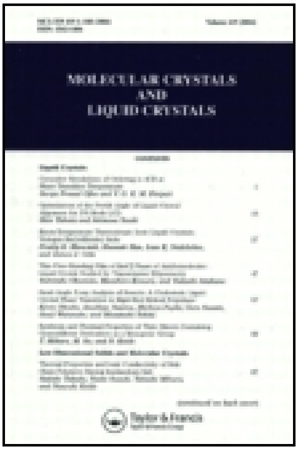

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# Electrosynthesized Doped Polypyrrole Films on Pure Zinc Electrode

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*Polypyrrole films have been successfully synthesized on zinc surface in absence and presence of sodium bis(2-ethylhexyl) sulfosuccinate and sodium dodecylbenzosulphonate as dopants. The synthesis was achieved by galvanostatic method. The electrochemical behaviour of doped-polypyrrole films was investigated by electrochemical impedance spectroscopy and polarization studies. The films were characterized by scanning electron microscopy. Considering the surfactant anions entrapment inside the polymer matrix, the obtained results showed that the dopant concentration plays an important role in the response of the obtained coatings which proved to inhibit the corrosion of zinc substrate at anodic polarization in 0.1 M NaCl.*

**Keywords:** corrosion; doped; polypyrrole; zinc

## INTRODUCTION

The electrodeposition of conducting polymers such as polypyrrole (PPy) is now recognized as a method for obtaining organic coatings with strong corrosion protection properties. PPy can be prepared on zinc by electropolymerization from aqueous solutions in special conditions which strongly passivate the zinc without impeding the synthesis process [1,2]. As it was found by Bazzaoui et al., the tartrate counteranions inhibit the zinc electrode dissolution by leading to the formation

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of a passivation layer on its surface [2]. Conducting polymers like polyaniline, polypyrrole etc. can improve the corrosion protection of unnoble metals but it is impossible that the porous films protect the metal surface completely [3]. It is expected that protective properties of PPy can be improved by dopant anion [4]. During pyrrole (Py) electropolymerization, positive charge is incorporated into PPy matrix and compensated by anions doped from the electrolyte. The kind of counter ions doped in the polymer matrix significantly affects the properties of the PPy film. There have been many reports concerning electrochemical synthesis of PPy films using various types of dopants, including organic [5] and inorganic ions [6]. Among organic anions, aliphatic and aromatic sulfonates provide good electrical and mechanical properties and good stability to PPy layer [7]. The size of counter ions plays an important role in the exchange of doped anions [8].

In this study we obtained new PPy coatings doped with two surfactants namely sodium dodecylbenzosulphonate (SDBS) and sodium 1,4-bis(2-etylhexyl) sulphosuccinate (AOT) are doped. The corrosion protection properties of the coatings were examined in 0.1 M NaCl solution.

## EXPERIMENTAL

A conventional three-electrode cell connected to a GillAc potentiostat/galvanostat was used for electrodeposition of PPy on zinc substrate. The counter electrode was a platinum wire. All the potentials were measured versus a saturated calomel electrode used as reference electrode. The working electrode was a pure zinc cylinder (geometrical surface of 0.3 $cm^2$). The Zn electrode was mechanically polished with abrasive paper down to 1200 grade and degreased in acetone before use. The undoped PPy and doped-PPy films were synthesized galvanostatically at 27°C. Electrochemical impedance spectroscopy and polarization curves were used to investigate the corrosion performances of the obtained coatings. The Nyquist plots were recorded at anodic potential of $-600$ mV in a frequency range of 10 mHz–100 kHz, the amplitude was 30 mV. The polarization curves were recorded with a scan rate of 1 mV $s^{-1}$ upon 30 minutes of immersion in 0.1 M NaCl. The scanning electron microscopy (SEM) micrographs were obtained on a JEOL JSM-5400 instrument and the metallographic images on a Hund microscope.

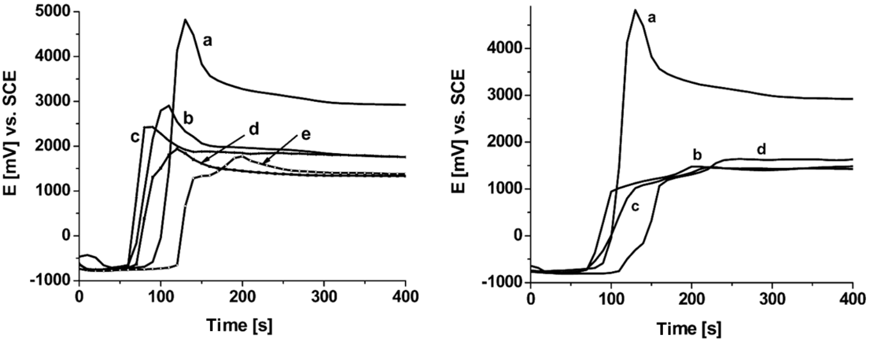
## RESULTS AND DISCUSSION

There have been many reports concerning electrosynthesis of PPy films on zinc surface [1,2]. The tartrate counter ions proved to inhibit the zinc dissolution by leading to the formation of a passivation layer on its surface. Any preliminary passivation pre-treatment was unnecessary. In what follows, we will present the results relative to the effect of different dopants concentration on the electrochemical properties of the obtained films will also be exposed.

Doped polypyrrole films were electrosynthesized on zinc in an aqueous solution of $Na_2C_4H_4O_6$ (0.2 M) in the presence of 0.5 M Py and different concentrations of surfactant. All the electropolymerization processes were carried out galvanostatically by applying to the working electrode a current density of $15\,mA\,cm^{-2}$ for 10 minutes. Previously, undoped PPy was synthesized on zinc electrode as reference for comparison.

Two types of PPy films were prepared on zinc: PPy film doped with SDBS and AOT, respectively. The concentration range for each dopant includes the critical micelle concentration (CMC) and values below and above it. As it is well known the CMC represents the range of the concentration in which the surfactants, in solution, change their initial molecular solvated state (nonaggregate) in the aggregate dispersive state.

The potential change versus electropolymerization time during the constant current synthesis of the SDBS-doped PPy film on zinc is presented in Figure 1(A). It can be seen that the addition of SDBS cause significant decrease of polymerization potential ($E_p$). This dependence may be attributed to the simultaneous doping process of electrons and anions dependent on the concentration of the anions in



(A) (B)

**FIGURE 1** Potential-time curves for galvanostatic electropolymerization of Py doped with (A): different concentrations of SDBS (a) 0 mM; (b) 1 mM; (c) 1.4 mM; (d) 1.8 mM; (e) 2.2 mM and (B): different concentrations of AOT (a) 0 mM; (b) 1.6 mM; (c) 2.2 mM; (d) 2.8 mM.

aqueous solution. The electropolymerization process can be explained by a nucleation phenomenon which leads to polymer seeds on the zinc surface. As it can be observed from data in Figure 1(A) and Table 1 the nucleation time increases and the potential plateaux stabilize at slightly lower values as SDBS concentration increases from 1 mM to 2.2 mM, respectively. However the potential stabilizes at values corresponding to the monomer oxidation and the electropolymerization reaction starts.

Also, it can be seen that the addition of SDBS in lower concentration leads to decrease of the induction time with respect to the undoped PPY film formation, but as the dopant concentration increases, the increase of the induction time and the decrease of the nucleation potential ($E_n$) are observed. It is believed that SDBS concentration above the CMC leads to micelles formation that hinder the film formation–less monomer in the solution converts to oligomers and the chain length of the oligomers in the solution decreases as well.

In conclusion, these results indicate that SDBS-doped PPy can be synthesized on zinc surface by using the galvanostatic mode. The shortest induction time is observed at the lowest value of SDBS concentration (1 mM) studied which is close to its CMC.

The corrosion performances of the obtained SDBS-doped PPy films were investigated in 0.1 M NaCl. Electrochemical impedance spectroscopy experiments were carried out under anodic polarization. Figure 2(A) illustrates a typical Nyquist plot obtained after 15 minutes immersion time of the SDBS-doped PPy coated zinc electrode in 0.1 M NaCl.

It can be seen that the impedance obtained at high frequencies for the undoped PPY coated zinc electrode can be represented by one depressed capacitive loop followed by a well defined large inductive

**TABLE 1** Electropolymerization of Doped PPy Films on Zinc Electrode as a Function of Dopant Concentration

| $C_{dopant}$ [mM] | | Induction time [s] | $E_n$ [V] | $E_p$ [V] |
|---|---|---|---|---|
| | 0 | 90 | 4.82 | 2.87 |
| SDBS | 1 | 60 | 2.91 | 1.76 |
| | 1.4 | 60 | 2.42 | 1.75 |
| | 1.8 | 70 | 1.94 | 1.39 |
| | 2.2 | 120 | 1.78 | 1.33 |
| AOT | 1.6 | 55 | 1.46 | 1.47 |
| | 2.2 | 60 | 1.48 | 1.39 |
| | 2.8 | 100 | 1.59 | 1.67 |

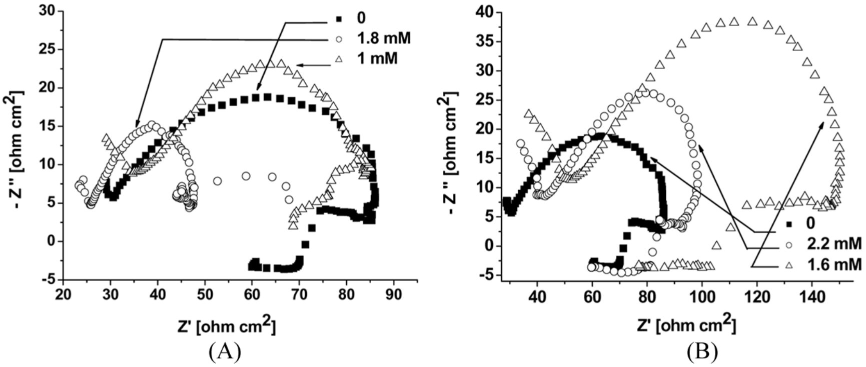


**FIGURE 2** Nyquist plot of EIS of the zinc electrode coated with (A): undoped PPy (■), 1 mM SDBS-doped PPy (Δ) and 1.8 mM SDBS-doped PPy (○) and (B): undoped PPy (■), 1.6 mM AOT-doped PPy (Δ) and 2.2 mM AOT-doped PPy (○).

loop at low frequencies. In this range of low frequency adsorption of some ionic species takes place and a relaxation phenomenon follows.

The use of large anions could improve the corrosion protection of the Ppy film by preventing the penetration of chloride [9]. The corrosion inhibition can be explained by the fact that the surfactant anions competitively adsorb on the electrode surface blocking the active sites and therefore the $Cl^-$ ions are impeded from reaching the zinc surface and corrosion inhibition is achieved.

The diagrams in Figure 2(A) show an increase in the polarization resistance with decreasing SDBS concentration. The value corresponding to zinc electrode covered with PPy doped with 1 mM SDBS is higher than the one corresponding to the undoped PPy coated zinc. These results indicate an inhibition of zinc corrosion when PPY is doped with SDBS at a concentration close to CMC.

As complementary experiments, potentiodynamic polarization curves have been plotted for SDBS-doped PPY coated zinc in 0.1 M NaCl as a function of SDBS concentration (see Fig. 3(A)).

Corrosion rate information can be obtained by the Tafel extrapolation method. Tafel extrapolations show a positive shift in the corrosion potential compared with bare zinc. The kinetic parameters of corrosion for pure zinc and zinc coated with undoped and doped PPy in 0.1 M NaCl are presented in Table 2. The results show that SDBS lead to decrease of the corrosion inhibition properties of the doped films as its concentration increases.

In case of electropolymerization of Py doped with AOT on zinc substrate, the transient potentials obtained as a function of the dopant

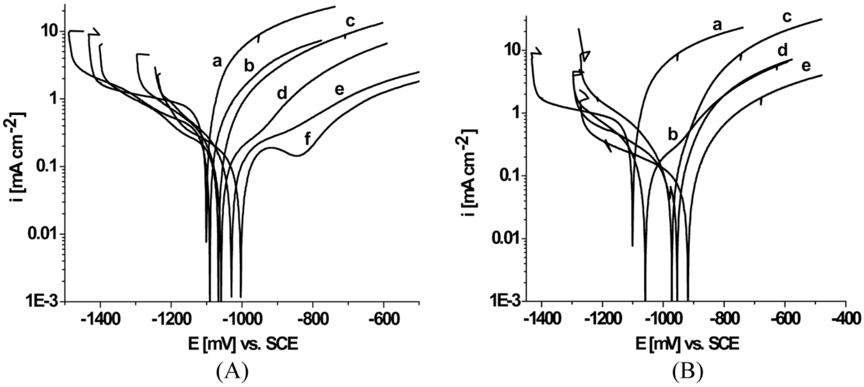


**FIGURE 3** Polarisation curves of (a) pure zinc, (b) undoped PPy coated zinc and zinc coated with (A) PPy doped with SDBS: (c) 2.2 mM, (d) 1.8 mM; (e) 1.4 mM; (f) 1 mM and (B) PPy doped with AOT: (c) 1.6 mM; (d) 2.2 mM; (e) 2.8 mM in 0.1 M NaCl.

concentration are presented in Figure 1(B). The application of current density to the specimen increased the potential in all cases after their respective induction periods. It appears that nucleation begins at potentials lower than the ones for undoped PPy and SDBS-doped PPY, respectively. The dopant concentration appears to have only slight influence on the nucleation potential. It can be noted that the addition of AOT also cause significant decrease of polymerization potential with respect to the one corresponding to undoped PPy. The induction time increases as AOT concentration increases from

**TABLE 2** Kinetic Parameters of Corrosion for Doped PPy Coated Zinc in 0.1 M NaCl

| Electrode | $i_c$ [mA cm$^{-2}$] | $-E_c$ [mV] | Rmpy [mils y$^{-1}$] | P [mm y$^{-1}$] | E [%] |
|---|---|---|---|---|---|
| Zn | 0.34 | 1101 | 202.45 | 5.13 | 0.00 |
| PPY/Zn | 0.061 | 1056 | 36.32 | 0.92 | 82.06 |
| PPY-SDBS 1 mM/Zn | 0.053 | 989 | 31.56 | 0.80 | 84.41 |
| PPY-SDBS 1.4 mM/Zn | 0.057 | 1033 | 33.94 | 0.86 | 83.24 |
| PPY-SDBS 1.8 mM/Zn | 0.091 | 1067 | 54.18 | 1.37 | 73.24 |
| PPY-SDBS 2.2 mM/Zn | 0.169 | 1083 | 100.63 | 2.55 | 50.29 |
| PPY-AOT 1.6 mM/Zn | 0.037 | 916 | 22.03 | 0.55 | 89.12 |
| PPY-AOT 2.2 mM/Zn | 0.04 | 956 | 23.81 | 0.6 | 88.24 |
| PPY-AOT 2.8 mM/Zn | 0.054 | 971 | 32.04 | 0.81 | 84.18 |

1.6 mM to 2.8 mM, as it can be observed from data in Table 1. Nevertheless, the induction periods for electropolymerization of Py doped with AOT are shorter than the one necessary for electropolymerization of undoped Py. It can be said that in case of AOT doping the potential stabilizes at values corresponding to the monomer oxidation and the electropolymerization reaction starts as well. Therefore, the obtained results indicate that AOT-doped PPy can be successfully synthesized on zinc surface by using the galvanostatic method.

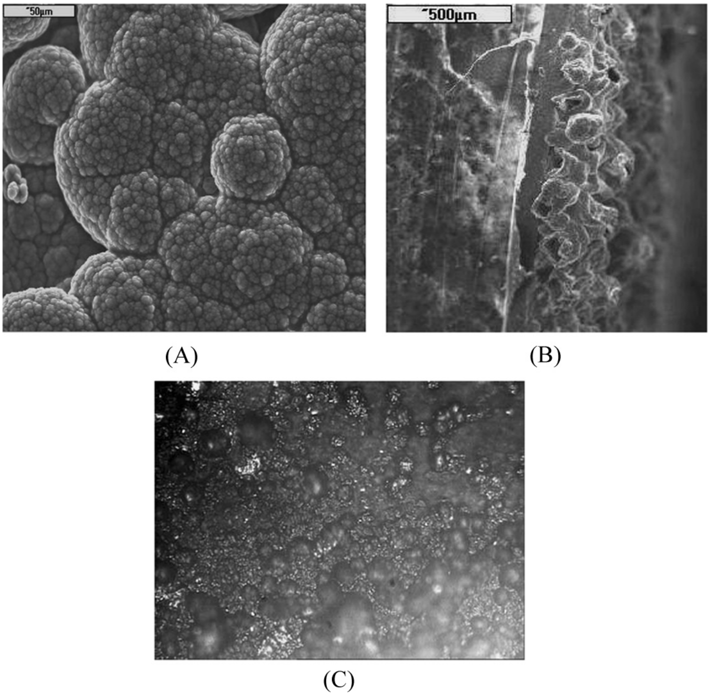
Further, the corrosion performances of the obtained AOT-doped PPy films were investigated in 0.1 M NaCl. Impedance experiments were carried out under anodic polarization. Figure 2(B) illustrates the Nyquist plots obtained after 15 minutes immersion time of the AOT-doped PPy coated zinc electrode in 0.1 M NaCl as a function of AOT concentration. It can be seen that the impedance obtained at high frequencies for the AOT-doped PPy coated zinc electrode can be represented by one capacitive loop more clearly evidenced than in the case of SDBS followed by one large inductive loop at low frequencies. The inductive loop probably corresponds to relaxation processes of the electrode coverage. Decreasing AOT concentration leads to bigger capacitive loop. The diagrams in Figure 2(B) show an increase in the polarization resistance with decreasing AOT concentration. Thus, the values of polarization resistance corresponding to zinc electrode covered with PPy doped with AOT are higher than the one corresponding to the undoped PPy coated zinc. These results indicate a better inhibition of zinc corrosion when PPY is doped with AOT for whole concentration range studied.

Potentiodynamic polarization curves for AOT-doped PPY coated zinc in 0.1 M NaCl as a function of dopant concentration have been plotted (see Fig. 3(B)). The polarization curves presented in Figure 3(B) show a more evident positive shift in the corrosion potential in comparison with SDBS-doped PPY. The kinetic parameters of corrosion obtained by Tafel extrapolation in case of pure zinc and zinc coated with undoped and AOT-doped PPy in 0.1 M NaCl are presented in Table 2. The results show that AOT lead to decrease of the corrosion inhibition properties of the doped films as its concentration increases. The corrosion inhibition efficiency is highest for the PPy film doped with the lowest concentration of AOT namely 1.6 mM which is close to its CMC. Nevertheless, the addition of AOT leads to improved corrosion inhibition properties of the PPy film for all concentration values studied. It can be concluded that the EIS measurements confirm the potentiodynamic results for both dopants.

Using SEM and metallographic microscope, morphology of the polymer coatings produced on zinc substrate was investigated.

Examples are shown in Figure 4. The PPy film prepared galvanostatically on zinc substrate by applying 15 mA cm$^{-2}$ current densities for 10 minutes has been imaged by SEM (Fig. 4a). It can be observed that its surface is characterized by a cauliflower-like structure consisting of microspherical grains with different sizes. It has been reported that the cauliflower structure seems to be due to the difficulty of dopant intercalation in the disordered polymeric chain [10]. The obtained PPy film is uniform, thick and strongly adherent to the zinc surface.

Homogenous and adherent doped PPy films are obtained at dopant concentrations close to the corresponding CMC while at dopant concentrations higher than the CMC value the film surface presents some inhomogeneities which are believed to be the cause of the poor inhibition properties of the films. In case of AOT the films present better homogeneity and inhibition properties than in the case of SDBS. The SEM micrograph of the PPy film doped with 1.6 mM



(A) (B)

(C)

**FIGURE 4** Images of films synthesized galvanostatically: SEM micrographs of (a) undoped PPy (b) PPy doped with 1.6 mM AOT and (c) metallographic image of zinc electrode coated with 2.2 mM AOT-doped PPy after polarization study in 0.1 M NaCl; magnification 200× .

AOT synthesized by the same method is presented in Figure 4b and it shows an adherent coating with a structure constituted of clusters of globules. The metallographic image in Figure 4c shows the morphology of the PPy doped with AOT in 2.2 mM concentration synthesized on zinc substrate after polarization study in 0.1 M NaCl. It can be observed that the globular structure is maintained after polarization suggesting a good corrosion inhibition exhibited by this coating.

## CONCLUSIONS

In this study we have shown that doped PPy films can be successfully achieved on zinc substrate in tartrate aqueous solution by galvanostatic method. The addition of dopant cause significant decrease of polymerization potential in both cases: SDBS and AOT. However the potential stabilizes at values corresponding to the monomer oxidation and the electropolymerization reaction starts.

The electrochemical measurements and potentiodynamic curves show that polypyrrole doped with SDBS and AOT can act as protective layers on zinc surface improving the overall corrosion performance. The corrosion protection properties of the doped PPy films are best when concentration of dopant used is close to the corresponding CMC. The activation of the zinc surface with anodic potential is lessened by SDBS and AOT when added in concentration close to their CMC. Their inhibiting effect on zinc dissolution is associated with deceleration of different steps implied in the reaction pattern.

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