



Impedance spectroscopic study of corrosion inhibition of pure iron by poly (4-vinylpyridine isopentyl bromide) in molar H₂SO₄

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ABSTRACT

A brief review is given of the application of impedance measurements to electrochemical processes. Only very few applications for corrosion processes have been reported. The inhibitive action of the poly (4-vinylpyridine isopentyl bromide) (P4VPIBr) in three degrees of quaternisation (6%, 18% and 79 %) on the corrosion behaviour of pure iron was investigated in deaerated molar sulphuric acid solution, by means of electrochemical impedance spectroscopy measurements (EIS) at free corrosion potential. The parameters, which characterise the corrosion behaviour, can be determined from plots and diagrams of Nyquist. Their inhibition efficiency (E%) increases with the concentration of all inhibitors. Trends in the increase of charge transfer resistance and decrease of capacitance values also show the adsorption of the molecules on the metal surface.

Key words: Electrochemical impedance spectroscopy, Iron, poly (4-vinylpyridine), inhibition, corrosion.

INTRODUCTION

The cost of corrosion has been reported from many studies to be in the order of 1 to 5 per cent of GNP for any country. Corrosion never stops but its scope and severity can be lessened. In a sense, the use of inhibitors is one of the best-known methods of corrosion protection [1-2]. Organic compounds are of interest as corrosion inhibitors in acid pickling baths. The compounds used as inhibitors act through a process of surface adsorption, so the efficiency of an inhibitor depends not only on the characteristics of the environment in which it acts, the nature of the metal surface and electrochemical potential at the interface, but also on the structure of the inhibitor itself, which includes the number of adsorption active centres in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metallic surface [2-6]. Adsorption of inhibitors at the metal/solution interface is usually accepted as the formation of electrostatic or covalent bonding between the metal surface atoms and the adsorbents [3,5].

The application of electrochemical impedance spectroscopy technique (EIS) as a new tool in corrosion research has resulted in a wealth of information concerning the methods of corrosion protection, which were difficult to study with traditional DC techniques. This includes corrosion protection by conversion coatings [7], polymer coating, and anodic films [8]. EIS has also provided information concerning corrosion protection by inhibitors [9]. In addition to specification of the physical properties of the system, the technique leads to important mechanistic and kinetic information [10–12]. AC impedance technique are finding increasing in corrosion research also due to their promise in obtaining mechanistic data and due to the possibility of using the technique for corrosion monitoring. Some of advantage of AC impedance techniques are the use of only very small signals which do not disturb the electrode proprieties to be measured, the possibility of studying corrosion reactions and measuring corrosion rates in mow conductivity media where traditional DC methods fail, and the fact that polarisation resistance as well as double layer capacitance data can be obtained in the same measurements [13]. The electrochemical impedance spectroscopy has become a very important method and tool in the analysis of an equivalent circuit of an electrochemical cell. This method permits to surimpose a small sinusoidal excitation to an applied potential and then the electrochemical interface metal/solution offers impedance. Recently Taylor and Gileadi proposed a new model for the better understanding of the Warburg process. The model describes an equivalent circuit consisting of capacitance in series with resistance to replace the conventional Warburg impedance in the Randels equivalent circuit. Discusses the above model highlighting the defects in their assumption. Attempts to find a better understanding of the Warburg impedance and discusses various possibilities. The inhibitive performances of organic inhibitors are widely discussed on the basis of EIS characteristics [1-14]. Usually the values of R_p (defined as the zero frequency limit of the real part of the complex faradic impedance) are used to obtain the electrode corrosion rates and the corresponding percent inhibiting efficiencies (E%).

The application of water-soluble polymers as corrosion inhibitors of metals in aggressive media with AC impedance technique takes recently more attention. The inhibitive power of the polymers is related structurally to the various active centres of adsorption such as cyclic rings and heteroatoms as oxygen, nitrogen and sulphur, which are the major active centres of adsorption. PVP and derives, polyvinyl pyridine, polyvinylbipyridine, polyvinylpyrrolidine, polyvinylpyrrolidone (PVP), polyethylenimine (PEI) and polyvinylimidazoles (PVI) has been widely examined, has received particular attention and has been applied to the inhibition of Fe, Cu, Al, Zn and their alloys in various acidic media [13-19]. Recently, the encouragement result obtained by addition of poly (4-vinylpyridine) (P4VP) derivatives on the corrosion of pure iron in 1M H₂SO₄ has incited us to modify the molecular structure by introducing the poly-3-oxide ethylene group [16-20]. P4VP and its derivative, the poly (4-vinylpyridine poly-3-oxide ethylene) (P4VPPOE), obtained good results [21] and Poly (4-vinylpyridine isopentyl bromide) P4VPIPBBr on the corrosion of pure iron in 1M H₂SO₄ [22].

The aim of this work is to investigate how the poly (4-vinylpyridine isopentyl bromide) (P4VPIPBBr) in three degrees of quaternisation (6%, 18% and 79 %) inhibits the pure iron corrosion in desaerated 1M H₂SO₄ by using electrochemical impedance spectroscopy (EIS) and to propose the adsorption models of (P4VPIPBBr) on the pure iron surface.

2. Experimental

2.1. Inhibitors

The Poly (4-vinylpyridine isopentyl bromide) (P4VPIPBr) is fractionated by partial precipitation from methanol solution with ethyl petrol. The polymer has been obtained by mixing P4VP to isopentyl bromide (IPBr) in chloroforme (CHCl_3) in a thermostatic bath (70°C).

Poly (4-vinylpyridine isopentyl bromide) is obtained in three degrees of quaternisation (6%, 18% and 79 %). The first polymer (6%) P4VPIPBr (I) is obtained after 3 hours, the second (18%) P4VPIPBr (II) after 24 hours and the tertiary (79%) P4VPIPBr (III) after 72 hours.

After that, they are precipitated in petrol ether, ished in ethanol, then precipitated again in ether petrol and dried. The structure is checked by NMR and IR spectra. The molecular weight is estimated by the viscosity technique using ethanol as solvent. P4VPIPBr (I), (II) and (III) of average molecular weight $4.2 \cdot 10^5$, $4.7 \cdot 10^5$ and $7.16 \cdot 10^5 \text{g/mol}$, respectively.

The molecular structure of the new synthesised Poly (4-vinylpyridine isopentyl bromide) (P4VPIPBr) is shown in Figure (1).

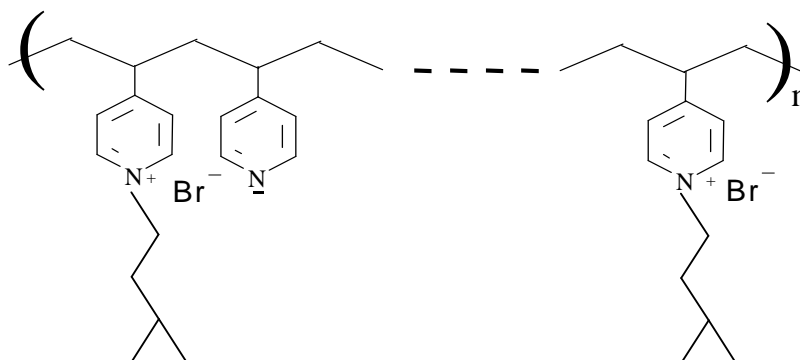


Figure 1: The molecular structure of P4VPIPBr.

2.2. Chemicals

Prior to all measurements, the iron samples (99.5%, thickness = 0.05 cm from Good Fellow, Cambridge, England) are polished with different emery paper up to 1000 grade, ished thoroughly with bidistilled water degreased and dried with acetone. The aggressive solution (1M H_2SO_4) is prepared by dilution of Analytical Grad 98% H_2SO_4 with bidistilled water.

2.3. Impedance spectroscopy measurements

Impedance spectroscopy measurements are carried out in a conventional three electrodes electrolysis cylindrical pyrex glass cell. The working electrode (W.E) had the form of a disc cut from iron sheet. The exposed area to the corrosive solution is 1cm^2 . A saturated calomel electrode (SCE) and a disc platinum electrode are used, respectively, as a reference and auxiliary electrode. The temperature is thermostatically controlled at $298 \pm 1 \text{K}$.

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Volta lab PGZ 100 computer at E_{cor} after immersion in solution without bubbling. After the determination of steady-state current at a given potential, sine wave voltage (10mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure.

The impedance diagrams are given in the Nyquist representation. Before recording the curves the test solution is de-aerated in magnetically stirred for 30 min in the cell with nitrogen.

RESULTS AND DISCUSSION

The corrosion behaviour of iron, in acidic solution in the presence and absence of polymer compounds, is investigated by the electrochemical impedance spectroscopy (EIS) at 298 K after 30 min of immersion.

The charge-transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al [23]. To obtain the double layer capacitance (C_{dl}) the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) is found as represented in equation.

$$C_{dl} = \frac{1}{\omega R_t} \quad \text{Where } \omega = 2\pi f_{max}$$

The inhibition efficiency obtained from the charge transfer resistance is calculated by:

$$E(\%) = \left[\frac{R_{t/inh} - R_t}{R_{t/inh}} \right] \cdot 100$$

R_t and $R_{t/inh}$ are the charge transfer-resistance values with and without inhibitor, respectively.

The data fig 2 reveal that, each impedance diagram of pure iron electrode exposed for 30 min at the free corrosion potential in inhibited and uninhibited acidic solution containing at 10^{-6} M of P4VPIBBr in three degrees of quaternisation (6%, 18% and 79 %) consists of a large capacitive loop at high frequencies (HF) and a small inductive one at low frequency values (LF).

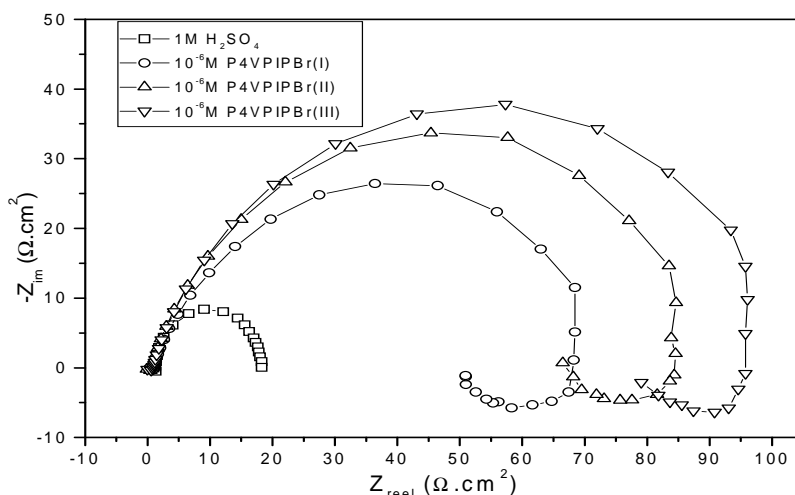


Figure 2: Impedance diagrams of iron electrode in 1M H₂SO₄ at Ecorr in presence and absence of P4VPIBBr (I), (II) and (III) inhibitors at 10⁻⁶M.

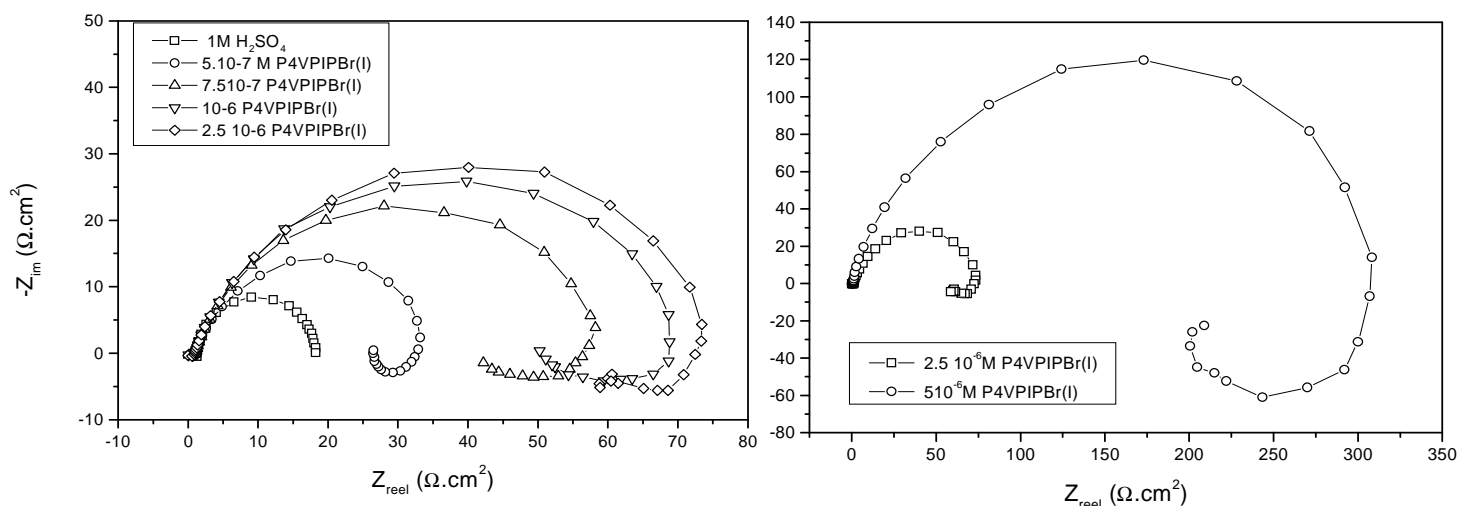
The HF capacitive loop could be assigned to the relaxation process and its dielectric properties [24,25]. The effect of P4VPIBr in three degrees of quaternisation on the impedance response of pure iron in deaerated 1M H₂SO₄ solution at 298K is independent of degrees of quaternisation of these polymers. This loop makes an angle with the real axis and its intersection gives a value of the resistance of the solution enclosed between the working electrode and the counter electrode (R_s). The inductive loop may be attributed to the relaxation process obtained by adsorption species.

The inductive loop may be attributed to the relaxation process obtained by adsorption species. The point of intersection between the inductive loop and the real axis represents (R_s+R_p) where R_p is the polarization resistance, which is defined as the DC limit of the impedance [26]. It is essential to develop the appropriate models for the impedance, which can then be used to fit the experimental data and extract the parameters, which characterize the corrosion process.

Fig (3) shows a set of Nyquist impedance diagrams obtained from the pure iron electrode exposed for 30 min at the free corrosion potential in inhibited and uninhibited acidic solutions containing various concentrations of P4VPIBr (I). It is seen from this figure that the impedance diagrams are almost semicircular in appearance but not perfect semicircles. We deduce the centre of the semicircles does not lie on the Z_{reel} axis, but is shifted to negative Z_{im} values. This difference has been attributed to the frequency dispersion [19,21]. These circles are constructed with the inductive loop at high frequency.

The occurrence of inductive loop, which becomes in the presence of poly (4-vinylpyridine isopentyl bromide) (P4VPIBr), the corrosion inhibition efficiency depends on inhibitors concentration. The presence of the inductive loop attributed in the relaxation of intermediate reactions.

Figure 3: Impedance diagrams of iron electrode in 1M H₂SO₄ at E_{corr} in presence and absence of P4VPIBr (I) at different concentration.



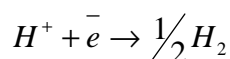
The inductive loop associated with metal dissolution and hydrogen adsorption is not observed on the Nyquist diagram for acidic solution alone. As the impedance diagram obtained has a semicircle appearance, it shows that a charge transfer process mainly controls the corrosion of

iron. It is apparent also from these figures 2-3, that the charge transfer-resistance value of pure iron in uninhibited H₂SO₄ solution significantly changes after the addition of (P4VPIPBr).

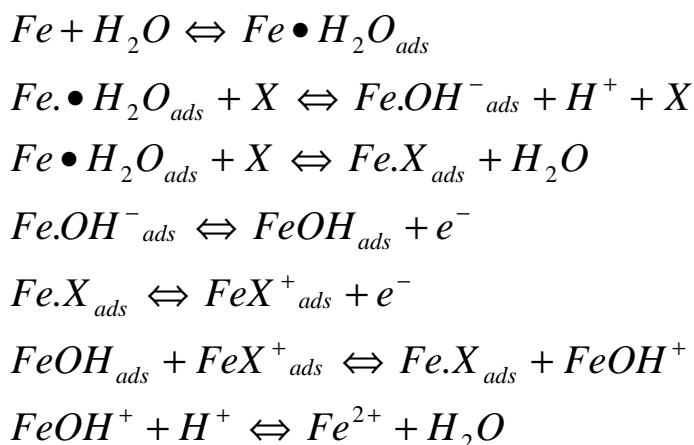
The size of capacitive loop significantly decreased with the further increase of concentration of (P4VPIPBr). The former shows that the mass transport has high influence on the corrosion reaction after 30mn of immersion, whereas latter indicates that the corrosion resistance is increasing.

Generally, the pure sulphuric acid and (P4VPIPBr)-containing sulphuric acid solution used in our experiments were all desaerated. Dissolved oxygen may be reduced on iron surface and this will enable some corrosion to take place [27]. Theoretically, pure iron can hardly be corroded in the deoxygenated dilute sulphuric acid [28], as iron can displace hydrogen from acid solutions according to theories of chemical thermodynamic.]. It is a good approximation to consider the hydrogen evolution reaction and only consider oxygen reduction in the des-aerated sulphuric acid solutions at corrosion potential.

Cathodic reduction of hydrogen can be expressed either by a direct two electron transfer as shown by Equation. (1).



Dissolution of iron in sulphuric acid is described by the following equations. . This behaviour can be explained by considering the mechanism of iron oxidation in acidic solution proceeding via one adsorbed intermediate, while in the presence of inhibitor a different mechanism has to be developed, involving to adsorbed intermediates. It is commonly accepted that the kinetics of iron anodic oxidation in acid depends on the adsorbed intermediate FeOH_{ads} [27,29]. An iron anodic oxidation mechanism, which is valid in the presence of inhibitor, could be one similar to that discussed by Hackerman [27,30].



The species X is the inhibitor molecule, in our case. This mechanism shows that the anodic reaction kinetics is affected by two intermediates: one involving adsorbed hydroxyl (/FeOH_{ads}) and the other involving the adsorbed inhibitor molecule (FeX_{ads}). The rate of anodic dissolution (step 4) depends to the product of step 2, but the two competitive steps 2 and 3 are based on the FeH₂O_{ads}. Displacements of the adsorbed water molecule by the species X, can affect the step 4. Every condition, such as molecular shape or localized partial charges or by another view, strict hindrance of X molecule to the metal surface, can variegate the above competition.

The polymer is endowed besides centres nitrogenous strongly coordinate, which facilitate the adsorption to the surface of the metal. The adsorption of P4VPIBBr on the metal surface can occur either directly via donor-acceptor interactions between the π -electrons and free pair electrons of the heterocyclic compound and the vacant d-orbitals of surface iron atoms [19-22]. The polymer may be adsorbed on the metal surface in the form of neutral molecules involving the replacement of water molecules from the metal surface and sharing of electrons between the nitrogen atoms and the metal surface [31-34].

It may result from the fact that adsorption amount and the coverage of the polymers on the electrode surface increases with increasing concentration. Thus, the electrode surface is efficiently separated from the medium. It is worthy noting that, the presence of the inhibitor does not alter the profile of the impedance spectra, suggesting similar mechanisms for the metal dissolution in H_2SO_4 solution in the absence and presence of the inhibitor. The impedance parameters derived from these investigations are given in Table 2 and I.

Inhibitors	R_t ($\Omega.cm^2$)	R_p ($\Omega.cm^2$)	f_o (Hz)	C_{dl} ($\mu F/cm^2$)	E%
Blank	17.5	-	100	91.20	-
$10^{-6}M$ P4VPIBBr (I)	72.02	8.64	25	74.98	75
$10^{-6}M$ P4VPIBBr (II)	89.13	12.12	25	66.11	80
$10^{-6}M$ P4VPIBBr (III)	100.5	12.34	25	64.47	82

Table 1: Characteristic parameters evaluated from the impedance diagrams in presence and absence of P4VPIBBr (I), (II) and (III) inhibitors at $10^{-6}M$.

Concentration of P4VPIBBr (I)	R_t ($\Omega.cm^2$)	R_p ($\Omega.cm^2$)	f_o (Hz)	C_{dl} ($\mu F/cm^2$)	E%
Blank	17.5	-	100	91.20	-
5.10-7	33.53	4.82	63.29	74.98	47
7.510-7	60.27	8.57	40	69.11	71
10-6	69.47	8.64	25	65.47	75
2.5 10-6	76.12	12.2	25	64.12	77
5.10-6	317.0	15.34	15.823	31.72	95

Table 2: Characteristic parameters evaluated from the impedance diagrams in presence and absence of P4VPIBBr (I) inhibitor at different concentration.

We note again, the inhibitory efficiency is independent of quaternisation degree of poly (4-vinylpyridine-isopentyl bromide). These results are in good agreement with the study of the action of a poly (4-vinylpyridine poly-3-oxide ethylene) in two degree of quaternisation 20% and 80% in corrosion of iron in molar sulphuric acid [32]. It is apparent also, from the impedance results shown in the Table (1-2), the value of R_t increase with increase in the concentration of P4VPIBBr (I) inhibitor and amelioration in the protection of the surface, this indicated an increase in the corrosion inhibition efficiency. The decrease in C_{dl} may be due to the adsorption of this compound on the metal surface leading to the formation of film from acidic solution [33-38].

An equivalent circuit of this polymer depicted in Fig 3 was used in simulation of the impedance data, as previously reported [25,39]. In this circuit, C_{dl} is the double layer capacitance R_t is the interfacial charge-transfer resistance, L is the inductance, and R_L is the inductive resistance. When an inductive loop is present, the polarization resistance R_p can be calculated from Eq. (2) [25,40-41]:

$$R_p = (R_L \times R_t) / (R_L + R_t)$$

It has been observed that derivations from the results expected for equivalent circuits such as shown in figure (4) for real, corroding system, while the results for iron in acid media counting poly (4-vinylpyridine isopentyl bromide) (P4VPIBr) in three degrees of quaternisation.

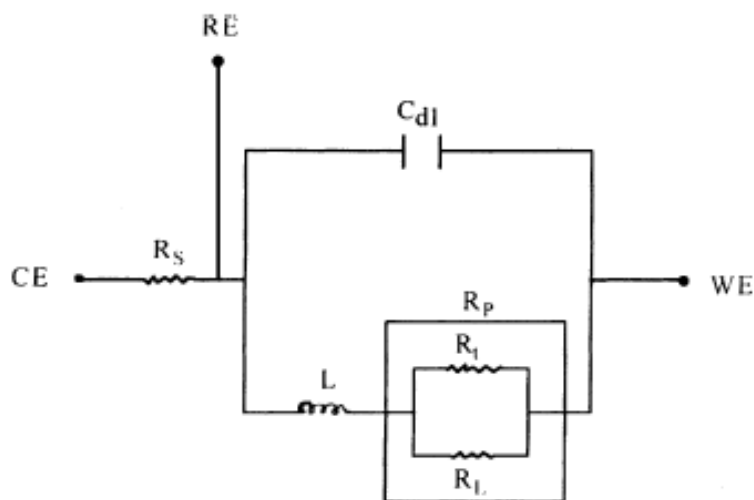
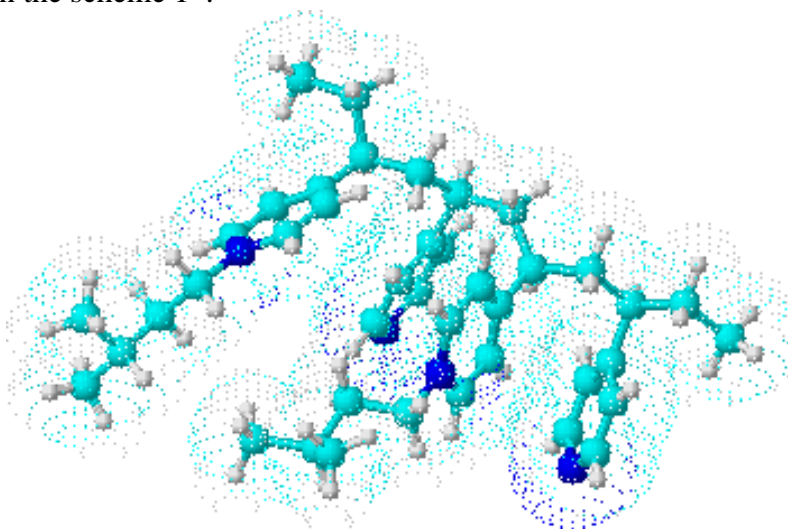


Fig. 4. The equivalent circuit model used to fit the experimental data.

The high inhibition efficiency of P4VPIBr is attributed to the presence of additional electron donor atoms and N-heterocyclic, active centre of adsorption, which facilitates the strong binding of this compound to the surface. The chart in the results in the table (1-2) is explicated of difference of time necessarily of the formation of layer adsorption of the polymers. This can be explained by the forming of a protective coating under shape painting on the surface of the electrode shows in the scheme 1 .



Scheme 1. Mode of adsorption of P4VPIBr suggested on the surface of iron.

CONCLUSION

The use of impedance measurements particularly for corrosion studies in extremely resistive medium in increasing. We verified:

- The type molecules have been low-cost and stable corrosion inhibitors.
- Their inhibition efficiency (E%) increases with the concentration for all inhibitors.

- The inhibitory efficiency is independent of quaternisation degree of Poly (4-vinylpyridine-isopentyl bromide)
- The decrease in C_{dl} may be due to the adsorption of these compounds on the metal surface leading to the formation of film from acidic solution.
- Nyquist diagrams of P4VPIBBr present a semicircle with the inductive loop at high frequency. The presence of the inductive loop attributed in the relaxation of intermediate reactions.

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