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Effect of povidone–iodine addition on the corrosion behavior of cp–Ti in normal saline

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Abstract The effect of various concentrations of povidone–iodine (PI) on the corrosion behavior of a commercially pure titanium alloy (Ti-1) has been investigated in normal saline solution to simulate the povidone–iodine addition in an oral environment. The open circuit potential, electrochemical impedance spectroscopy and potentiodynamic polarization measurements have been used to characterize the electrochemical phenomena occurring on the alloy surface. The open circuit potential values for Ti-1 in various concentrations of PI shift considerably towards noble direction as compared to pure normal saline. In the potentiodynamic polarization curve for Ti-1 in various solutions, the cathodic current density has increased for all concentrations of PI and the anodic current density has decreased. Only the 0.1% PI concentration is able to inhibit corrosion of Ti-1 in normal saline and the other higher concentrations studied, accelerate corrosion. The EIS data for Ti-1 in normal saline and in various concentrations of PI follows a one time constant circuit, suggesting the formation of a single passive film on Ti-1 which is not altered by the addition of PI to normal saline.

1 Introduction

Povidone–iodine (PI) is a commonly used anti-bacterial agent in dental applications such as periodontal treatments & oral and maxillofacial surgeries. Povidone–iodine is a water-soluble combination of molecular iodine and the solubilizing agent and polymer, polyvinyl-pyrrolidone (iodophor). It has a bactericidal effect similar to that of pure iodine [1]. Polyvinyl-pyrrolidone is the most widely used specialty polymer [2] and the ability of its complex to release iodine in a controlled fashion is the basis for some of its important and diverse applications, most of which are related to various fields of medicine.

The difference between a conventional iodine solution and an iodophor is that the latter carries almost all the iodine in a complexed form, so that the concentration of free iodine in the solution is very low and the negative aspects related to iodine such as irritation and staining power are minimized [3]. The bulk of the iodine exists in the triiodide form, which is in equilibrium with iodide and the active iodine.

In aqueous solution, the solvated povidone–iodine complex can be described as a swollen polymer, which carries a definite number of HI_3 units in complexed form. In addition, a cloud of various iodine species is attached to the polymer [3]. It is proposed that during solvation, the expanded polymer chain might get transformed to a coiled form and the complex might undergo dissociation to give PVP–H^+ poly-cations and I_3^- poly-anions [3].

Studies have shown that in the povidone–iodine system, for every two amide groups complexed with HI_3, there is an average of seventeen uncomplexed vinylpyrrolidinone units in a molecule [3]. The polymer structure, thus, contains one charged unit for every 19 pyrrolidone units along the polymer chain. It is therefore considered a highly reactive polymer, with strong complexing ability and also a true polyelectrolyte that carries charges along the polymer chain [4].

Many attempts have been made to determine the structure of povidone–iodine complex [5–8]. The most acceptable structure (Fig. 1) of the complex involves the linkage of the HI_3 proton with two pyrrolidonyl carbonyl groups with split bonds. The pyrrolidolyl pair represents the cation

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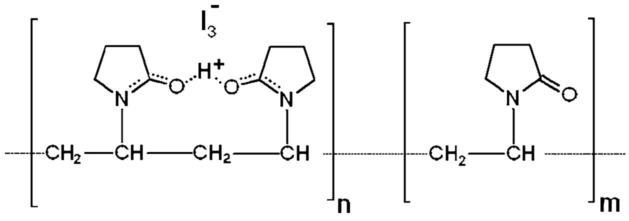


Fig. 1 Structure of povidone–iodine

of the system and the I_3 unit is the counter anion. The atoms of each ring system are coplanar and the plane lies parallel to the plane of iodine atoms which are also coplanar. The hydrogen atoms are located outside of that plane with two IO units oriented at an angle of 135°.

Many studies have reported the efficacy of povidone–iodine as an effective bactericide for dental and oral use [3–9]. The usual procedure is oral rinsing with dilute solutions of povidone–iodine or chlorhexidine gluconate in normal saline before the dental procedures. Povidone–iodine is also used directly as higher concentrations in surgical scrubs and bandages. A newly inserted implant and various surrounding tissues may get exposed to povidone–iodine from minutes [10, 11] (during oral prophylaxis, alveolar socket irrigation following extraction, surgical rinses before operative procedures) to days [11–14] (during odontogenic infections, dentoalveolar abscesses, facial space infections following implant placement and retrognathic and orthognathic reconstruction surgeries), depending upon the therapy performed and the local and systemic patient factors. The local factors include localized hypersensitivity, local health of the adjoining hard and soft tissues, localized body fluid (saliva, blood, bone cells) chemistry and localized inflammatory and toxic body responses. Systemic factors may include cardiovascular conditions, renal diseases, endocrinal disorders (diabetes mellitus), bleeding disorders, hypertension and severe auto-immune diseases such as hepatitis and AIDS. These factors allow for the variability in the application of PI in various treatment procedures.

The aim of this paper is to study the effect of various concentrations of povidone–iodine as a function of time on the corrosion behavior of a titanium alloy (commercially pure Ti-1) in normal saline solution using electrochemical techniques.

2 Materials and methods

2.1 Materials preparation

Commercially pure titanium grade 1 alloy (ATI Wah-Chang) (composition: 0.1%C, 0.2%Fe, 0.015%H, 0.03%N, 0.18%O and 99.47% Ti) was used for the present investigation. Available cuboidal rod was cut to expose cross-section area of 0.855 cm^2 for use as a working electrode. The alloy specimens were joined at one end with an insulated copper wire using a conducting silver epoxy and left overnight to dry. The coated samples were finally mounted in an epoxy resin, leaving the base exposed for corrosion studies. The exposed surface of specimens was finished and polished with different grades of SiC grit papers (2400 grit max, and polished over the diamond abrasive wheel) and washed with detergent, double distilled water and acetone.

Normal saline solution (sodium chloride inj, USP, HOSPIRA) (composition: 5.26 g l^{-1} sodium chloride, 2.22 g l^{-1} anhy. sodium acetate, 5.02 g l^{-1} sodium gluconate, 0.37 g l^{-1} potassium chloride and 0.3 g l^{-1} magnesium chloride hexahydrate) having pH 6.6 was used to carry out the electrochemical testing of the alloy. A 10% betadine solution (betadine solution HOSPIRA) was used to prepare various compositions such as 0.1, 0.2, 0.4 and 1% in normal saline solution, which were used for the electrochemical measurements.

2.2 Measurements

A three-electrode cell assembly consisting of Ti-1 alloy as the working electrode, platinum wire as the counter electrode and a saturated calomel electrode as the reference electrode was used for all the following corrosion measurements in normal saline solution (N.S.) and 0.1, 0.2, 0.4 and 1% povidone–iodine (PI) solutions at the ambient temperature (298 K).

Open circuit potential (OCP): OCP values were obtained at various immersion times for all the solutions.

Electrochemical impedance spectroscopy (EIS): Impedance measurements were performed using a PAR 1255 FRA, at the open circuit potential, for various immersion hours such as 0, 6, 24 and 48 h. The frequency sweep was applied from 10^5 to 10^{-1} Hz with the AC amplitude of 10 mV.

Potentiodynamic polarization: Potentiodynamic polarization measurements were performed using a PAR Potentiostat 273A, after 48 h of immersion by polarizing the working electrode from an initial potential of −250 mV versus the open circuit, up to a final potential of 2 V versus the reference. The ASTM standard scan rate of 1 mV/s was used for the polarization sweep [15].

3 Results and discussion

The evolution of the OCP with time for Ti-1 in various PI solutions and normal saline is shown in Fig. 2. The OCP stabilizes in approximately 6 h of immersion in each

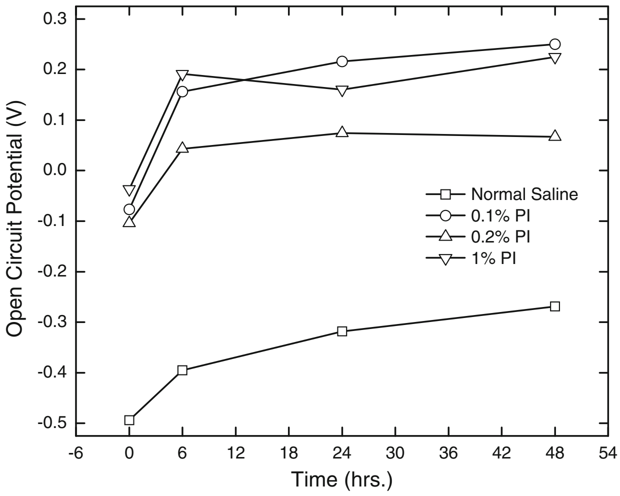


Fig. 2 Open circuit potential as a function of time for Ti-1 in normal saline and various concentrations of PI

solution. The increase in stabilized OCP values with time is observed in all cases. The OCP increase for titanium alloys in simulated body fluid solutions has been related to the thickening of the passive oxide film with time [16]. The OCP values for various concentrations of PI are more positive as compared to pure normal saline. The mechanism of action of PI in normal saline on titanium can be identified by EIS and potentiodynamic results below.

The EIS data for Ti-1 in normal saline in the absence and presence of various concentrations of PI were fitted using the equivalent circuit shown in Fig. 3, where R_s is the solution resistance, R_p is the polarization resistance and CPE is the constant phase element. The impedance of CPE is given by,

$$Z_{CPE} = Y_0^{-1}(j\omega)^{-\alpha}$$

where ω is the angular frequency in radians/s, Y_0 is the admittance magnitude of the CPE and α is the exponential term which can vary between 1 for pure capacitance and 0 for a pure resistor [17]. α is a measure of surface inhomogeneity, the lower is its value, the higher is the surface roughening of the metal/alloy [18]. The surface inhomogeneity can also be due to an inhomogeneous distribution of reaction rates or current and due to the differences in the thickness or properties of a coating on the alloy surface [19]. In case of titanium alloys, a distributed relaxation feature for titanium oxide films is often observed and CPE is used over pure capacitance to account for this behavior [20, 21]. This equivalent circuit has been generally used to fit EIS data in case of a single passive film present on the surface of the metal [22].

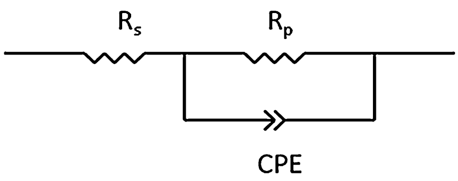


Fig. 3 Circuit model used to fit EIS data

Figure 4 shows the impedance plots at various immersion times for normal saline in the absence and presence of different concentrations of PI and the corresponding impedance parameters have been listed in Table 1.

It can be seen in Fig. 5 and also from the size of the Nyquist plots in Fig. 4 that the polarization resistance values increase with time for pure normal saline and normal saline with added concentrations of PI. Correspondingly, the capacitance values decrease with time. This observation suggests that the oxide film formed on Ti-1 in the solutions examined becomes thicker with time. The phase angle Bode curves for pure normal saline and 0.1% PI show a near capacitive response with phase angles approaching −80° for most of the intermediate and low frequency region, except for 0.1% PI at 0 h of immersion, where the phase angle shows a decrease at the low frequency end of the spectrum. Phase angle curves for 0.2% PI and 1% PI, on the other hand show phase angles dropping at the low frequency end of the spectrum, more so on immersion; and are increasing with time. This suggests that these solutions show a decrease in polarization resistance values as compared to the above two solutions but the polarization resistance still increases with time.

Figure 6 shows the impedance plots for Ti-1 in normal saline and various concentrations of PI at 0 and 48 h of immersion. The polarization resistance values for Ti-1 in various concentrations of PI just on immersion are almost similar (also in Fig. 5) and less than the polarization resistance of Ti-1 in pure normal saline, whereas after 48 h of immersion, the order is 0.1% > N.S. > 1% > 0.2%. All other time intervals obey the similar order as 48 h. This implies that on immersion, the corrosion rate (combined effect of cathodic and anodic reactions) of Ti-1 in the presence of PI solutions is higher as compared to pure normal saline. On the other hand, at all other immersion times, the corrosion rate of Ti-1 in the presence of 0.1% PI is less than in pure normal saline.

Figure 7 shows the potentiodynamic polarization curves for Ti-1 in normal saline and various concentrations of PI.

It can be seen from Fig. 7 that the solutions containing PI show much noble corrosion potential value for Ti-1 as compared to pure normal saline. The cathodic current density has increased for all concentrations of PI and the anodic current density has decreased. These shifts have made the corrosion potential to rise in the anodic direction. In case of 0.1% PI the anodic current has decreased to a maximum and the cathodic current has increased to a minimum, which makes 0.1% PI to show an inhibition effect towards the corrosion of Ti-1. The combined current

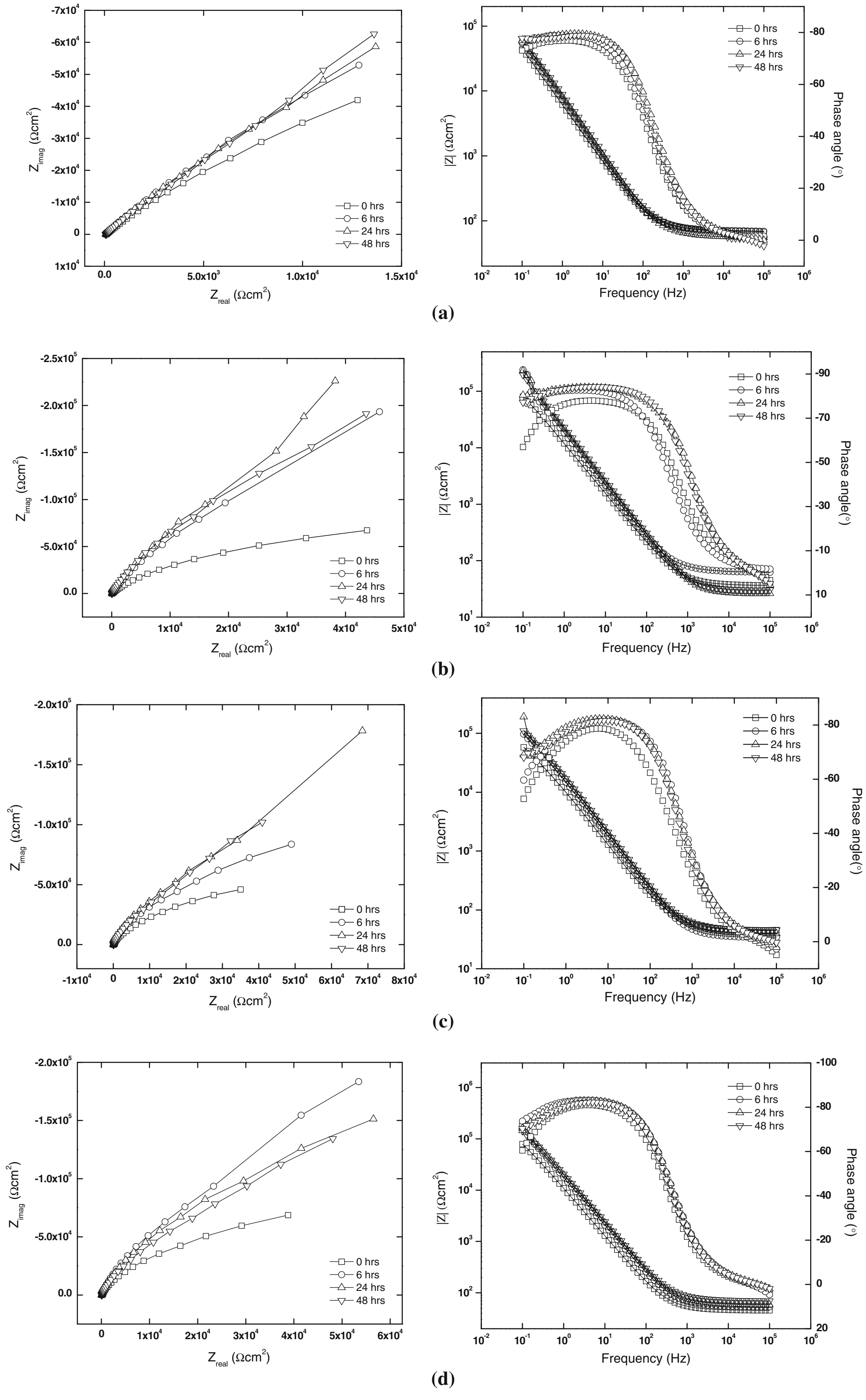


Fig. 4 Impedance plots (Nyquist & Bode) for normal saline and various concentrations of PI at various immersion times. **a** Normal saline, **b** 0.1% PI in normal saline, **c** 0.2% PI in normal saline, **d** 1% PI in normal saline

Table 1 Impedance parameters for normal saline and various concentrations of PI using the equivalent circuit shown in Fig. 3

Ti-1 (h)	R_s (Ωcm^2)	R_p ($\times 10^5$) (Ωcm^2)	CPE ($\times 10^{-5}$) [$S(srad^{-1})^n/cm^2$]	α	Chi-square	Weighted sum of squares
Normal saline						
0	71.25	5.58	3.36	0.86	3.4×10^{-3}	0.43
6	71.91	12.93	2.74	0.88	3.1×10^{-3}	0.39
24	57.44	14.59	2.44	0.88	2.9×10^{-3}	0.36
48	64.20	34.24	2.34	0.87	28.9×10^{-3}	3.53
0.1% PI						
0	37.38	2.08	1.66	0.88	1.2×10^{-3}	0.14
6	65.15	15.14	1.02	0.92	4.3×10^{-3}	0.49
24	26.44	24.95	0.79	0.93	15.2×10^{-3}	1.79
48	30.39	44.94	0.81	0.93	6.2×10^{-3}	0.84
0.2% PI						
0	46.13	1.32	2.05	0.87	$4.8 \times x10^{-3}$	0.62
6	34.86	2.18	1.26	0.91	2.7×10^{-3}	0.32
24	40.86	3.31	1.13	0.91	4.4×10^{-3}	0.51
48	46.98	3.57	1.14	0.90	5.4×10^{-3}	0.64
1% PI						
0	46.84	2.11	1.71	0.91	2.7×10^{-3}	0.33
6	55.26	7.43	1.02	0.92	4.3×10^{-3}	0.50
24	60.67	9.13	0.95	0.92	4.7×10^{-3}	0.62
48	70.87	15.35	1.01	0.90	12.4×10^{-3}	1.72

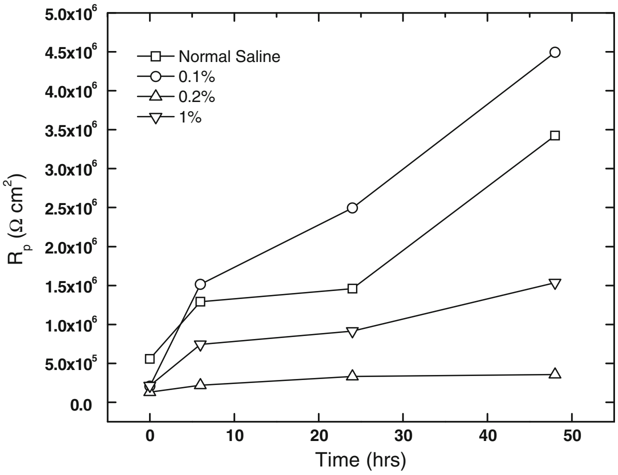
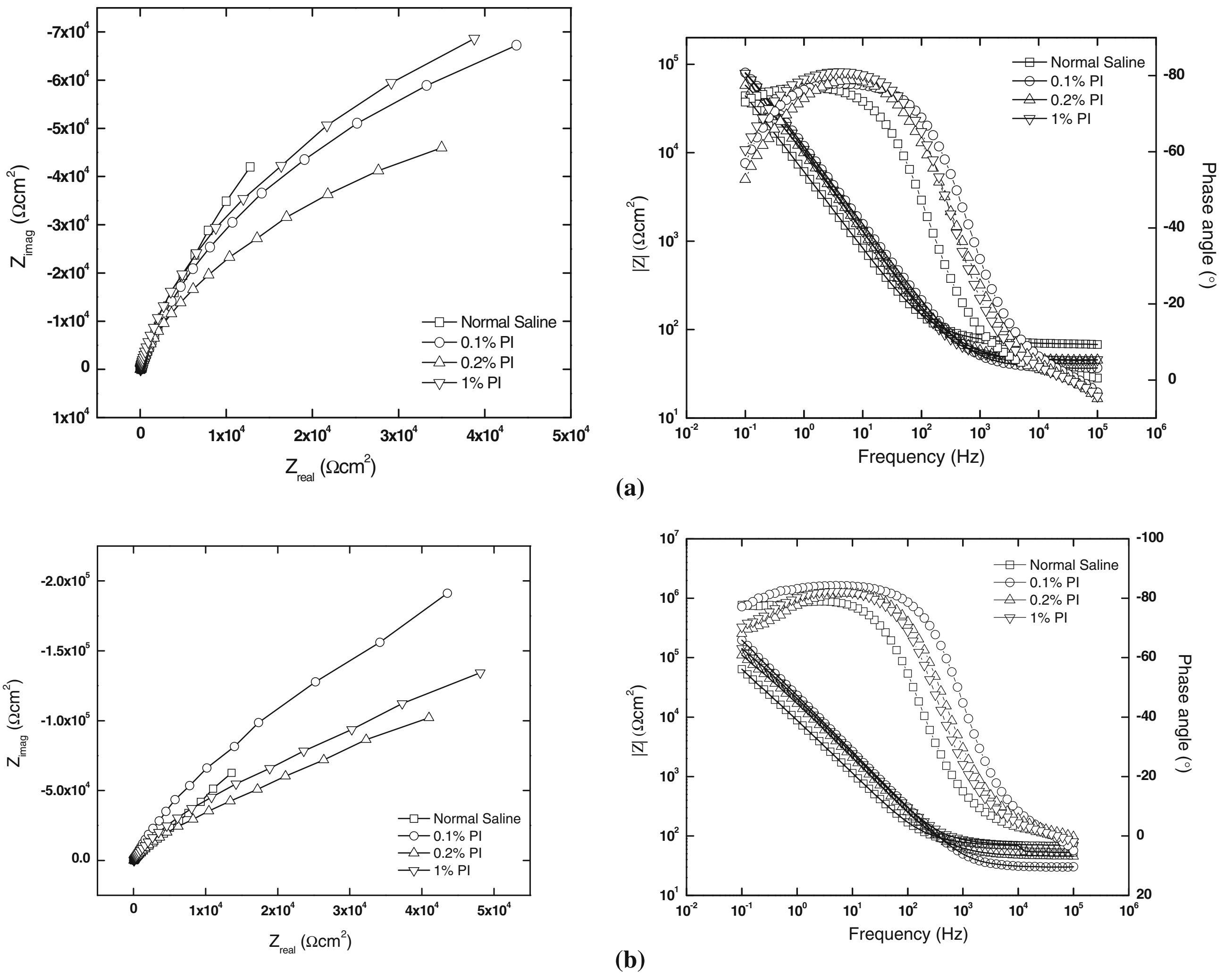


Fig. 5 Variation of R_p as a function of time for Ti-1 in normal saline and various concentrations of PI

density from the cathodic and anodic reactions for 0.2 and 1% PI solutions is, on the other hand, more than that of pure normal saline. Hence these concentrations are unable to show an inhibition effect, however the lowest concentration out of the range of concentrations studied, is able to show an inhibition effect. In addition, from Table 1, it can be seen that the values of the parameter α show an increase for various PI concentrations as compared to pure normal saline. This means that on adding PI to normal saline, the adsorption of povidone iodine molecules on the oxide film allows the formation of a more homogeneous surface. The values of alpha are highest in case of 0.1% PI, which also suggests a more homogeneous distribution of PI molecules over the surface of the alloy as compared to the other concentrations. This observation further supplements the fact that 0.1% PI shows an inhibition effect and better adsorption over the other two lower concentrations.

For a good surface coverage, adsorption should be favored more to desorption. The complex adsorption–desorption equilibria that operates in case of polymers involves the role of steric effects in the adsorption process of such compounds, which could possibly lead to a least steric effect and an inhibition action of 0.1% PI towards the alloy [23, 24].

The above findings imply that the PI complex accelerates the cathodic reduction reaction, either by making another redox reaction amongst the various iodine species in aqueous solution possible or by consuming the cathodic reduction reaction products for its redox reactions and hence shifting the cathodic reaction more in the forward direction. In contrast, there is a fall in the anodic reaction rate in the presence of PI, suggesting that PI molecules are able to adsorb on the anodic sites at positive potentials, either through the lone pair of electrons on N and O or by a synergistic effect of I^- ions and protonated PI molecules. Iodide ion is known for its inhibitive effect on metal



(a)

(b)

Fig. 6 Impedance plots (Nyquist & Bode) for Ti-1 in normal saline and various concentrations of PI at 0 and 48 h of immersion. **a** 0 h of immersion, **b** 48 h of immersion

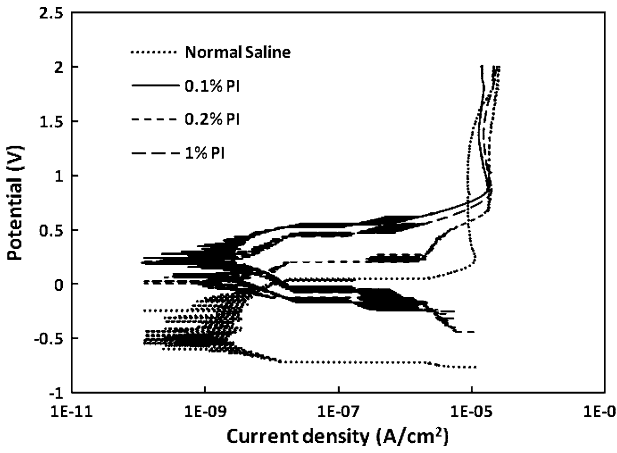


Fig. 7 Potentiodynamic polarization curves for Ti-1 in normal saline and various concentrations of PI

surfaces by specific adsorption and further promoting the adsorption of organic cations by forming intermediate bridges between the positively charged metal surface and the positive end of the inhibitor [25]. Umoren et al. [25] have shown the efficacy of polyvinyl pyrrolidone (PVP) as a corrosion inhibitor for mild steel in dilute sulphuric acid and also studied the synergistic effect with iodide ions. There have also been reports on the effect of PVP as a corrosion inhibitor for aluminium in HCl solution [26]. The authors have suggested that PVP could be adsorbed by the interaction between the lone pair of the electrons of the oxygen and nitrogen atoms respectively on the polyvinyl pyrrolidone moiety and metal surface (chemical adsorption). It could also be protonated at the N atom in the acidic solution to interact with the metal surface through electrostatic attraction (physical adsorption).

In aqueous solution, as has already been mentioned, the solvated povidone–iodine complex can be described as a swollen polymer and during solvation, the expanded polymer chain might get transformed to a coiled form and the complex might undergo dissociation to give PVP–H^+ poly-cations and I_3^- poly-anions [3]. Besides the role of steric effects taking part in adsorption, it is further proposed that the lower concentration of 0.1% might dissociate more to give such poly-ions due to increased solvation in case of a low concentration (also due to the fact that the degree of dissociation of a compound increases on dilution) which in turn might allow for the adsorption of free I_3^- ions on the anodic sites of the alloy followed by this another layer of polycations, as opposed to the weaker adsorption in case of the higher concentrations studied. More work needs to be performed to understand the detailed adsorption kinetics of PI on the titanium alloy surface.

4 Conclusions

The EIS data for Ti-1 in both normal saline and in various concentrations of PI follows a one time constant circuit, suggesting the formation of a single passive film on Ti-1. The polarization resistance values for Ti-1 in various concentrations of PI follow the order, $0.1\% > \text{N.S.} > 1\% > 0.2\%$, at all times of immersion other than 0 h. At 0 h of immersion, the values for all PI concentrations are almost equal and slightly less than that for pure normal saline.

Povidone–iodine increases the cathodic current density for Ti-1 and decreases the anodic current density due to which the corrosion potential rises in the anodic direction. PI molecules are able to adsorb on the anodic sites at positive potentials, either through the lone pair of electrons on N and O or by a synergistic effect of I^- ions and the protonated PI molecules. In case of 0.1% PI the anodic current has decreased to a maximum and the cathodic current has increased to a minimum, which makes 0.1% PI to show an inhibition effect towards the corrosion of Ti-1 in normal saline. The combined current density from the cathodic and anodic reactions for 0.2 and 1% PI solutions is more than that of pure normal saline. These concentrations are therefore unable to show an inhibition effect.

Bactericidal action of povidone iodine is well acknowledged in the clinical community. Besides, it has been found in our results that low concentrations of PI show an inhibition effect towards the corrosion of an implant or prostheses, though higher concentrations were found to enhance their corrosion. This corrosion increase could be detrimental to the surrounding tissues and bring about an adverse body reaction. This investigation needs to be extended further to understand the role of PI addition towards the corrosion behavior of other clinically used alloy systems.

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