

CORROSION INHIBITION OF BRASS IN INDUSTRIAL COOLING WATER SYSTEMS

Florina Branzoi¹ and Viorel. Branzoi²

¹Institute of Physical Chemistry, 202 Splaiul Independenței, Bucharest, Romania,

E-mail fbrinzoi@chimfiz.icf.ro,

²University Politehnica of Bucharest, 132 Calea Griviței, Bucharest, Romania,

e-mail iv_branzoi@chim.upb.ro

ABSTRACT

The inhibitory effect of PASAC1, PASAC 11 and PASAC13 on the corrosion behavior of brass in cooling water system at temperature of 25°C was studied by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FT-IR) and metallurgical microscopy techniques. The effect of inhibitor concentration on the corrosion rate, surface coverage and inhibition efficiency is investigated. Results show that these organic inhibitors exert a strong inhibiting effect on brass corrosion and acts as a mix-type inhibitor. The inhibition efficiency of organic polymers may be due to either the adsorption of inhibitor molecules building a protective film or the formation of an insoluble complex of the inhibitor adsorption obeys the Langmuir model. Further, characterization using FT-IR demonstrates the adsorption of inhibitors and the formation of corrosion products on the brass surface. EIS results confirm its corrosion inhibition ability.

Keywords: organic inhibitor, brass, cooling water, potentiodynamic polarization, electrochemical impedance spectroscopy and FT-IR

INTRODUCTION

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 copper and brass corrosion inhibition in the different environments. Some researches [1-5] have reported the inhibiting effects of alkyl amines, phenyl-alkyl amines, imines derivatives and polymer inhibitors. Among all the inhibitors the most important are the organic ones, also called adsorption inhibitors. They control the corrosion acting over the anodic or cathodic reaction or

both. Because they usually affect the whole metal surface, when they are presenting sufficient concentration, they can not be called anodic or cathodic inhibitors. Therefore, a systematic study of adsorption processes of organic inhibitors, effective in protection enhancement, contributes to a better understanding and ultimately control of corrosion.

Wet corrosion is a manifestation of the significance of electrochemistry and electrochemical adsorption in environmental degradation of industrial materials [6-8]. Electric field-assisted mechanisms of corrosion initiation processes involve a local penetration or degradation of passive films by activating ions and/or a coordination of surface metal sites by such ions. These interfacial events facilitate dissolution of metals, ultimately leading to corrosion. Conversely, adsorption/incorporation of corrosion inhibitors may prevent environmental corrosive attacks on the surface sites.

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. 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. 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 [5-9]. 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, aromaticity, electron density at the donor and π orbital character of donating electrons and also on the electronic structure of molecules [2, 6, 8-14]

Brass materials are relatively noble for which brass possesses attractive properties, namely, good corrosion resistance, high thermal and electrical conductivity and better resistance to biofouling. It has been widely used in water distribution systems, water treatment units, condensers, desalination, power plant condensers and petrochemical heat exchangers, shipboard condensers, and many other applications [4-18]. Brass with 65% Cu and 35% Zn is prone to corrosion attack when exposed to a corrosive media because of the brass α -phase. Increasing the

zinc content in the alloy changes the α -phase to β -phase and accelerates corrosion damage [12]. Dezincification of brass is one of the well-known and common processes by means of which brass loses its valuable physical and mechanical properties leading to failure of structure [9-18]. Therefore, the corrosion mechanism and corrosion prevention of brass in different corrosive media has been attracted many investigators. Several researchers have investigated brass in view of resistance to corrosion [17-23]. Many techniques are used to improve the corrosion resistance of the brass used as mechanical parts in industry.

In this paper, the inhibition of brass corrosion in cooling waters by organic polymers was investigated by potentiodynamic polarizations, EIS measurements, FT-IR and metallography analysis. Electrochemical measurements are used to assess the relevant physical properties of new corrosion inhibitors.

EXPERIMENTAL

Electrochemical polarization curves and electrochemical impedance spectroscopy measurements were performed out by using a single –compartment cell with the conventional three electrode set up at temperature 25⁰C. The cell was connected to a VoltaLab potentiostat coupled to a PC running VoltaMaster software. A saturated calomel electrode (SCE) was employed as the reference electrode and a bright platinum gauze as an auxiliary electrode. The working electrode was a brass with a surface area 0.5 cm². The electrochemical techniques employed were corrosion potential monitoring, anodic and cathodic polarization curves. Experimental methods were described previously [13-14]. The determinations were repeated with each solution until a good reproducibility of the results was obtained.

The inhibiting action was studied through the plotting of the polarization curves obtained using the potentiodynamic method and calculation of the kinetic parameters of corrosion (especially the corrosion current densities of solutions with inhibitors) and the comparison with the kinetic parameters of the solution without inhibitors. The EIS experiments were performed at open circuit potential disturbed with amplitude of 10mV ac sine wave and over a frequency range of 100 kHz to 40 mHz. The studied material was the brass. The used organic inhibitor were three polymers namely PASAC1 (maleic anhydride and urea molar ratio 1.5:1 at temperature of 140⁰C), PASAC-11 (polyaspartic acid and H₃PO₄ molar ratio 1:0.025 in propylene carbonate with sodium tartrate at temperature of 200⁰C) and PASAC-13 (polyaspartic acid 0.07M and H₃PO₄, in ethylene carbonate/propylene carbonate, gravimetric ratio 1/1 with

trisodium citrate at temperature of 150°C) which were obtained by radicalic polymerization in presence of microwave field from.

The corrosion medium was industrial cooling water type S1 with the chemical composition given in Table 1.

Table 1 The chemical composition of the cooling water type S₁

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
Calciu 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
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
Copper, Cu ²⁺	mg/L	<0.015
Zinc, Zn ²⁺	mg/L	<0.1

The chemical composition of the working electrode is: Fe% 0.29, Cu% 65.60, Zn% 34, Si% 0.060, Pb% 0.059. Brass was obtained from MISUMI, Japan. The working electrode was brass in the form cylindrical with an exposed area of 0.5 cm². This shape is preferred, because it assures a greater surface and a reduce number of edges. The working electrode was mechanically polished with emery papers of varied granulation (600, 1200, 2600, 4000 grid) up to mirror-luster, degreased in benzene at boiling temperature in order to remove all traced of fat. After that, the working electrode was washed with distilled water and inserted in the polarization cell, which was the usually three-electrode cell. All tests have been performed at temperature of 25°C under atmospheric oxygen without agitation. Surface analysis on the brass electrode of the formed adsorbed film was analyzed by both FT-IR (FT-IR spectrometer Bruker optik) and metallographic micrographies (Hund H660).

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 and alloys 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.

The typical potentiodynamic polarization curves of the brass in industrial cooling water type S₁ (it was not aerated) in absence and presence of various concentrations of PASAC1, PASAC11 and PASAC13 are presented in Figures 1-3. Electrochemical corrosion kinetics parameters, i.e. corrosion potential, cathodic and anodic Tafel slopes and corrosion current density obtained from the Tafel extrapolation of the polarization curves, were given in Tables 2-4, where the inhibition efficiency were calculate. The presence of inhibitor causes a significant decrease in corrosion rate; change the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This may be ascribed to adsorption of inhibitor over the surface.

Analyzing the cathodic polarization curves from Figures 1-3- it can be observed that, on the large range of the potential the brass electrodes behave very close to a passive behaviour. Practically, we can say that, in this potential range the electrode surface is passivated. We consider that, in this potential range, the cathodic reaction is hindered by the oxide film (passive film) from the electrode surface. In this potential range takes place the oxygen reduction cathodic reaction according to equation:



As it can be seen, both cathodic and anodic reactions of brass electrode were inhibited with the increase of organic inhibitor concentration in cooling water system. The addition of PASAC 13, PASAC 11 and PASAC 1 decreases the i_{corr} values significantly for all the studied concentrations due to increase in blocked fraction of the electrode surface by adsorption. This confirms that these inhibitors behave as a mixed inhibitor.

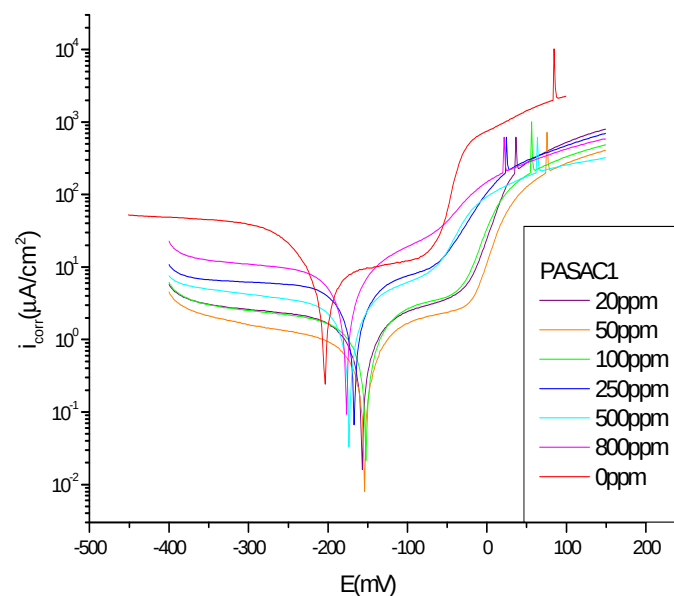


Figure 1 Polarization curves of brass in cooling water S_1 +Xppm PASAC 1 at temperature of 25°C

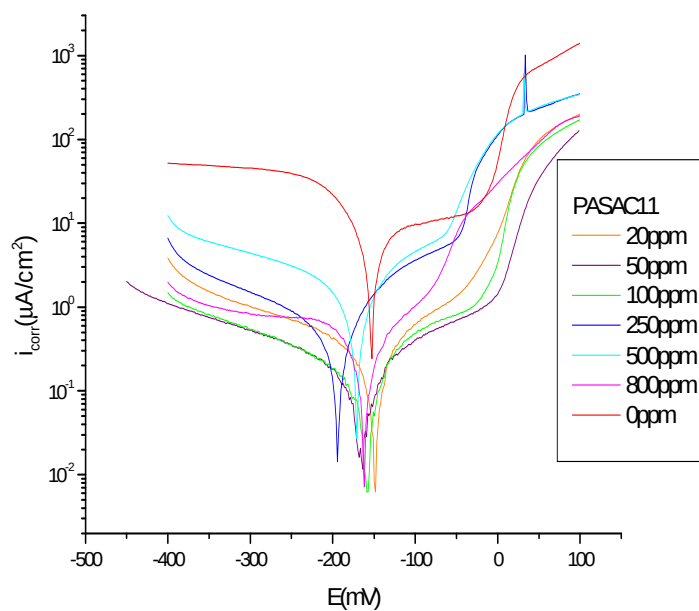


Figure 2 Polarization curves of brass in cooling water S_1 +Xppm PASAC 11 at temperature of 25°C

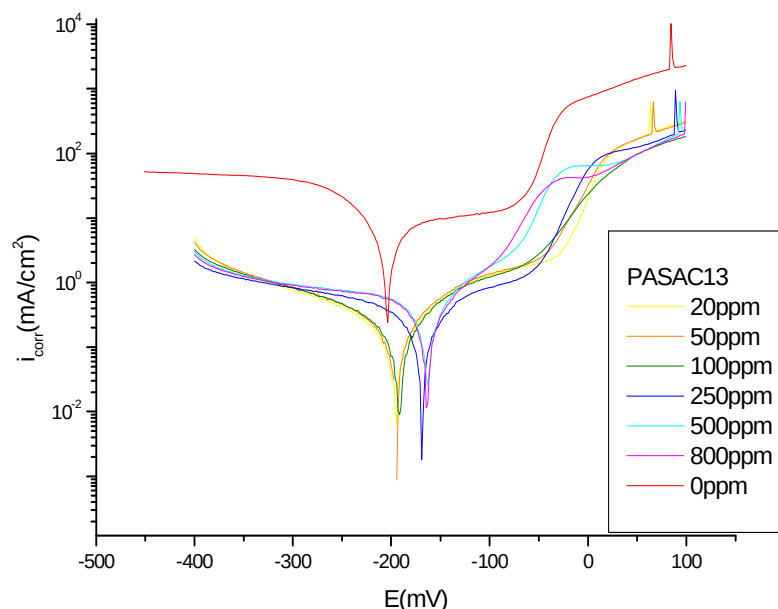


Figure 3 Polarization curves of brass in cooling water S₁ +Xppm PASAC 13 at temperature of 25⁰ C

Analysis of the polarization curves from figures 1-3 indicates that at low overvoltages, the Tafel relationship are followed, showing that both anodic and cathodic reactions are activation-controlled. At higher overvoltages a limiting current appears on the anodic and cathodic polarization curves showing that, the transport of ions towards the electrode surface becomes the rate-determining step (concentration polarization). The electrochemical parameters derived from the polarization curves at different concentrations are given in Tables 2-4. Analyzing these tables, it can be observed that, the addition of the organic inhibitor to the amounts shown in the Tables 2-4 leads in all the cases to inhibition of the corrosion process. This case can be explained taking into account the effects of organic compounds on the electrochemical properties of the brass. All the studied of organic inhibitors (PASAC11, PASAC13 and PASAC1) showed a very good inhibition properties for the corrosion of brass in cooling water system type S1 and the corrosion current density decreased and the inhibitor efficiency increased with increasing inhibitors concentrations. Analyzing in comparison the corrosion rate of organic inhibitors, in the same condition, one can see that, the PSAC13 had a higher efficiency for corrosion system brass in S1 and PASAC11 had a very good efficiency for same system and PASAC1 had a good efficiency. 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 Cu). The maximum efficiency is obtained at the inhibitor concentration for PASAC 13 is 20ppm and 100ppm, for

PASAC11 is 50ppm and 100ppm and for PASAC1 is 50ppm. These results suggest that these polymers can be classified as mixed type corrosion inhibitors.

Table 2 Kinetic corrosion parameters of brass in cooling industrial water type S_1 in presence and absence of organic inhibitor type PASAC1 at temperature of 25 °C

Concentration (ppm)	i_{corr} (μAcm^{-2})	R_p $K\Omega cm^{-2}$	R_{mpy}	$P_{mm/year}$	K_g g/m^2h	E (%)	$-E_{corr}$ (mV)	b_a (mVdec ⁻¹)	$-b_c$ (mVdec ⁻¹)	θ
0	5.31	2.92	2.60	0.066	0.064	-	207	186	76	
20	1.225	20.93	0.65	0.0164	0.016	77	160	193	296	0.77
50	0.915	34.17	0.45	0.0113	0.011	83	157	134	291	0.83
100	1.16	19.95	0.567	0.0144	0.014	78	155	147	305	0.78
250	2.662	6.97	1.301	0.033	0.032	50	167	135	196	0.50
500	2.59	9.86	1.267	0.032	0.031	51	175	189	293	0.51
800	2.03	10.05	0.9584	0.025	0.0246	62	174	187	206	0.62

Table3 Kinetic corrosion parameters of brass in cooling industrial water type S_1 in presence and absence of organic inhibitor type PASA-11 at temperature of 25 °C

Concentration (ppm)	i_{corr} (μAcm^{-2})	R_p $K\Omega cm^{-2}$	R_{mpy}	$P_{mm/year}$	K_g g/m^2h	E (%)	E_{corr} (mV)	b_a (mVdec ⁻¹)	b_c (mVdec ⁻¹)	θ
0	5.31	2.92	2.60	0.066	0.064	-	207	186	76	
20	0.151	89.92	0.074	0.0018	0.0018	96	151	117	196	0.96
50	0.126	181.26	0.061	0.0016	0.0015	97	168	127	186	0.97
100	0.116	170.25	0.056	0.0014	0.0014	98	162	89	183	0.98
250	0.449	43.88	0.219	0.0055	0.0054	91	197	87	184	0.91
500	1.158	17.52	0.567	0.0144	0.014	78	172	111	172	0.78
800	0.296	62.19	0.145	0.0037	0.0036	94	163	113	142	0.94

Table 4 Kinetic corrosion parameters of brass in cooling industrial water type S_1 in presence and absence of organic inhibitor type PASAC13 at temperature of 25 °C

Concentration (ppm)	i_{corr} (μAcm^{-2})	R_p $K\Omega cm^{-2}$	R_{mpy}	$P_{mm/year}$	K_g g/m^2h	E (%)	$-E_{corr}$ (mV)	b_a (mVdec ⁻¹)	$-b_c$ (mVdec ⁻¹)	θ
0	5.31	2.92	2.60	0.066	0.064	-	207	186	76	
20	0.167	106	0.081	0.002	0.002	97	199	92	137	0.97

50	0.194	96	0.091	0.0023	0.0022	96	198	95	145	0.96
100	0.185	98	0.09	0.0022	0.0022	96.5	195	96	146	0.965
250	0.280	78.6	0.137	0.0034	0.0033	95	172	136	224	0.95
500	0.462	47.38	0.226	0.0057	0.0056	91	166	109	205	0.91
800	0.330	51.36	0.161	0.0041	0.0039	94	167	87	180	0.94

The variation of inhibition efficiency and current density with inhibitor concentrations is shown in Figure 4. The inhibition efficiency increased with increase in concentration and from figures, one can see much better the influence of these parameters on the polarization behaviour of the brass in cooling water system see Figure 4). It is obvious from the figures that all these compounds inhibit the corrosion of brass in cooling water system at all concentrations used in this study.

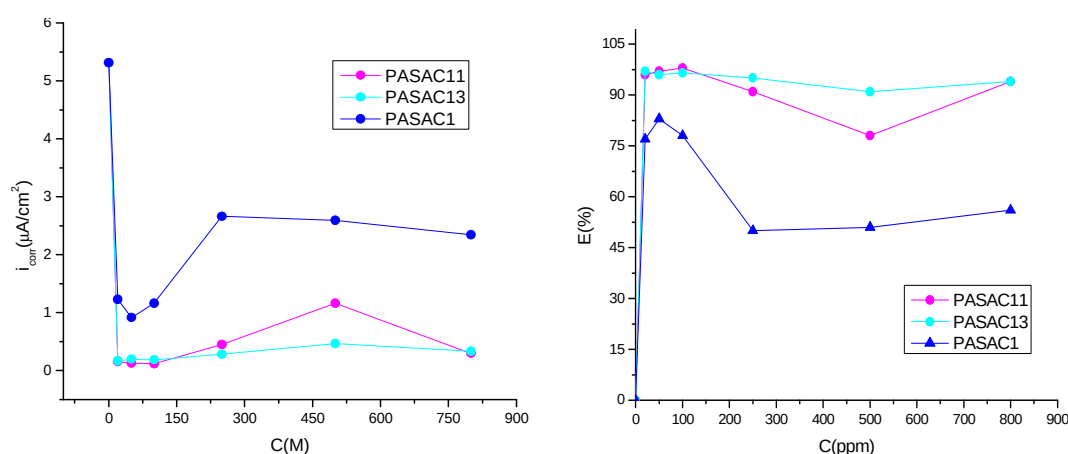


Figure 4 The influence of the inhibitors PASAC11, PASAC13 and PASAC1 concentration on the corrosion rate and efficiency of the brass in cooling water type S1 at 25⁰C.

Adsorption isotherm is very important in determining the mechanism of organo-electrochemical reactions. Also, the higher inhibitor efficiency is a result of the adsorption process. The adsorption isotherm can give important information on the interaction of inhibitor and metal surface. 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 degree of the coverage on the metal surface 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. All

correlation coefficient (R^2) exceeded 0.99 (PASAC13- $R^2=0.99939$; PASAC11- $R^2=0.99879$; PASAC1- $R^2=0.99338$) indicates that the inhibition was attributed to adsorption of these compounds on the metal surface.

Utilization of the Langmuir behavior is often justified with the argument that inhibition must involve adsorption.

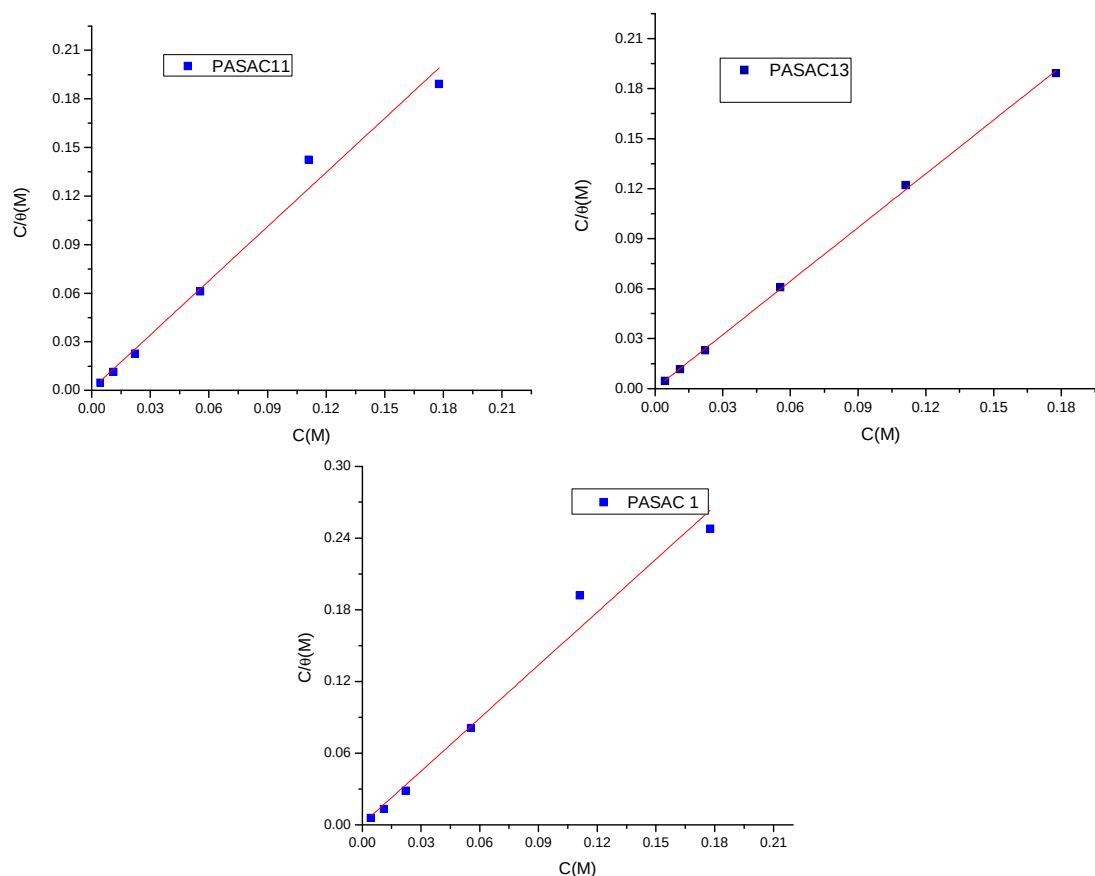


Figure 5 Langmuir plot for PASAC 11, PASAC 13 and PASAC 1 on brass in S1 at different inhibitor concentrations

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 Figure 5). Moreover, we shall try to show what kind type of adsorption process takes place on the electrode surface. The high value of the adsorption equilibrium constant reflects the high adsorption ability of this inhibitor on brass surface.

The adsorption equilibrium constant (K_{ads}) is related to the standard free energy of reaction (ΔG_{ads}^o) by the equation: $\ln K_{ads} = -(\Delta G_{ads}^o / RT)$.

The deduced value of ΔG_{ads}° obtained is negative and means that the adsorption of organic inhibitor is a spontaneous process, and furthermore the negative values of ΔG_{ads}° also show the strong interaction of the inhibitor molecule with the surface.

The obtained values ΔG_{ads}° around -20KJmol^{-1} or lower are consistent with electrostatic interaction between the charged molecules (the inhibitor molecules) and the charged electrode surface (physical adsorption see Table 5), 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).[28-30]

Table 5.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}° KJmol^{-1}	Type of adsorption
Cooling water type S_1 +PASAC 1	Brass	1.088×10^2	-12.447	Physical adsorption
Cooling water type S_1 +PASAC 11	Brass	1.171×10^3	-17.497	Physical adsorption
Cooling water type S_1 +PASAC 13	Brass	7.366×10^3	-22.051	Physical adsorption

Mechanism of inhibition - From the results obtained, it was concluded that all the organic inhibitors (PASAC 1, 11 and 13) inhibit the corrosion of brass in cooling water systems by adsorption at brass/cooling water interface. Adsorption of organic compounds can be described by physical adsorption process. This process is influenced by the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte. The inhibition efficiency of organic inhibitors (PASAC 1, 11 and 13) against the corrosion of brass in cooling water systems can be explained on the basis of the number of adsorption sites, molecular size and mode of interaction with the metal surface. Physical adsorption requires presence of both electrically charged surface of the metal and charged species in the bulk of the solution.

By EIS was investigated the corrosion behavior of brass in cooling water system in the absence and presence of various concentrations of PASAC 1, PASAC 11 and PASAC13 at temperature of 25°C . Impedance measurements were performed at open circuit potential on the frequency range between 100 kHz and 40 mHz with an AC wave of $\pm 10\text{ mV}$ (peak-to-peak) and the impedance data were obtained at a rate of 10 points per decade change in frequency.

Figure 6 showed a typical set of Nyquist plots for brass in cooling water system in absence and presence of various concentrations of organic inhibitors. The impedance spectra of brass electrode exhibit one capacitive loop and the diameter of the semicircles increases on

increasing the inhibitor concentration suggesting that the formed inhibitive film was strengthened by the addition of inhibitors. However, these diagrams are not perfect semicircles and this fact is attributed to frequency dispersion, largely attributed to roughness and inhomogeneities of the solid surface. The semicircular appearance shows that the brass is controlled by charge transfer reaction and the presence of inhibitor does not change the mechanism of dissolution.

Figure 6 also indicates that the diameters of the capacitance loops in the presence of 50ppm PASAC1+Brass-S1, 50ppm and 100ppm PASAC11+Brass-S1 and for 50ppm PASAC13+Brass-SC1 are bigger than those in the absence of organic inhibitors, suggesting that has good anticorrosion performance on the brass in S1

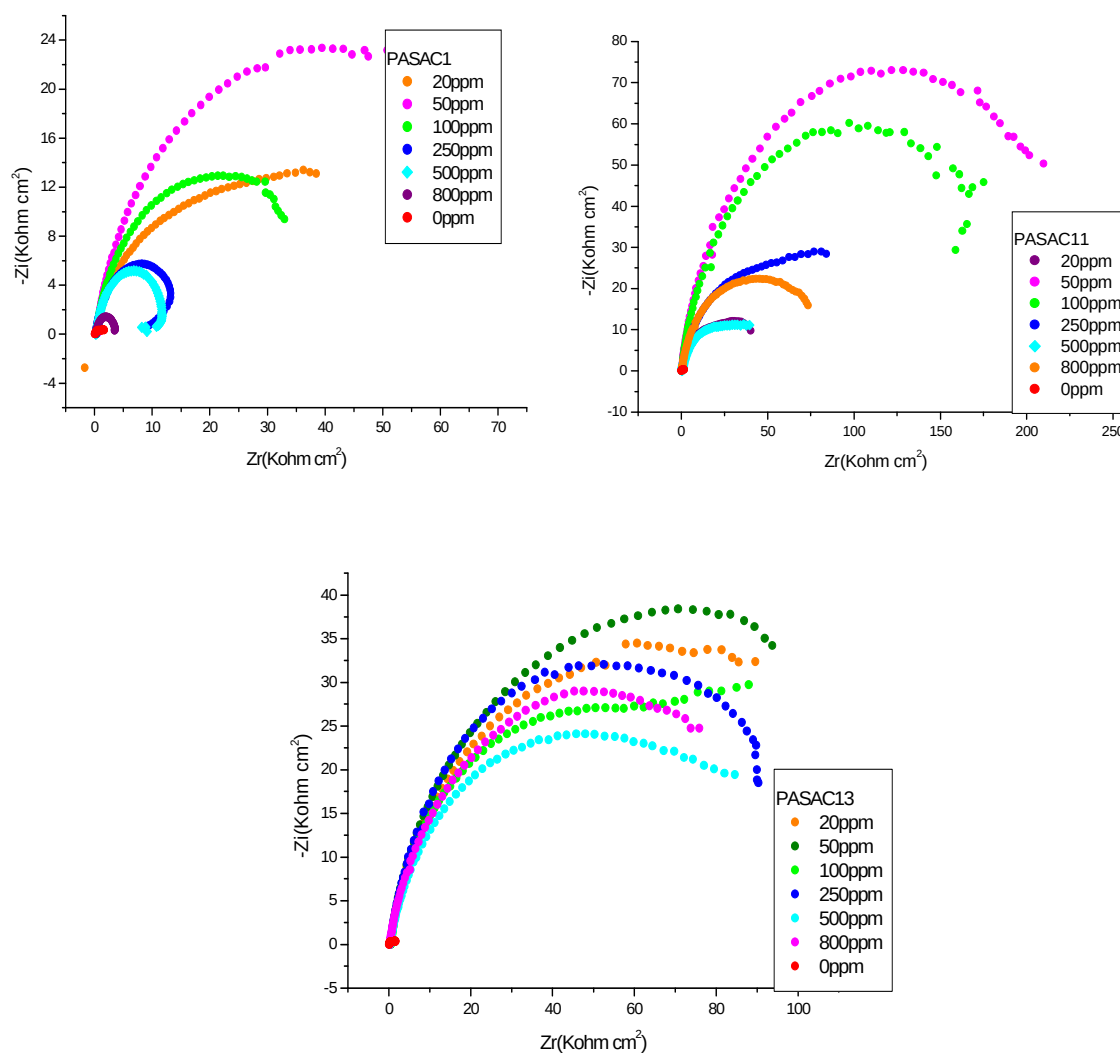


Figure 6 The Nyquist plot for brass in S1 with and without organic inhibitor

Bode diagrams presented in Figures 7-9 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 30° 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 75° 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. Similar results were reported in several studies [13-14].

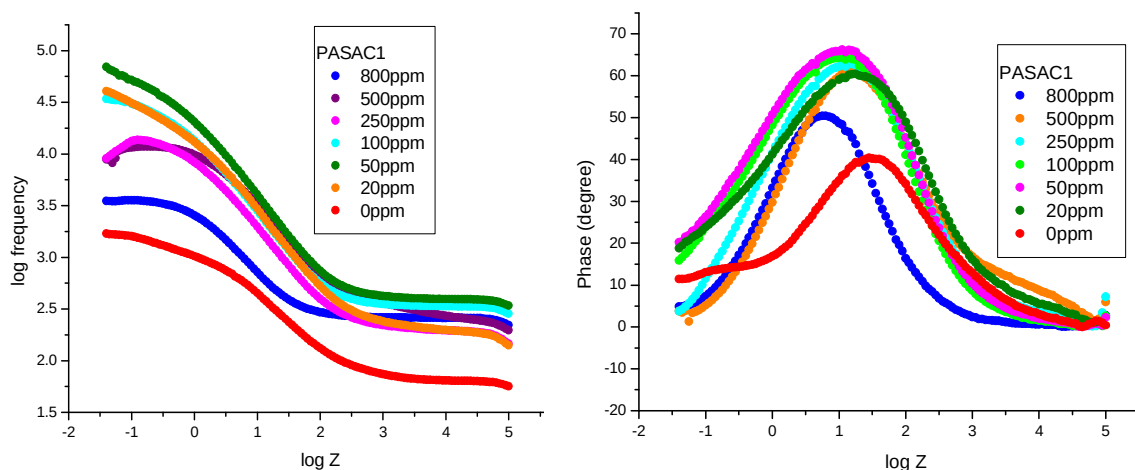


Figure 7 The Bode plot for brass in S1 with and without organic inhibitor PASAC-1

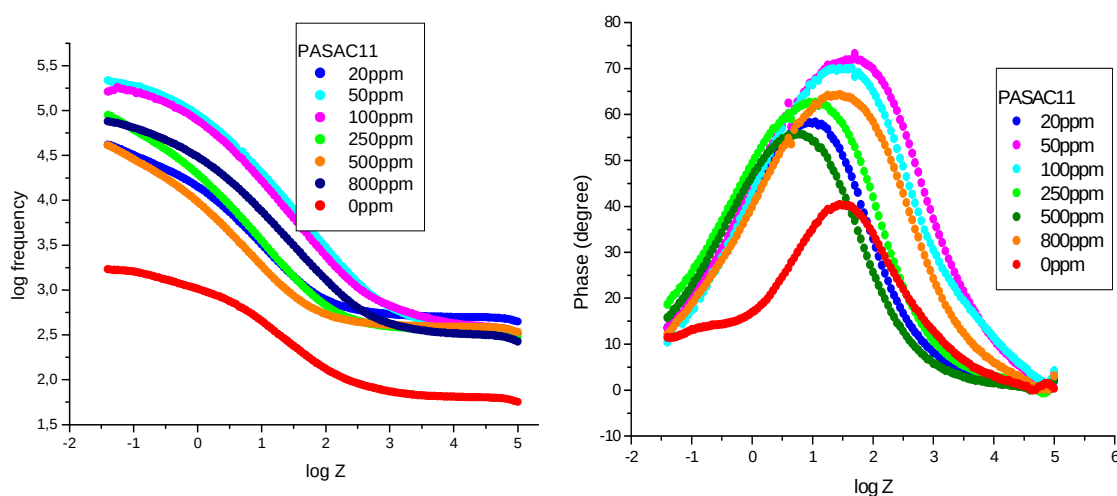


Figure 8 The Bode plot for brass in S1 with and without organic inhibitor PASAC-11

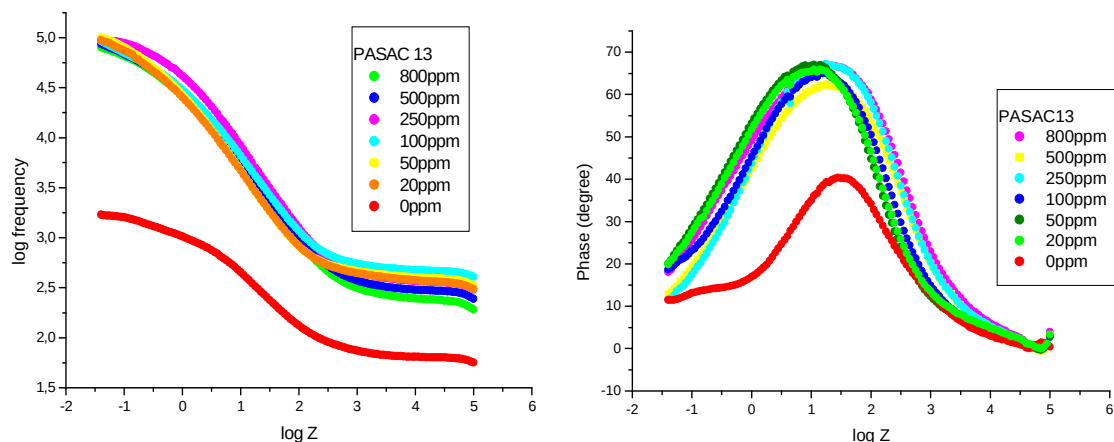


Figure 9 The Bode plot for brass in **S1** with and without organic inhibitor PASAC-13

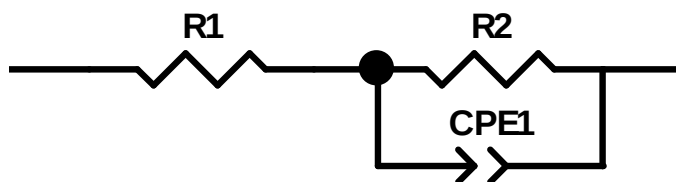


Figure 10 Equivalent circuit

All the obtained plots show only one semicircle and they were fitted using one time constant equivalent mode with capacitance (C), the charge transfer resistance (R_{ct}) and R_s solution resistance. The lower capacitance values for systems: cooling water system -S1+Brass with PASAC-11, PASAC-13 and PASAC-1, indicate the inhomogeneity of the metal surface roughened due to corrosion. The C_{dl} values decreases once with the increasing of the inhibitor concentration and reaches very low values for the optimum concentrations of inhibitors for all the studied systems indicating the reduction of charges accumulated in the double layer due to the formation of adsorbed inhibitor layer.

Several researchers have confirmed that FT-IR spectrometry is a powerful tool that can be used to determine the type of bonding for organic inhibitors adsorbed on the metal surface [24-30].

In this study, FT-IR spectrometry was used to identify whether there was adsorption and to provide new bonding information on the brass surface after immersion in the cooling water system containing organic inhibitors. All spectra in these experiments were obtained at a resolution 4cm^{-1} in the region $4000\text{-}650\text{ cm}^{-1}$. In order to evaluate the protective layer formed on

the metal surface in presence of inhibitor also to provide new bonding information on the brass surface was analyzed by FT-IR spectra.

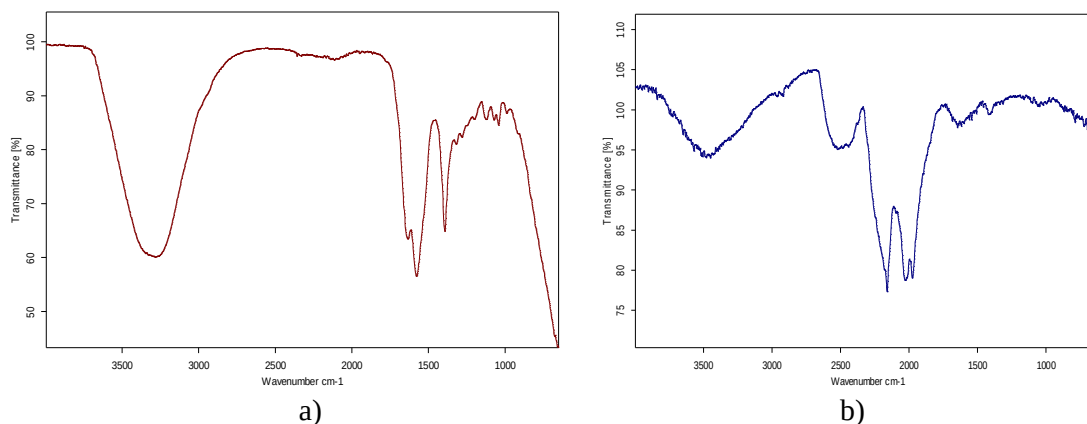


Figure 11 FT-IR spectra of (a) PASAC11 and (b) Brass+100 ppm PASAC11+S1

The FT-IR spectrum of organic polymer PASAC11 is shown in Figure 11a. The FT-IR spectra of the adsorbed protective layer formed on the surface after immersion in S1 containing optimum concentration of inhibitor 100 ppm PASAC11 is shown in Figure 11b. As can be seen, all important peaks in pure compounds (PASAC11) appeared in the adsorption layer on the metal surface. The band around 3350 cm^{-1} is attributed to O-H stretching, which indicates that the protective film contains H_2O . The peak around 2780 cm^{-1} is assigned to C-H stretching vibration, the peaks at 1540 and 1413 cm^{-1} correspond to the C=O and N-H. The presence of C-N and C-O is indicated by their stretching modes at 1100 and 900 cm^{-1} . The characteristic peaks at 1090 and 3335 cm^{-1} correspond to the C-O and O-H stretching of the COOH. Comparing figures 11a and b, it can be suggested that PASAC11 is adsorbed on the brass surface.

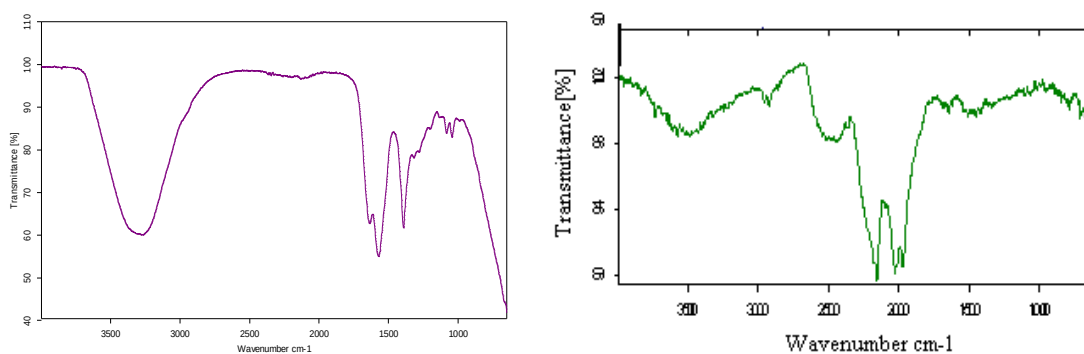


Figure 12 FT-IR spectra of (a) PASAC13 and (b) Brass+20 ppm PASAC13+S1

A transmission vibrational spectrum of pure organic polymer PASAC 13 is depicted in Figure 12a. From figure 12a, a broad peak at 3200 cm^{-1} indicates the presence of the C-H bond of the PASAC13. The presence of C=O and N-H stretching frequencies are manifest in the region 1642

cm^{-1} and 1491 cm^{-1} . The weak band at 1325 to 1210 cm^{-1} respectively is attributed to C-H bending. The FT-IR spectra obtained for the brass with 20ppm PASAC13 inhibitor organic is presented in Figure 12b. This shows the characteristic band for the adsorbed PASAC 13 on the metal surface. A broad band in the range from 3340 cm^{-1} is attributed to C-H, the appearance of the peak in region 1520 cm^{-1} is assigned to N-H symmetric stretching vibration. The band around 3500 cm^{-1} is attributed to O-H stretching, which indicates that the protective film contains H_2O . The peaks for C-N stretching modes can be assigned in the region around 1450 cm^{-1} . The bands 1200 cm^{-1} and 1050 cm^{-1} are attributed to C-O and C-N.

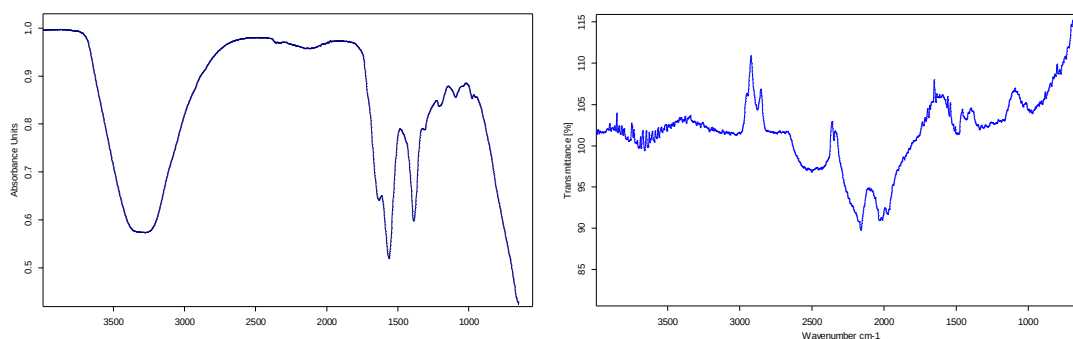
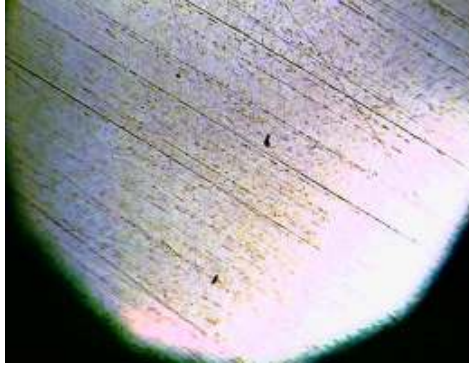


Figure 13 FT-IR spectra of (a) PASAC1 and (b) Brass+50 ppm PASAC1+S1

The transmission FT-IR spectra obtained of pure organic polymer PASAC 1 and for the brass immersed in cooling water systems type S1 containing 50ppm PASAC1 inhibitor organic is presented in Figures 13a and 13b. This shows the characteristics the bands for the adsorbed PASAC1 on the electrode surface. A weak band in the range from 3300 cm^{-1} is attributed to C-H. The medium band approximately 1582 cm^{-1} is assigned to N-H symmetric stretching vibration. The peaks for C-N stretching modes can be assigned in the region around 1396 cm^{-1} . The bands 1200 cm^{-1} and 1020 cm^{-1} are attributed to C-O and C-N.

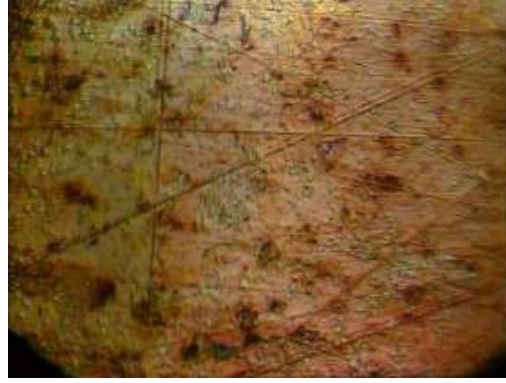
Comparing figures 11a-b, 12a-b and 13a-b it can be suggested that these organic inhibitors (PASAC11, PASAC13 and PASAC1) are adsorbed on the brass surface.

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. Figure 14 shows a few micrographies obtained by us for the following systems: brass +S1 before and after a certain immersion in cooling water type S1 with and without organic inhibitor. Analyzing in comparison the Figures 14b, 14c, 14d and 14e-f, it can be observed that, on the surface of micrographies there are the adsorbed films of inhibitor and corrosion products. These films behave like a barrier between corrosive medium and metal surface and as a consequence the corrosion process is inhibited - see in comparison the figures 14(a, b, c, d, e and f).[33-36]



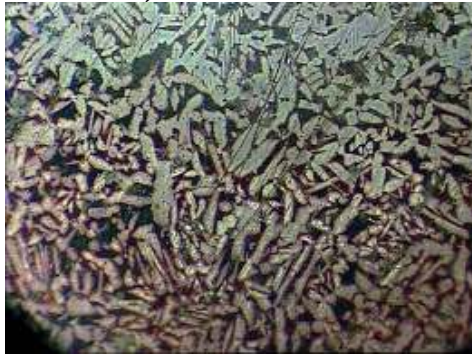
Brass polished-200x

a)



Brass+S1-200x

b)



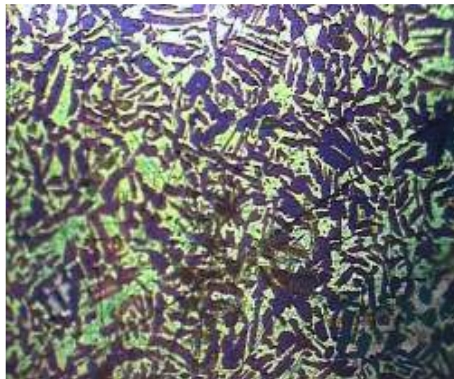
Brass+50ppm PASAC-11+S1-200x

c)



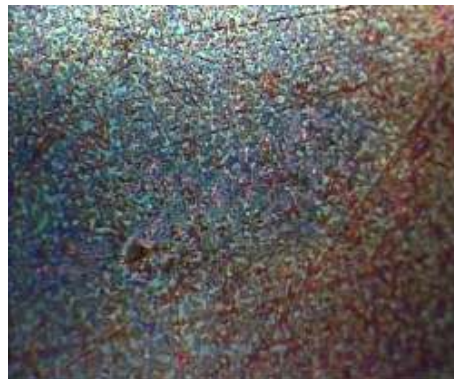
Brass+100ppm PASAC-11+S1-400x

d)



Brass+20ppm PASAC-13+S1-200x

e)



Brass+50ppm PASAC-1+S1-200x

f)

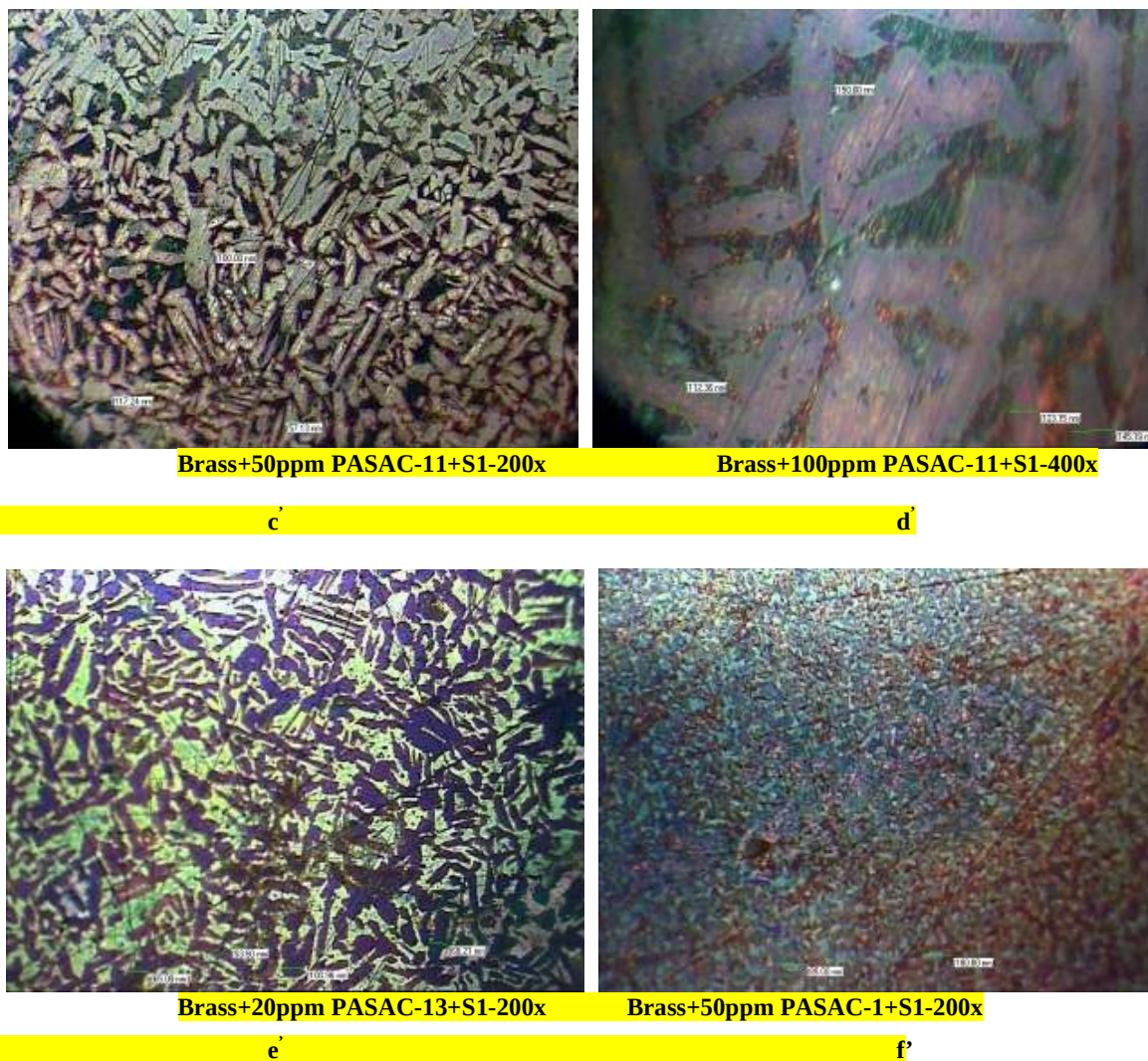


Figure 14 Micrographies of the brass in cooling water type S1 with and without organic inhibitor PASAC-11, PASAC13 and PASAC-1 at different magnitudes (200x-400x)

Analyzing in comparison the figures 14(a-f), it can be observed that, the corrosive attack is much more accentuated in the case of brass+ cooling water type S1 system than in the case of brass+ cooling water type S1 +Xppm inhibitor system. Hence, the protective nature of the film formed on the brass surface is confirmed by metallurgical microscopy techniques examination and with the results obtained by electrochemical method –see Tables 2-4 and the polarization curves from Figures 1-3.

CONCLUSIONS

All the studied of these organic inhibitors (PASAC11, PASAC13 and PASAC1) showed

a very good inhibition properties for the corrosion of brass in cooling water system type S1 and the corrosion current density decreased and the inhibitor efficiency increased with increasing inhibitors concentrations.

The adsorption of all organic inhibitors studied on the brass electrode obeyed the Langmuir adsorption isotherm model.

The results of FTIR, also reveals the adsorption of inhibitor molecule on the electrode surface and blocking the active sites.

PASAC11, PASAC13 and PASAC1 acted as mixed type corrosion inhibitor.

In all of the studies, the organic inhibitor type PASAC-13 and PASAC11 had a higher efficiency; PASAC-1 had a good efficiency.

The inhibition efficiency follows the order: PASAC13>PASAC11>PASAC1

Acknowledgments Financial support from National Research Grant PN-II-32-137/2008 (Romanian Ministry of Education and Research/CNMP) is gratefully acknowledged

REFERENCES

1. JM Maciel, R.Jaimes, PCorio, P.LVolpe, SMI Agostinho, *Corros Sci*, **2008**, 50, 879-886
2. L.Yohai, Mvasquez, MB Valcarce, *Corros Sci*, **2011**, 53, 1130-1136
3. R.Karpagavalli, R Balasubramaniam, *Corros Sci*, **2007**, 49, 963-979
4. L.Campanella, O.C Allessandri, M Ferretti, *Corros Sci*, **2008**, 50, 2183-2191
5. R.Nishimura, T.Yoshida, *Corros Sci*, **2009**, 51, 1205-1213
6. A.M Beccaria, C.Bertolotto, *Electrochim Acta*, **1997**, 48, 1361-1371
7. D. Jones, "Principle and Prevention of Corrosion", MacMillan Publishing Company, New York, **1992**.
8. V. Branzoi, and F. Branzoi, *Rev Roum Chim.*, **2002**, 47, 1193-1203
9. V.Branzoi, F. Branzoi and L.Pilan, *Materials Chemistry and Physics*, **2009**.118, 197-202
10. H. H.Uhlig and R.W.Revie, "Corrosion and Corrosion Control", Wiley, New York, 3rd edn., **1985**.
11. D. P. Schwensberg and V. Ashworth, *Corros.Sci.* **1988**, 28, 539.
12. J. L. Rozenfeld, "Corrosion Inhibitors", McGraw-Hill, New York, **1981**, p.109.
13. V.Branzoi, F. Branzoi and I Harabor, *Rev Roum. Chim.*, **2010**.55, 48
14. F. Branzoi, and V. Branzoi, *Rev Roum Chim.*, **2013**, 58, 747-757

15. .E .M. Sherif and Su-Moon Park, *J. Electrochemical. Soc*, **2005**, 152,B428
16. . E .M. Sherif and Su-Moon Park, *Corros. Sci*, **2006**, 30, 61.
17. .E .M. Sherif, *J.Appl.Surf. Sci*, **2006**, 252, 8615.
18. D.Held Kulwasser, Vulkan Verlag Essen, **1994**.
19. J.Steber, P.Wierich, *Chemosphere*, **1986**, 15, 929-949.
20. . E .M. Sherif and Su-Moon Park, *Electrochim.Acta*, **2006**, 51, 6556.
21. Y.A.Aleksanyan, I.I.Rformatskaya and A.N.Podobaev, *Protection of Metals*, **2007**, 43, 125-128.
22. E .M. Sherif and Su-Moon Park, *Electrochimica Acta*, **2006**, 51, 4665-4673.
23. F. Mansfeld, "Corrosion Mechanism", Marcel Dekker (Ed.), New York, **1987**, p.119.
24. V.Branzoi, F. Branzoi and L.Pilan, *Molec. Crystal & Liquid Crystals*, **2006**,446, 305-318.
25. F. Zucchi,G.Trabanelli, *Corrosion*, **1996**, 38, 2019.
26. V. Branzoi, A. Pruna and F. Branzoi, *Rev Roum de Chim.*, **2007**, 52, 587-595
27. K. Aramaki, J.Uehre and H. Nishihare, *Proc. of the 11th International Corrosion Congress*, Florence, Italy, **1990**, 3, 331.
28. G.B Hunt and A.K.Holiday, *Organic Chemistry* **1981**, 14, 229.
29. Braun R.D., E.E Lopez and D.P. Vollmer, *Corros. Sci.* **1993**, 34, 1251.
30. H.W. Shen and Z.S Smialowskya., *Corrosion Sci.***1989**, 45, 720.
31. Loupy A., *Chemistry Today*, **2006**, 24, 36.
32. Q.Qu, S.Jiang, W.Bai and L.Li, *Electrochim.Acta*, **2007**, 52,6811
33. Q.Quing, L.Li, S.Jing and Z.Ding, *J.Appl.Electrochem.*,**2009**, 39,569
34. M.F.L. Granero, P.H.L.S. Matai, I.V.Aoki and I.C.Guedes, *J.Appl.Electrochem.* **2009**, 39, 1199.
35. D. Gopi, K.M. Govindaraju and L. Kavitha, *J.Appl.Electrochem.* **2010**, 40, 1349.
36. A.Prună, V Branzoi and F. Branzoi, *Materials and Technologies*, **2007**, 23, 233-239.