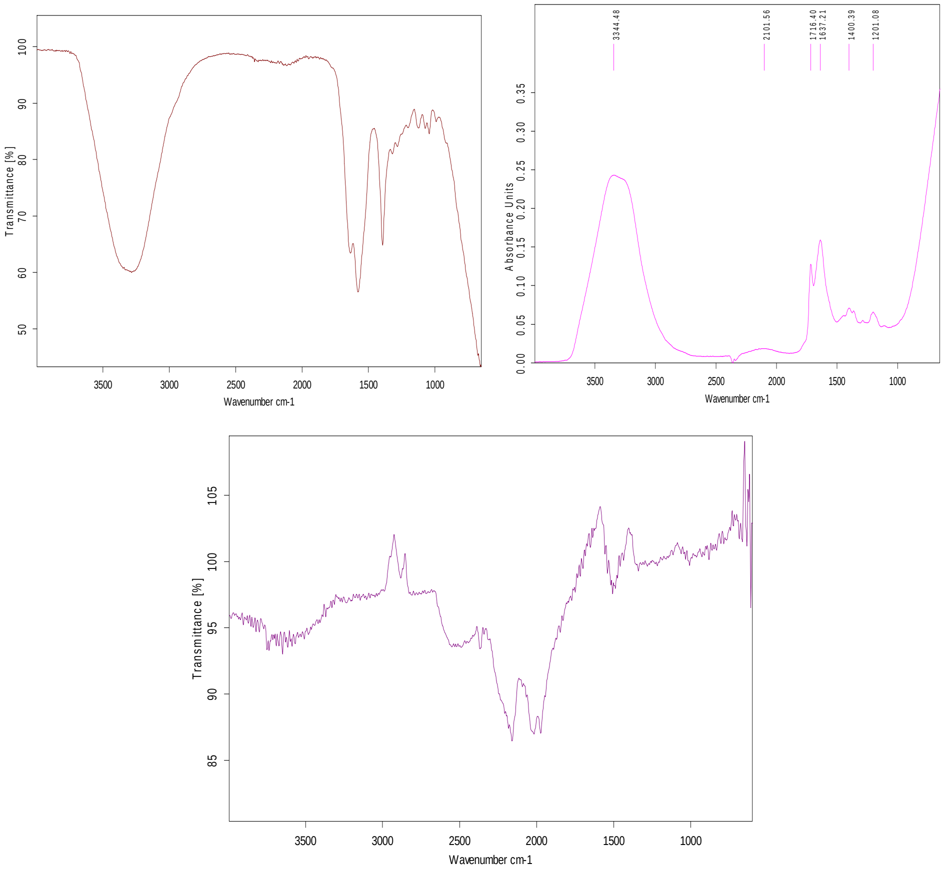


Fig. 7 FT-IR transmittance spectrum of (a) PASAC11 (b) PASAC3 and (c) ) OL3720/80 ppm PASAC3/PASAC11/OL37/S1

Transmission spectra of polymer PASAC11 and PASAC3 is show in FIG. 7a and 7b. FT-IR transmittance spectrum of protective film adsorbed on the carbon steel surface in S1 containing of 20/80ppm PASAC3/PASAC11/OL37/S1 is presented in FIG. 7c. From Fig. 7c it can be observed all important peaks of polymer PASAC11 and PASAC3 appeared in the protective film. A broad band in the range from 3500-3400 $cm^{-1}$ is attributed to O-H stretching, which indicates that the protective film contains $H_2O$.[25-28] The band in the region 3000-2500 $cm^{-1}$ are attributed to C-H stretching vibration, the band at 1650 and 1540 $cm^{-1}$ corresponds to the C=O and N-H. The presence of C-N and C-O is indicates stretching at 1100-1000 and 900-800 $cm^{-1}$. Moreover, these FT-IR measurements indicated at 3860 cm-$^{1}$ the direct bonding between Fe atoms and PASAC3/PASAC11 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. [27-29] Comparing Figs. 7a, b and c, it can be suggested that PASAC3/PASAC11 is adsorbed on the carbon steel surface.

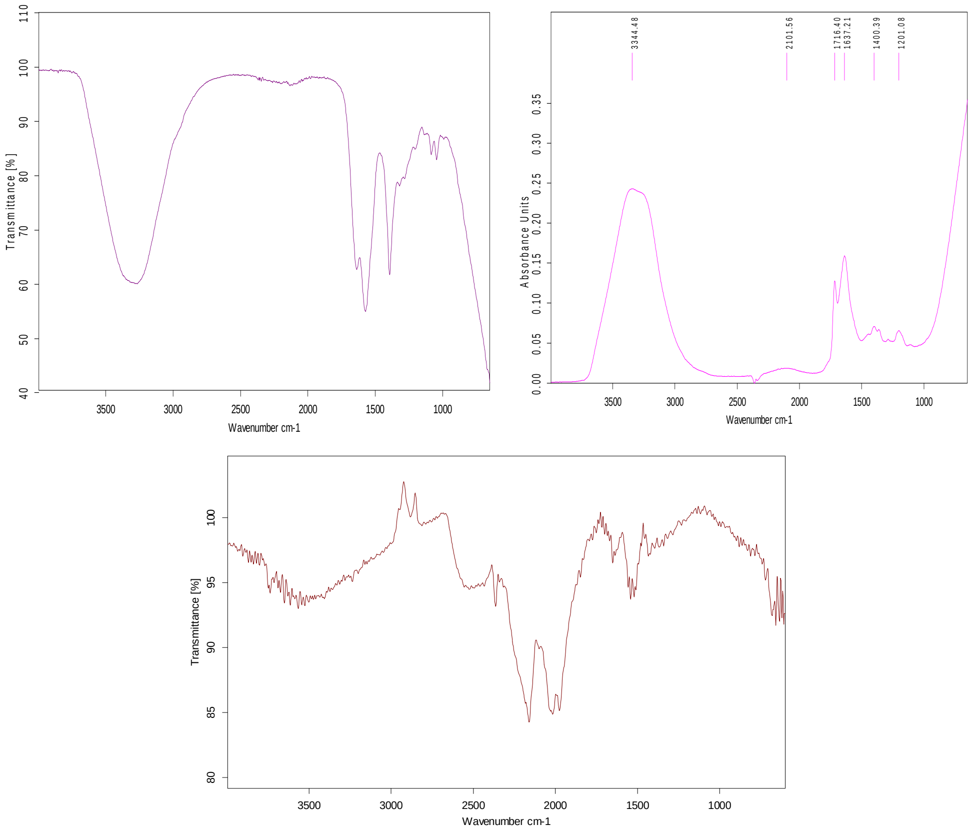
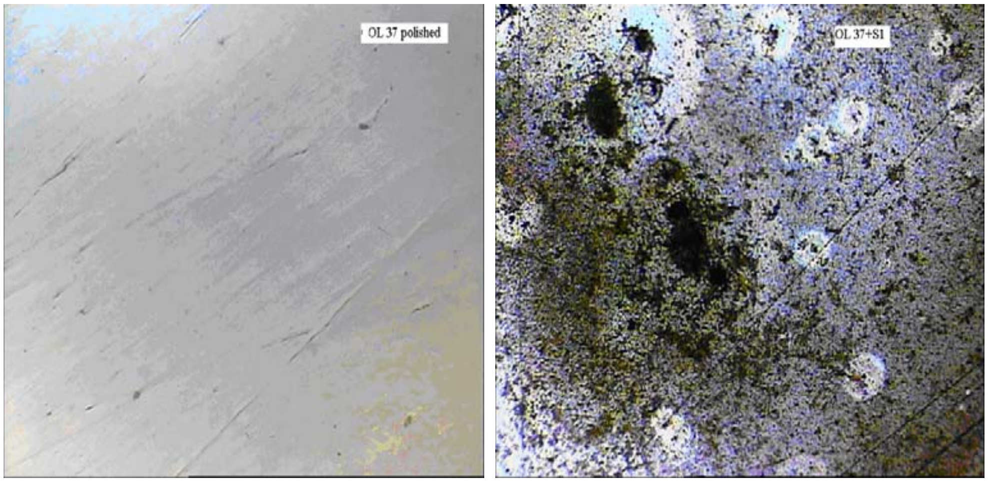


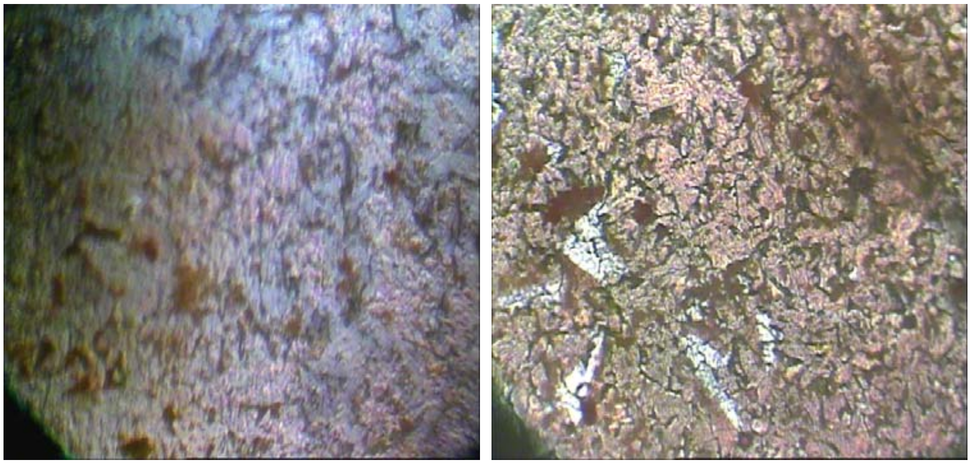
Fig. 8 FT-IR transmittance spectrum of (a) PASAC13 (b) PASAC3 and (c) OL3720/80 ppm PASAC3/PASAC13/OL37/S1

Transmission vibrational spectra of polymer PASAC 13 and PASAC3 is depicted in FIG. 8a and 8b. From Fig. 8a, a weak peak at 3000 cm$^{-1}$ shows the existence of the C-H. The N-H and C=O stretching frequencies are manifest in the region 1631 and 3300 cm$^{-1}$and 1521 cm$^{-1}$. The weak band at 1300 to 1200 cm$^{-1}$ respectively is attributed to C-H bending. The FT-IR spectra obtained for the carbon steel with 20/80 ppm PASAC3/PASAC13 inhibitor organic is presented in FIG. 8c. This shows the characteristic band for the adsorbed PASAC3/PASAC13 on the metal surface. A broad band in the region from 3300 cm$^{-1}$ is assigned to C-H. At range 1520cm$^{-1}$ and 3560, the appearance of the peak is assigned to N-H. The presence of C-N is indicates stretching at 1456 cm$^{-1}$. The C-O bends are shown around at 1100-1000 cm$^{-1}$. The peaks at 3780 cm$^{-1}$and 3850 cm$^{-1}$ are related to Fe-O bending. Comparing Figs. 8a, b and c, it can be suggested that PASAC3/PASAC13 is adsorbed on the carbon steel surface.

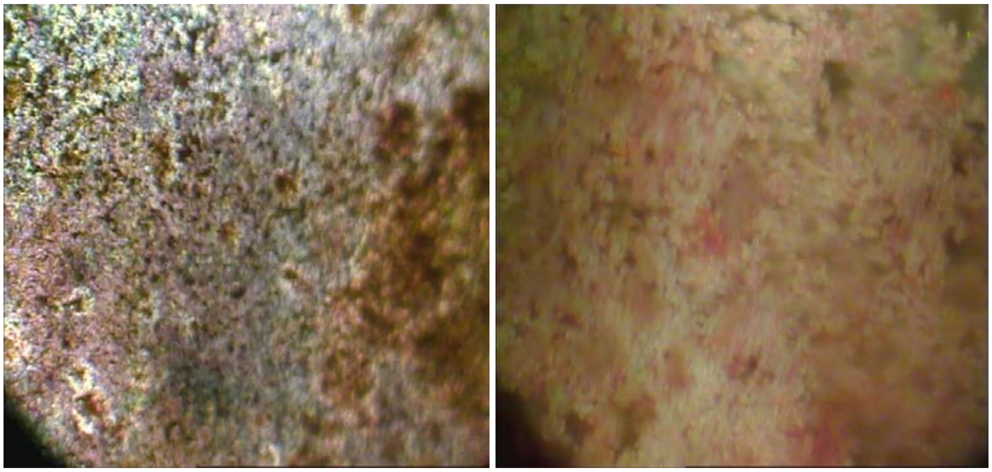
The formation of the protective surface film of organic inhibitor on the electrode surface was confirmed by metallurgical research microscope observation on the electrode surface. Fig. 9 shows some micrographies were analyzed for our systems: carbon steel/S1 before and after a certain immersion in S1 in presence and absence of various combination organic inhibitor of type PASAC. [29-33]



a) OL 37 polished b) OL 37/S1



c) 20/80ppm PASAC3/PASAC13/OL37/S1 d) 40/60ppm PASAC3/PASAC13/OL37/S1



e) 20/80ppm PASAC3/PASAC11/OL37/S1 f) 20/80ppm PASAC3/PASAC11/OL37/S1

Fig. 9 Micrographies of the carbon steel OL 37 in cooling water type S1 with and without different combinations of organic inhibitor: PASAC3, PASAC11 and PASAC13

From Figs. 9b-f it is evident that the inhibited carbon steel surface is smoother than the uninhibited surface where showing protective layers are formed of adsorbed films of inhibitor and corrosion products. These films act as a barrier between aggressive medium and metal surface and as a result the corrosion process is protected. [30-33]

## 6. Conclusions

The combinations of polymers: PASAC3/PASAC11 and PASAC3/PASAC13 presented a good inhibitory action and a significant efficiency for OL 37 in cooling water system S1.

FT-IR technique has been performed in order to confirm the formation of protective film on the carbon steel surface.

The results obtained from EIS and polarization curves are in reasonably good agreement.

The organic polymers PASAC3/PASAC11 and PASAC3/PASAC13 acted as mixed type corrosion inhibitors.

In all of the studies, the inhibitors PASAC3/PASAC11 and PASAC3/PASAC13 have a very good efficiency.

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