Electropolymerization of N-Salicyly tetrahydro phthalamic acid for anticorrosion and antibacterial action applications

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Abstract: Poly (N-salicyly tetrahydrophthalamic acid) (PSP) synthesized from corresponding monomer N-salicyly tetrahydrophthalamic acid (NSP) in aqueous solution by using electrochemical polymerization process at room temperature. The polymeric film formed on stainless steel (316) surface (working electrode) and its structure examined by Fourier Transmission Infrared Region (FTIR). The anticorrosion action of the polymeric film on stainless steel (S.S316) was studied by using electrochemical polarization method in 0.2M HCl solution and temperature range (293-323)K. Kinetic and thermodynamic of activation parameters for corrosion process of S.S were calculated. The biological activity of polymeric film determined toward gram positive bacteria which is Staphylococcus aureus (Staph.Aure) and negative bacteria which is Escherichia coli (E.Coli). The effect of nanomaterials was studied by adding to the monomer solution in different concentrations to increase the efficiency of polymeric film as anticorrosion and antibacterial. The nanomaterials used in this study which are Graphene (G) and Zinc Oxide (nano) (ZnOn).

Key words: Electropolymerization, anticorrosion, antibacterial, Graphene

1. Introduction

The term “conductive polymer” first used in 1977 after synthesis polyacetylene and discovery its conductivity of metallic structure [1]. Conductive polymers have a wide field in many applications, they commonly used in a chemical transistor, rechargeable batteries, production of indicators and ion selective electrodes, and biochemical analysis [2]. The common method to prepare a thin film of conductive polymer on S.S (working electrode) by using electrochemical polymerization which included polymerizing the monomer in suitable electrolyte [3-5]. The film of conductive polymer used as anticorrosion and antibacterial. Corrosion defined as destruction of metal by reaction or chemical attack with its environment causes serious of problems [6], hence, corrosion is an economic problem. Therefore, the corrosion behavior of metals is an important consideration in the economic evolution of any research. The using of coating have antimicrobial activity is an effective method for decreasing microbial numbers on healthcare surface. Antimicrobial agents are materials have the ability for killing pathogenic microorganism [7]. The good antimicrobial polymers should have the following properties: a- biocidal to a broad spectrum of pathogenic microorganism, b- it can be regenerated upon loss of activity, c- it cannot soluble in water for variable applications, d- it cannot be decomposed to toxic materials [8]. In this paper, electrochemical polarization technique employed for studying the protection efficiency of the polymeric film against corrosion of S.S in 0.2 M of HCl solution in the temperature range (293-323) K. In addition,
the effect of addition nanomaterials (ZnO and G) to the polymer was studied for improving the efficiency of the polymeric coating against corrosion and bacteria.

2. Experimental

The electrochemical polymerization of NSP on S.S surface (working electrode) carried out by using DC power supply (galvanostatic technique). The solution involved for electropolymerization process 0.1 g of monomer (NSP) in 100 (ml) H₂O with three drops of concentration (95% H₂SO₄) [9]. For corrosion studies, S.S used as a working electrode (WE). It is grading by (2000 mesh) of carbide silicon and washed by distilled water and acetone, saturated calomel electrode (SCE) used as a reference electrode, platinum used as auxiliary electrode. All experiments studied in 0.2 M of HCl solution and at a temperature range (293-323) K. Also, nanomaterials (4% ZnO and 0.4% G) added into the solution of a monomer for improvement the coated-layer against bacteria and corrosion.

3. Results and discussion

3.1 Mechanism of polymerization

Cationic mechanism [10-11] and radical mechanism [12-15] explained electrochemical polymerization and growth of PSP film. The mechanism is depicted in Scheme (1-A).

A1- anodic potential applied to monomer solution (NSP) to transfer one electron from monomer to the working electrode (WE).

A2- the transfers of an electron in (A1) refer to formation radical cation adsorbed on the surface of the electrode.

A3- the radical cation desorbed and reacted in solution to increase the molecular weight of species.

A4- NSP added by a cationic mechanism at the charged end of desorbed oxidized NSP.

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\begin{align*}
A1 & \rightarrow A2 \\
A3 & \rightarrow A4
\end{align*}
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Scheme (1-A): Cationic mechanism for growth for PSP film.

The radical mechanism (Scheme1-B): The radical mechanism proceed by hemolytic scission of double bond hemolytic rupture double bond highly improbable considered initial polarization of bond which improved under field produced by electric double [16].
Scheme (1-B): Radical mechanism for growth PSP film.

3.2 Structure of PSP

FTIR spectrum of PSP coating film from NSP show in Figure 1-A. In this spectrum the characteristic bands of PSP is obtained in Fig. 1-B. aliphatic double bond at C=C at 3026.10 cm$^{-1}$ disappeared and confirm the formation of PSP.

Fig. 1-A FTIR of NSP.
The band appeared at 1697.24 cm\(^{-1}\) for C=O of carboxylic acid, the band appeared at 1670.24 cm\(^{-1}\) according to C=O of amide group, the band of OH of carboxylic acid appeared at 2530.43 cm\(^{-1}\) [17-19].

3.3 Potentiostate polarization measurement

The effect of polymeric layer on cathodic and anodic polarization curve of S.S in 0.2M of HCl solution and temperature range (293-303)K in absence and presence nanomaterials that shown in Fig. 2. The corrosion current density determined by extrapolation Tafel lines. The effect of polymeric layer in absence and presence nanomaterials which shown in Table1. The corrosion parameters involved corrosion potential (\(E_{corr}\)), corrosion current density (\(i_{corr}\)), cathodic Tafel slope (bc), anodic Tafel slope (ba), weight loss (WL) and penetration loss (PL) were found. Protection efficiency (PE %) was calculated by the following equation [20]:

\[
PE\% = \frac{(i_{corr}) \text{ uncoated} - (i_{corr}) \text{ coated}}{(i_{corr}) \text{ uncoated}} \quad \ldots (1)
\]

Where \((i_{corr}) \text{ uncoated}\) the corrosion current density for uncoated S.S, \((i_{corr}) \text{ coated}\) the corrosion current density for coated S.S. The corrosion potential (\(E_{corr}\)) shifted into more positive values (noble direction) and \(i_{corr}\) decreased after addition nanomaterials [21]. The polarization resistance (\(R_p\)) was determined by Stern-Gery equation [22]:

\[
R_p = \frac{babc}{2.303(ba + bc) i_{corr}} \quad \ldots (2)
\]

The polarization resistance (\(R_p\)) measurements have similar requirements to the measurements of full polarization curves and it is useful as a method to identify corrosion upsets and initiate remedial action [23]. The values of \(R_p\) are listed in Table1.
Fig. 2 polarization plots of S.S coated with PSP in absence and presence nanomaterials at 293K.

Table 1: Corrosion parameters of coated and uncoated S.S in 0.2M HCl.

|                  | T(K) | $-E_{corr}$ (mV) | $I_{corr}$ (μA/cm²) | $-bc$ (mV/sec) | $ba$ (mV/sec) | $WL$ (g/m².d) | $PL$ (mm/a) | PE% | $Rp$ (Ω/cm²) |
|------------------|------|------------------|----------------------|----------------|--------------|---------------|--------------|-----|--------------|
| Uncoated S.S     | 293  | 113.5            | 43.27                | 48.5           | 47.1         | 3.48          | 0.471        | -   | 239.786      |
|                  | 303  | 226              | 53.20                | 79.4           | 110.2        | 4.28          | 0.579        | -   | 376.668      |
|                  | 313  | 235.4            | 56.77                | 149.0          | 120.7        | 4.57          | 0.618        | -   | 510.035      |
|                  | 323  | 235.9            | 56.90                | 78.6           | 78.9         | 4.58          | 0.619        | -   | 300.286      |
| Coated S.S with PSP | 293  | 64.3             | 6.53                 | 100.6          | 61.3         | 0.525         | 0.0710       | 84.909 | 2532.821     |
|                  | 303  | 93.8             | 11.42                | 91.8           | 82.3         | 0.919         | 0.124        | 78.534 | 1649.999     |
|                  | 313  | 99.4             | 14.29                | 102.9          | 84.3         | 1.15          | 0.155        | 74.828 | 1408.027     |
|                  | 323  | 109.1            | 17.63                | 127.4          | 105.6        | 1.42          | 0.192        | 69.016 | 1422.103     |
| Coated S.S with PSP modified with ZnOn | 293  | 62.9             | 2.81                 | 219.4          | 226.0        | 0.226         | 0.0306       | 93.506 | 17202.619    |
|                  | 303  | 121.9            | 6.52                 | 110.4          | 105.3        | 0.525         | 0.070        | 87.744 | 3589.269     |
|                  | 313  | 144.6            | 8.68                 | 64.0           | 74.3         | 0.698         | 0.0944       | 84.710 | 1720.018     |
|                  | 323  | 146.0            | 16.29                | 74.3           | 82.7         | 1.310         | 0.177        | 71.371 | 1043.229     |
| Coated S.S with PSP modified with G | 293  | 66.9             | 2.10                 | 122.6          | 121.2        | 0.169         | 0.0228       | 95.147 | 12602.204    |
|                  | 303  | 97.4             | 2.81                 | 98.8           | 131.8        | 0.226         | 0.0305       | 94.718 | 8725.950     |
|                  | 313  | 104.0            | 6.75                 | 117.6          | 83.5         | 0.543         | 0.0734       | 88.109 | 3141.117     |
|                  | 323  | 217.3            | 9.81                 | 82.9           | 115.6        | 0.790         | 0.107        | 82.759 | 2136.923     |

3.4 Thermodynamic and kinetic activation parameters

Thermodynamic activation parameters involved activation energy Ea, enthalpy of activation $\Delta H^*$ and entropy of activation $\Delta S^*$ calculated by using Arrhenius equation and its alternative formulation called transition state, activation energy determined from the plot that represent the relationship between Log C.R and reciprocal of absolute temperature ($1/T$) [24] as shown in Fig.3.

$$\text{Log C.R} = \text{Log A} - \frac{Ea}{2.303 \times RT} \quad ........ (3)$$
Where C.R: corrosion rate, A: pre-exponential factor, Ea : Activation energy, R: Gas constant (8.315 JK⁻¹mol⁻¹), T: Absolute temperature (K).

While transition state expressed in the following equation [25]:

\[
\text{Log } \frac{C.R}{T} = (\text{Log } \frac{R}{Nh}) + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT} \quad \text{....... (4)}
\]

Where N: Avagadrous number (6.022 × 10²³mol), h: Blanks constant (6.62 × 10⁻³⁴ JS).

The entropy of activation ∆S* and enthalpy of activation ∆H* were determined from the plot that represent the relationship between log (C.R/T) and reciprocal of absolute temperature (1/T) as shown in Fig. 4. Where slope represent (- ∆H*/2.303RT) and the intercept represent (Log (R/Nh) + ∆S*/2.303R).

The free energy of activation determined from the following equation:

\[
\Delta G^* = \Delta H^* - T\Delta S^* \quad \text{....... (5)}
\]

**Fig. 3** Arrhenius plot of log C.R vs. 1/T in 0.2M HCl for coated and uncoated S.S.

**Fig. 4** Arrhenius plot of log C.R/T vs. 1/T in 0.2 M HCl for coated and uncoated S.S.
Table 2: Activation parameters for coated and uncoated S.S.

| coating                      | T(K) | ΔG* (kJ/mol) | ΔH* (kJ/mol) | -ΔS* (J/mol.K) | R²  | Ea (kJ/mol) | A (Molecule. Cm⁻². S⁻¹) | R²  |
|------------------------------|------|--------------|--------------|----------------|-----|-------------|--------------------------|-----|
| uncoated S.S                | 293  | 68.252       | 4.711        | 216.864        | 0.604| 7.373       | 5.605*10²⁶               | 0.784|
|                              | 303  | 70.421       |              |                |     |             |                          |     |
|                              | 313  | 72.589       |              |                |     |             |                          |     |
|                              | 323  | 74.758       |              |                |     |             |                          |     |
| coated S.S with SIP         | 293  | 72.651       | 23.937       | 166.261        | 0.922| 26.618      | 2.321*10²⁶               | 0.935|
|                              | 303  | 74.314       |              |                |     |             |                          |     |
|                              | 313  | 75.977       |              |                |     |             |                          |     |
|                              | 323  | 77.639       |              |                |     |             |                          |     |
| coated S.S with SIP modified with ZnOₙ | 293  | 74.764       | 43.527       | 106.612        | 0.964| 46.227      | 3.010*10²⁴               | 0.968|
|                              | 303  | 75.830       |              |                |     |             |                          |     |
|                              | 313  | 76.897       |              |                |     |             |                          |     |
|                              | 323  | 77.963       | 43.048       | 112.108        | 0.956| 45.767      | 1.567*10²⁴               | 0.967|
| coated S.S with SIP modified with G | 293  | 75.896       |              |                |     |             |                          |     |
|                              | 303  | 77.017       |              |                |     |             |                          |     |
|                              | 313  | 78.138       |              |                |     |             |                          |     |
|                              | 323  | 79.259       |              |                |     |             |                          |     |

Commonly the results shown the thermodynamic activation parameters (Ea and ΔH*) for S.S coated by polymer film are higher than S.S uncoated by polymer film, this indicated to increase the energy barrier. The values of the entropy of activation for S.S coated by polymer film and S.S uncoated by polymer film are negative, this refers to that the activated complex in the rate determining step was association rather than dissociation step, and refers to decrease the disordering which occurs on going from reactants to activated complex [26]. The free energy activation is had a positive values as shown in Table 2, and in addition showed almost small change with increasing temperature, this indicating that the activated complex not stable and the probability of its formation decreased with increasing of temperature [27].

3.5 Antibacterial study

The results were found a good inhibition for PSP against *E.coli* and *Stap.Aure* at concentration 800µg/(ml), these results listed in Table 3. Which indicated that the polymer in absence and presence nanomaterials have high activity against bacteria, ZnOₙ and G have special attention as an antibacterial agent against *E.coli* more than *Stap.Aure* [28].

Table 3: Antimicrobial activity of the polymer in absence and presence nanomaterials.

| compound                        | Stap.Aure (gram positive)(mm) | *E.coli* (gram negative)(mm) |
|---------------------------------|------------------------------|-----------------------------|
| PSP                            | 16                           | 17                          |
| PSP modified with G             | 25                           | 35                          |
| PSP modified with ZnOₙ           | 17                           | 22                          |
4. Conclusions

Electropolymerization of NSP on S.S surface was found to inhibit the corrosion rate in 0.2 M of HCl solution. The protection efficiency of PSP increased after addition nanomaterials. The protection efficiency of PSP in absence and presence nanomaterials decreased with increasing of temperature. The polymeric coating also provided antimicrobial activity against \( \text{Stap.Aure} \) and \( \text{E.coli} \) bacteria.

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