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Heat Treatment Effect of Polyphosphate Derivatives of Guanidine and Urea Copolymer on the Corrosion Inhibition of Armco Iron in Acid Solution and Antibacterial Properties

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The acid corrosion inhibition process of armco iron in hydrochloric acid 1 M HCl by a modified polyphosphate derivatives of guanidine and urea copolymer (PGUC) has been investigated using electrochemical impedance spectroscopy (EIS). The effect of a thermal treatment of the copolymer on the corrosion behaviour was studied. Data obtained from Electrochemical Impedance Spectroscopy (EIS) show a frequency distribution and therefore a modelling element with frequency dispersion behaviour, a constant phase element (CPE) has been used. The PGUC derivatives have also been used as biocides in aqueous environments and the bacterial killing efficiencies have been determined.

Keywords: PGUC, Heat treatment; Armco iron; HCl; Corrosion inhibition; Antibacterial activity

1. INTRODUCTION

The use of chemical inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media. Acid solutions are generally used in several industrial processes.

Hydrochloric acid HCl is widely used in the pickling solutions. Corrosion inhibition appears to result from the adsorption of inhibitors molecules and ions onto the metal surface. The adsorption is a very complex process and many factors may play a role on the mechanism of such process. It depends on the chemical structure of the inhibitors and their conformational changes, on the type of aggressive acid, pH, temperature and on the nature and surface charge of the metal. The presence of heteroatoms such as oxygen, nitrogen, phosphorus, and sulphur, as well as triple bonds or aromatic rings in their structures, increases the adsorption process [1-9]. Indeed, the phosphorous compounds are commonly used to inhibit materials corrosion in aqueous electrolytes [10-15]. Their use to protect iron and steel against corrosion has been the subject of various works [16-20]. Different bacterial taxa are involved in the biocorrosion processes, and causes severe damages of industrial and process equipments [21]. Corrosion inhibitors which possess an antimicrobial effect are of importance in preventing biological damage of equipments and service lines [22].

The present work is an extension of an earlier work on the influence of polyphosphate derivatives of guanylurea copolymer (PGUC) on the inhibition of corrosion of armco iron in molar hydrochloric acid (1 M HCl) [23]. We have previously shown that PGUC has an antibacterial activity in aqueous environments and that PGUC is an efficient corrosion inhibitor. Moreover, the inhibition efficiency increases with increasing the inhibitor content in the aggressive medium. Adsorption of PGUC on the Armco iron surface in 1 M HCl solution follows Temkin’s isotherm and the calculated thermodynamic parameters reveal that the adsorption mechanism on armco iron surface in 1 M HCl solution is typical of physisorption and the existence of a small attractive interaction between PGUC molecules in the adsorbed layer. In this study, PGUC was subjected to a heat treatment in order to modify its inhibition properties. Indeed, several conformational and structural changes can occur when PGUC is subjected to a heat treatment. In order to better understand the role played by the heat treatment on the efficiency of PGUC as corrosion inhibitor, the electrochemical impedance spectroscopy (EIS) technique has been used. The bacterial killing efficiencies of PGUC have been also investigated in order to evaluate the potential use of this compound as antibiocorrosion agent.

2. EXPERIMENTAL METHOD

2.1. Material preparation

Polyphosphate derivative of guanidine and urea copolymer (PGUC), resulting from the action of thermal treatment on an equimolecular mixture of urea, guanidine carbonate and ammonium phosphate were synthesised according to a slightly modified previously reported experimental procedure as follow [24]. A finely grinded of guanidine carbonate (45 g, 0.5 mole), urea (240 g, 4 moles) and ammonium dihydrogen phosphate (230 g, 2 moles) was heated up to melting point at about 100°C and then at 140°C under stirring for 2 hours with formation of foam which is due to the formation of ammoniac. The reaction mixture was then cooled at 110°C and diluted with 300 ml of an aqueous ammonium hydroxide solution at 1%. The molecular structure of PGUC is shown in Figure 1. The synthesized PGUC was heated under reflux during 15 min and the water was eliminated under vacuum using a rotating evaporator. The viscous product was washed using methanol in order to remove the excess of urea. Then the non dissolved PGUC is recuperated after a filtration step and subsequently subjected to a thermal treatment under air at 100 °C. The treatment duration was varied. The heating process leads to a release of ammonia which results from the reaction of guanidyl group with urea group inducing a mass loss.

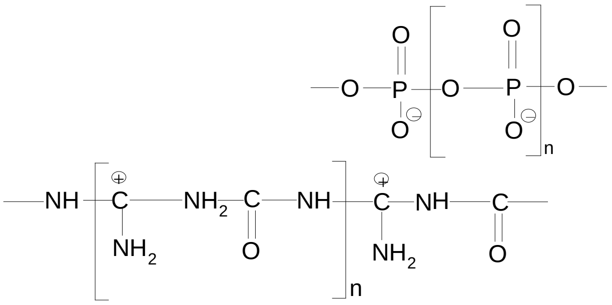
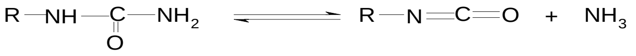
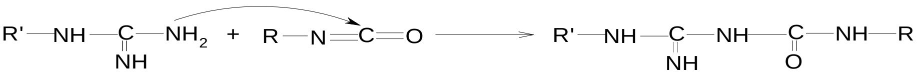


Figure 1. The molecular structure of investigated copolymer (PGUC).

The mass loss evolution versus heating duration is presented in Figure 2. It shows that the PGUC mass rapidly decreases and stabilises after 32 hours of heat treatment due to intermolecular and/or intramolecular reactions. Such intermolecular reactions lead to the formation of PGUC with longer chains according to the reactions shown in the following scheme:



$$R{-}NH{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}NH_2 \rightleftharpoons R{-}N{=}C{=}O + NH_3$$ **(1)**



$$R'{-}NH{-}\underset{\displaystyle NH}{\underset{\|}{C}}{-}NH_2 + R{-}N{=}C{=}O \longrightarrow R'{-}NH{-}\underset{\displaystyle NH}{\underset{\|}{C}}{-}NH{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH{-}R$$ **(2)**

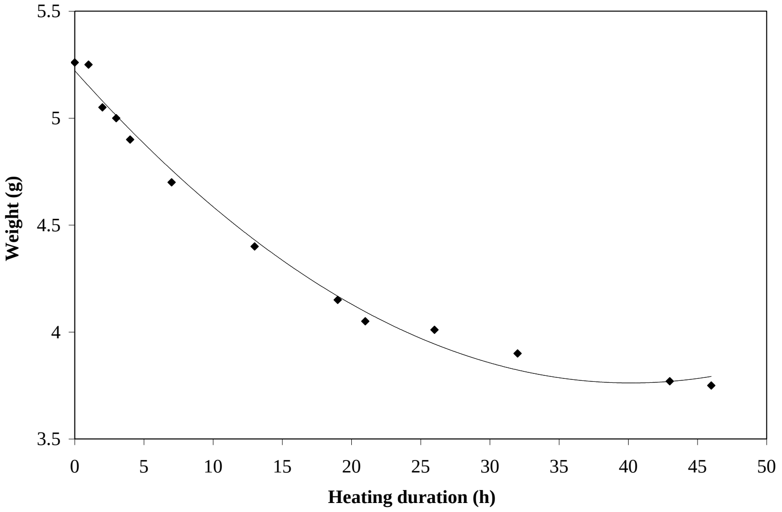


Figure 2. The Variation of weight loss of PGUC derivative with heating duration (the heating treatment temperature is 100° C).

Even through intramolecular reactions, marocyclic species can be also formed. After cyclisation, no more reaction can occurs. So after several hours of heat treatment, all the PGUC molecules will be transformed into a macrocyclic form. The heated PGUC derivatives employed for corrosion tests were tested at a constant concentration of 11.5 g/l. The acid solutions (1 M HCl) were prepared by dilution of an analytical reagent grade 37% HCl with doubly distilled water. Armco iron strips were pre-treated prior to each experiment by grinding with emery paper SiC (grades 600 and 1200), rinsed with distilled water, degreased in ultrasonic bath with acetone, washed thoroughly with doubly distilled water and finally dried at room temperature.

2.2. Electrochemical impedance spectroscopy (EIS)

The electrochemical behaviour of armco iron in 1 M HCl medium was characterised by electrochemical impedance spectroscopy (EIS). Ac impedance measurements were performed using a potentiostat Solartron SI 1287 and a Solartron 1255B frequency response analyzer in a frequency range of 10^5 Hz to 10^{-1} Hz with ten points per decade and a sine wave with 10 mV amplitude was used to perturb the system. ZPlot 2.80 software was used to run the tests, collect and evaluate the experimental data. Corrosion tests were performed in a polymethylmethacrylate (PMMA) cell with a capacity of 1000 ml at 30 ± 1°C, using a thermostat. A saturated calomel electrode (SCE) was used as the reference; a Pt electrode was used as the counter. All potentials are reported *vs*. SCE. The working electrode was prepared from a square sheet of armco iron such that the area exposed to solution was 7.55 cm^2. The impedance spectra were recorded 24 h after the exposure of the working electrode to the solution (no deaeration, no stirring). The impedance data were analysed and fitted with the simulation ZView 2.80, equivalent circuit software.

2.3. Bacteria and antimicrobial assays

The determination of the antibacterial activity of heated derivatives of the polyphosphate of guanidine and urea copolymer was performed using both Gram negative bacteria: *Escherichia coli* CIP 35218 and *Pseudomonas aeruginosa* SMH, and Gram-positive bacteria: *Listeria monocytogenes* ATCC 7644. All the bacterial species were conserved at −80 °C in glycerol containing nutrient broth and were sub-cultured twice in Muller-Hinton (Biokar Diagnostics, Beauvais, France) at 37 °C under agitation (60 rpm). The grown overnight bacteria were diluted in Mueller-Hinton broth to a cell density of *ca* 4×10^6 Colony Forming Unit/ml. The minimum inhibitory concentration (MIC) assays were carried out in sterilized 96 well microtiter plates (Corning, New York, USA) in a final volume of 200 µl, containing 100 µl of *ca* 2×10^6 bacteria in Mueller-Hinton broth and 100 µl of two fold serially diluted solution of the polyphosphate derivative of guanlyurea copolymer (1g/ml) prepared in Mueller-Hinton medium and 100 µl of the bacterial suspension. Three set 12 wells were used for each bacterium. The plates were incubated at 37 °C and bacterial growth was assayed by measurement of OD600 on a microplate reader MRX II (Dynex Technologies, Denkendorf, Germany) after 18 h incubation. The MIC was defined as the lowest concentration of PGUC that inhibited measurable growth of a bacterium following overnight incubation. Each set of experiments was repeated at least twice [25].

3. RESULTS AND DISCUSSION

3.1. Corrosion inhibition evaluation

The effect of the studied polyphosphate copolymer (PGUC) on the corrosion behaviour of armco iron in 1 M HCl was previously studied by ac impedance method at 30 °C after 24 h immersion period [23]. PGUC copolymer powders were thermally treated at a constant temperature of 100 °C for different time (Fig. 2). Such thermal treatment can significantly modify the copolymer structure which will affect the corrosion inhibition performance of the copolymer. The key objective of this ac impedance study is to provide insight into the characteristics of electrochemical processes occurring at the armco iron/HCl interface in presence of the modified PGUC derivatives. The impedance response of these systems at open-circuit potential is presented in Fig. 3. The Nyquist plots for all systems generally have the form of only one depressed semicircle (capacitive loop). The shape of the capacitive loops suggests that the charge transfer controls the corrosion of armco iron at E_{corr} [26]. However the results clearly show a distinct thermal treatment dependence on the effect of PGUC on the corrosion behaviour of armco iron. Compared to the semicircle reference (untreated PGUC), the size of the semi circle increases gradually with the heating duration of PGUC, which is an indication of the inhibition of the corrosion process. These PGUC derivatives inhibit the iron corrosion by adsorbing and blocking the available active centre on the iron surface.

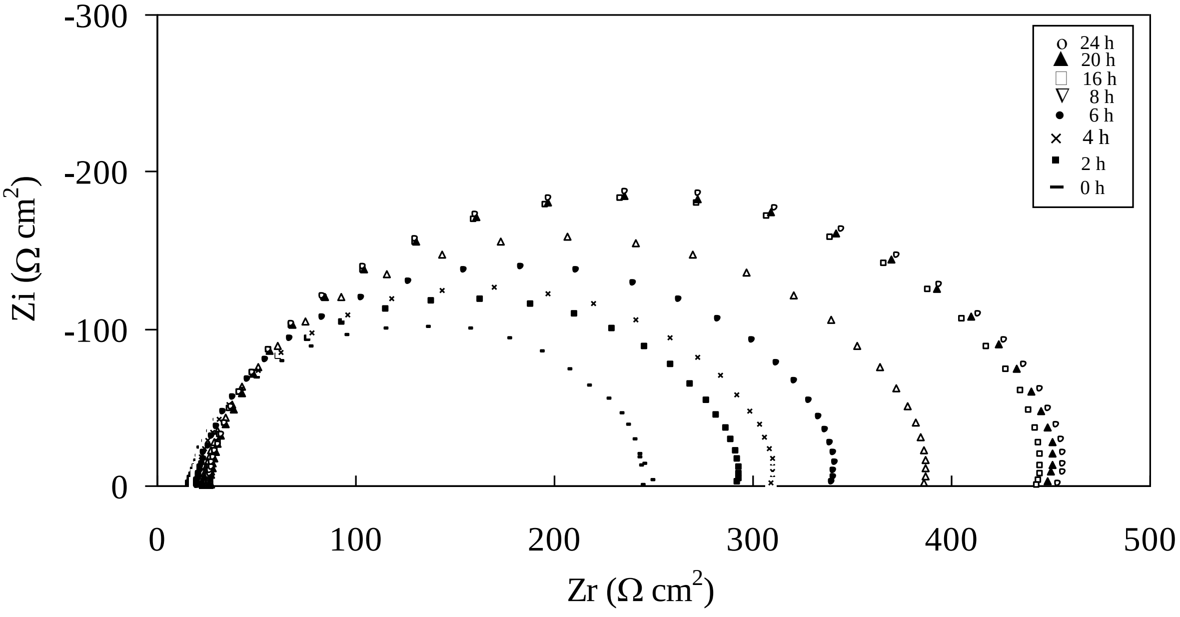


Figure 3. Nyquist diagrams for armco iron after 24 h immersion period in 1 M HCl containing 11.5 g/L of heated PGUC at different heating duration.

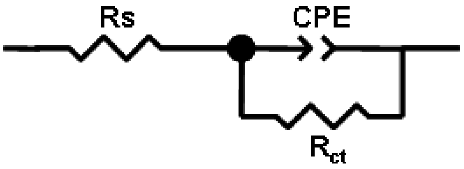


Figure 4. Electrical equivalent circuit used for modelling the interface of armco iron (heated PGUC /1 M HCl).

Electrical equivalent circuits are generally used to model the electrochemical behaviour and to compute the parameters of interest. When there is non-ideal frequency response, it is common practice to use distributed circuits elements in the equivalent circuit. The most widely used is the constant phase element (CPE) which has a non-integer power dependence on the frequency. In most times, CPE is required for modelling the frequency dispersion behaviour corresponding to different physical phenomena such as surface heterogeneity which results from surface roughness, impurities, dislocations, distribution of the active sites, adsorption of inhibitors and formation of porous layers [27,28]. The impedance, Z_{CPE}, associated with CPE is described as follows [29]:

$$Z_{\mathrm{CPE}} = A^{-1}(\mathrm{i}\omega)^{-n} \qquad (1)$$

where A is the CPE constant (in Ω^{-1} s^n cm^{-2}), ω is the sine wave modulation angular frequency (in rad s^{-1}), $i^2 = -1$ is the imaginary number, and n is an empirical exponent ($0 \leq n \leq 1$) which measures the deviation from the ideal capacitive behaviour [30]. The value of n can be used as a measure of the surface inhomogeneity [31].

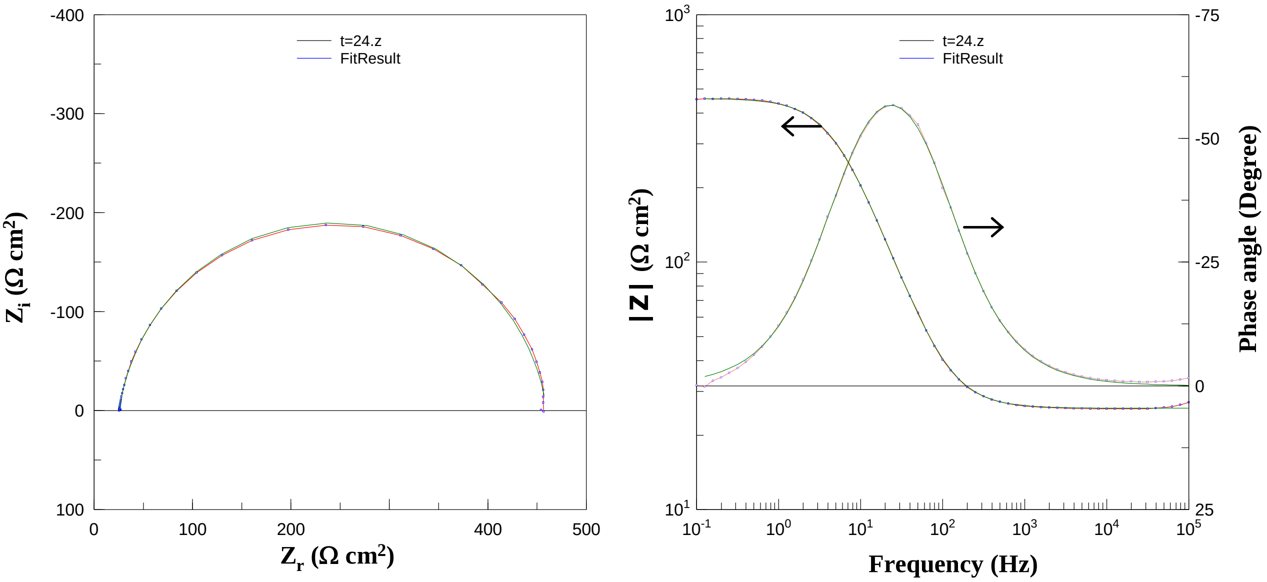


Figure 5. Nyquist and Bode plots for armco iron / 1 M HCl + 11.5 g/L heated PGUC during 24 h interface: (···) experimental; (—) fitted data.

The impedance parameters, such charge-transfer resistance (R_{ct}), the constant phase element (A) related to the capacity of the double layer and the exponent (n), relevant to the capacitive semicircle of the Armco iron/HCl/inhibitor system are given in Table 1. These parameters were calculated from the non-linear least square fit of the equivalent circuit shown in Fig. 4. Simulation of Nyquist and Bode plots with above model is very close to the experimental data (Fig. 5, representative example).

Table 1. Impedance parameters for the corrosion of armco iron after 24 h of immersion period in 1 M HCl containing 11.5 g/L of heated PGUC at different heating duration.

Heating duration (h)	Rct (Ω cm2)	10-4 A (sn □-1 cm-2)	n	Cdl (□F cm-2)	τ (s)	E (%)
Blank	21.62 ± 0.05	4.81 ± 0.01	0.906 ± 0.002	301.21	0.0065	—
0 [10]	239.4 ± 1.09	1.23 ± 0.01	0.898 ± 0.001	82.71	0.0198	90.97
2	275.8 ± 1.051	1.18 ± 0.01	0.902 ± 0.002	81.33	0.0224	92.38
4	293.1 ± 0.88	1.17 ± 0.01	0.901 ± 0.002	80.77	0.0237	92.83
6	323.6 ± 0.89	1.13 ± 0.01	0.902 ± 0.002	78.88	0.0255	93.51
8	367.6 ± 1.03	1.11 ± 0.01	0.902 ± 0.002	78.41	0.0288	94.29
16	423.9 ± 1.18	1.02 ± 0.01	0.910 ± 0.002	74.76	0.0317	95.05
20	429.6 ± 1.20	1.01 ± 0.01	0.910 ± 0.002	74.05	0.0318	95.11
24	434.9 ± 1.26	1.00 ± 0.01	0.911 ± 0.002	73.62	0.0320	95.17

The values of the double layer capacitance (C_{dl}) and the relaxation time constant (τ), given in Table 1, can be calculated for a parallel circuit composed of a CPE (A) and a charge-transfer resistance (R_{ct}), according to the following formulas [32]:

$$C_{dl} = (AR_{ct}{}^{1-n})^{1/n} \tag{2}$$

$$\tau = C_{dl}\, R_{ct} \tag{3}$$

The inspection of the impedance results, given in Table 1, clearly shows that the R_{ct} value increases when the heating duration of PGUC increases and reaches a maximum value of 434.9 Ω cm^2 in the case of 24 h of heating duration. A large charge-transfer resistance is associated with a slower corroding system, due to a decrease in the active surface necessary for the corrosion reaction [33]. In addition, the increase in R_{ct} values becomes stable from 16 hours of heating (Fig. 6). On the other hand, the increase of the n value after addition of heated PGUC in the corrosive solution indicates a reduction of surface inhomogeneity due to the adsorption of PGUC molecules on the most active adsorption sites at the iron surface. The value of the proportional factor A of the Z_{CPE} also varies in a regular manner with heating duration.

Its recalculation in terms of capacitor (Eq. 2), i.e. in F cm^{-2}, could serve as a basis of comparison, although roughly. Indeed, the addition of heated PGUC derivatives to the corrosive solution decreases the double layer capacitance (C_{dl}) and it increases the time constant (τ) value (Table

1). When the heating duration is increased to 24 h, the interface parameter (τ) increases from 0.0065 s (blank) to 0.0320 s while the capacitance (C) value decreases from 301.21 to 73.62 μF cm^{-2} signifying that the charge and discharge rates to the metal-solution interface is greatly decreased.

This shows that there is agreement between the amount of charge that can be stored (i.e. capacitance) and the discharge velocity in the interface (τ) [34]. The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of PGUC molecules on the Armco iron surface decreases its electrical capacity because they displace the water molecules and other ions originally adsorbed on the surface. The decrease in this capacity with increase in heating duration of PGUC may be attributed to the formation of a protective layer on the electrode surface [35]. The thickness of this protective layer increases with increase in heating duration of investigated polymer, since more PGUC will electrostatically adsorb on the electrode surface, resulting in a noticeable decrease in C_{dl}. This trend is in accordance with Helmholtz model, given by the following equation [36]:

$$C_{\text{dl}} = \frac{\varepsilon\varepsilon_0}{d} \qquad (4)$$

where d is the thickness of the protective layer, ε is the dielectric constant of the protective layer and ε_0 is the permittivity of free space (8.854×10^{-14} F cm^{-1}).

The inhibition efficiency of these PGUC derivatives was evaluated by R_{ct} values using Eq. 5, where R_{ct}^0 and R_{ct} are the charge-transfer resistance values without and with inhibitor [8], respectively:

$$E(\%) = \frac{1/R_{\text{ct}}^0 - 1/R_{\text{ct}}}{1/R_{\text{ct}}^0} \times 100 \qquad (5)$$

It can be observed, from the Table 1 and the Fig. 6 that the protection inhibition efficiency increases continuously with increasing of the heating duration of PGUC and becomes stable after 16 h of heat treatment. Indeed, the maximum E(%) of 95.05 % was achieved in the case of 16 h of heating and a further increase in the heating duration did not cause any more appreciable change in the performance of the inhibitor.

The heat treatment of PGUC molecules will induces a progressive formation of macrocyclic and longer chains PGUC which will be also transformed into a lager macrocycles for longer heat treatment time. The effect of the macrocyle size on the anticorrosion efficiency has been reported by Lebrini et al. [37,38]. The results shown give clearly evidence of an increase in the efficiency of marocyclic corrosion inhibitors when their size increases. The anticorrosion efficiency behaviour of the thermally treated PGUC can be then explained by the presence of a high content of larger PGUC macrocyles for longer heat treatment times.

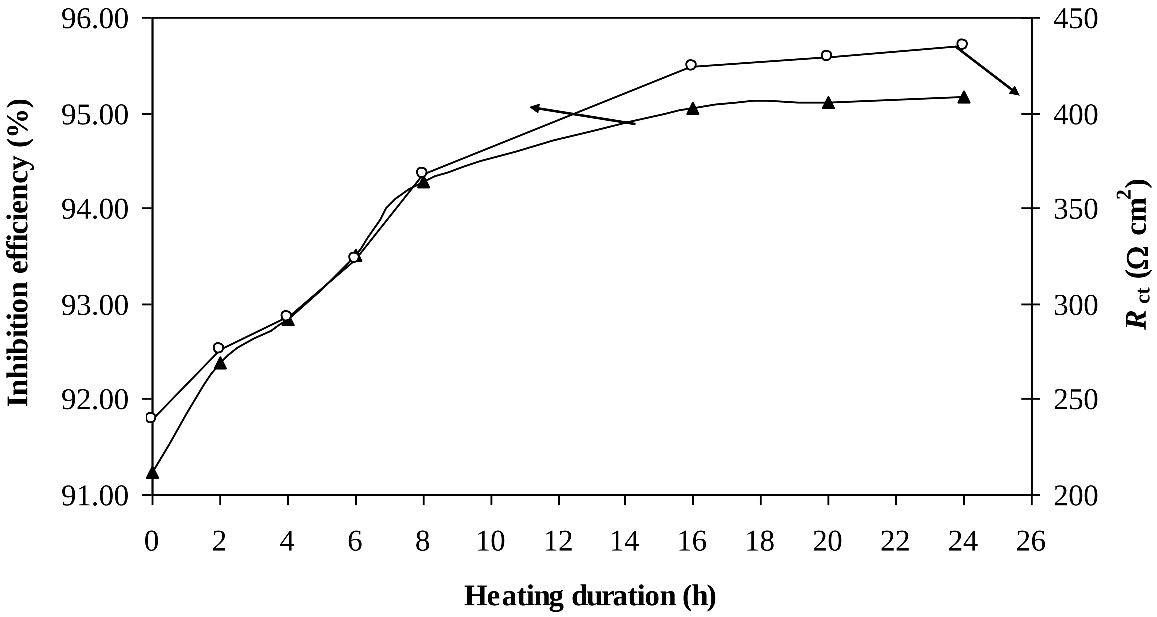


Figure 6. Variation of the charge-transfer resistance (R_{ct}) and the inhibition efficiency for armco iron in 1 M HCl with heating duration of PGUC derivative (11.5 g/L).

3.2. Effect of the duration of heat treatment on the antibacterial properties of PGUC

Assessment of the antibacterial properties of the PGUC was carried out using the MIC (minimal inhibition concentration). The results of Table 2 show that the MIC of PGUC against *Escherichia coli* is improved by the duration of heat treatment (100°C). Heat duration of the PGUC of 6h improve the MIC of PGUC almost four times. However, when the duration of the heat treatment applied is more than 6 hours no MIC decrease is measured (Table 2).

Table 2. The minimal inhibition concentration (MIC) of PGUC depending on the duration of heat treatment for (*Escherichia coli* CIP 35218).

Heat treatment duration* (h)	MIC of the PGUC derivatives (mg/ml)
0	31
2	31
4	15
6	7.8
8	7.8
12	7.8
15	7.8
18	7.8
24	7.8

* The heating treatment temperature is 100° C

In addition, Table 3 shows also that the MIC(s) of PGUC against *Pseudomonas aeruginosa* and *Listeria innocua* depend on the duration of the heat treatment. Thus, the MIC of PGUC decreases with the increase of the duration of heat treatment (100°C). The results of Table 3 show that for both *P. aeruginosa* and *L. innocua* the MIC decreases of *ca* 2-fold when the heat treatment (100°C) applied to the PGUC was 6 hours. However, as shown for *E. coli*, when the duration of the heat treatment applied is over than 6 hours no MIC decrease is measured (Table 2). Our results show also that the PGUC inhibitory corrosion effect is improved by the heat treatment. The PGUC efficient concentration used in this study for the armco-iron inhibition corrosion was of 11.5 g/l whatever the duration of the heat treatment. This concentration is of ca 2.7-fold lower than the MIC of *E. coli* when the PGUC is not heated. However, when the duration of the heat treatment is from 6 to 24h the PGUC efficient concentration used (11.5) is 1.5-fold higher than the MIC of *E. coli*. In PGUC polymer, the guanidyl group is basic; this means that these species carries positives charges at physiological pH. Consequently, PGUC is highly adsorptive to anionic surfaces such as bacterial cell surface and indeed its mechanism of biocidal action is considered to be related to the damage to the cytoplasmic membrane as reported for other antibacterial molecules [39]. The Heat treatment applied to the PGUC could also increase their bacterial trapping capacity due the formation of macrocyclic PGUC which could improve the antibacterial activity of the PGUC.

Table 3. The minimal inhibition concentration (MIC) of PGUC depending on the duration of the heating treatment.

	Heat treatment duration (h)	
	0	6
Bacteria	MIC (mg/ml)	
Escherichia coli CIP 35218	31 [10]	7.8
Pseudomonas aeruginosa MSH	125 [10]	62.5
Listeria innocua	31.2	15.6

4. CONCLUSION

The corrosion inhibition by polyphosphate derivatives of guanylurea copolymer has been experimentally investigated with the help of the Ac impedance method. It was shown that the heat treatment of PGUC increases the efficiency of corrosion inhibition of armco iron in 1 M HCl. Data obtained from ac impedance technique show a frequency distribution and therefore a modeling element with frequency dispersion behavior and constant phase element (CPE) has been used. The calculated corresponding parameters show an increase of the R_{ct} and a decrease of the capacitance values with heating duration. This last decrease is attributed to an increase in the thickness of the formed protective layer. And as a consequence, the inhibition efficiency was dependent on the duration of the heat treatment. The heat treatment of PGUC molecules induces an increase in the corrosion inhibition efficiency due to a progressive formation of PGUC polymers with larger macrocycles and longer chains. Moreover, the heat treatment applied to the PGUC improves also the antibacterial activity due to an increase in their bacterial trapping capacity and also their adsorption to bacterial cell walls which improves the MIC against the tested strains.

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