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Der Pharma Chemica, 2014, 6(6):285-293
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Effects of linseed oil additive on the electroplating of tin on mild steel

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ABSTRACT

In the present study an attempt was made, using cyclic and linear sweep voltammetry to explore the effects of Linseed oil extract additive on the electrodeposition of tin on mild steel in acid sulfutic solution. The experiments were performed under different plating time, different additive concentrations and fixed pH conditions. Tin electrodeposition on mild steel was performed using a DC - supply at defined operating parameters. The electrodeposition process was sensitive to the changes in the additive concentration and plating time. Polarization curves and electrochemical impedance spectroscopy demonstrated that corrosion current density decreased and charge transfer resistance increased in the presence of linseed oil in the electrolyte bath.

Keywords: Tin, electrodeposition, additive, kinetic, Linseed oil

INTRODUCTION

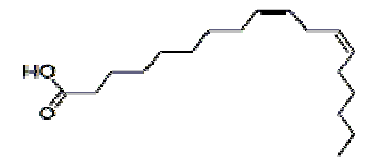
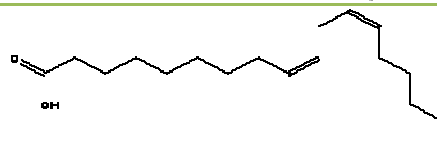

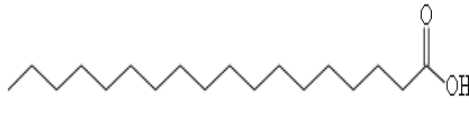

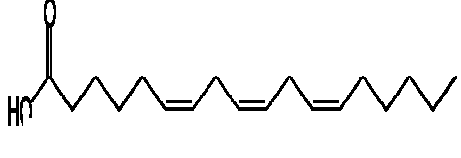
Tin and its alloys are involved in a large range of industrial applications including light engineering and electronics. An increasing interest or their deep investigation has been noticed in recent years due to the health and environmental concerns especially in electronic industry, but in the automotive or decorative plating ones as well, these coatings types being considered as ecological alternatives to replace lead based solders or nickel-chromium decorative coatings [1-3]. Tin and its alloys can be electrodeposited from various electrolytes, including aqueous fluoroborate, sulfate, and methanesulfonate solutions [4-6]. Porous or dendritic deposits are usually obtained. A lead compound is often added to inhibit the reduction of the stannous species and increase the polarization reaction [4]. To avoid pollution problems, organic additives, or surfactants are commonly used to improve the deposit morphology.

The interest in using natural organic compounds is because of its availability, cost and effect on the environment [7-10]. They pose no detrimental effect on the environment or hazard to human health. A number of natural organic compounds have been identified as good brightening agents in tin electroplating. Examples of these substances are linseed oil (LSO). These classes of organic compounds are biodegradable and non toxic.

Linseed (also known as flaxseed) is an important oil crop cultivated worldwide for oil and fiber. It has been cultivated in more than 50 countries. Canada is the major linseed producer, followed by China, United States and India [11]. Linseed contains about 36-40% of oil, generally used for the manufacture of paints, varnishes, inks, soap, etc. [12,13]. However, in recent time, linseed oil has become more popular as functional food in the health food market because of their reported health benefits and disease preventive properties on coronary heart disease, some kinds of cancer, neurological and hormonal disorders [14,15]. Most of the observed health benefits and disease preventive properties of linseed oil have been attributed to their omega-3 fatty acid, α -linolenic acid (ALA, 18:3) content. Linseed oil is the richest source of ALA, which makes about 55-60% of total fatty acids [16]. However, this high content of omega-3 fatty acid makes linseed oil highly sensitive to heat, oxygen and light [17]. Linseed oil is

generally getting exposed to heat, light and air during mechanical press oil extraction. Therefore, oil extraction is the crucial step which influences the quality of linseed oil.

Table 1. The systematic (IUPAC) name, 2D chemical structure of the main constituents of cosmetic linseed oil

The constituent	The systematic (IUPAC) name	The 2D chemical structure
Oleic acid (C18:1)	(Z)-Octadec-9-enoic acid	
Linoleic acid (C18:2)	(9Z, 12Z)-octadeca- 9,7-dienoic acid	
palmitic acid (C16:0)	hexadecanoic acid	
Stearic acid (C18:0)	octadecanoic acid	
alpha-Linolenic acid (omega-3fatty acid)	(9Z,12Z,15Z)-9,12,15-Octadecatrienoic acid	
gamma-Linolenic acid	all-cis-6,9,12-octadecatrienoic	

MATERIALS AND METHODS

Materials and Solutions

The standard bath compositions and deposition conditions for Sn deposits are given in Table 2. The solutions were prepared using distilled water and reagent grade chemicals. The bath temperature for electrodeposition was 298 K. The steel sheets having an exposed area of 1 cm² were used as cathodes. Materials used in this work was of analytical grade. The conventional three-electrode system was used. The potential was monitored against a KCl-saturated Ag/AgCl reference electrode (0.197 V vs.SHE). A platinum plate electrode was used as the counter electrode. Prior to each experiment, the surface of the working was abraded using emery paper up to 1500 grade and then being immersed in pure ethanol, and distilled water, respectively, to remove any surface impurity.

Table 2. The bath composition and deposition conditions

Operational condition	Quantity	Composition
Anode: Pt	-----	Platine electrode
pH: 1	0.56M	H ₂ SO ₄
Cathode: steel	0.14M	SnSO ₄
Temperature	-----	298 K 303 K
Linseedoil	1mL/10mL ethanol	bath : 50 mL

Corrosion study*Electrochemical impedance spectroscopy*

The electrochemical measurements were carried out using Volta lab (Radiometer PGZ 100) potentiostat and controlled by Tacussel corrosion analysis software model (Voltmaster 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a silver chloride electrode (Ag/AgCl). A platinum electrode was used as auxiliary electrode of surface area of 1 cm². The working electrode was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 60 minutes to establish steady state open circuit potential (E_{ocp}). After measuring the E_{ocp} , the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 303 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit

0.1 Hz at open circuit potential, with 10 points per decade, at the rest potential, after 60 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the x -axis.

The inhibition efficiency of the inhibitor was calculated from the polarization resistances values using the following equation:

$$\eta_{EIS} \% = \frac{R_p - R_p^I}{R_p^I} \times 100 \quad (1)$$

where R_p and R_p^I are the polarization resistances in the presence and absence of additive, respectively

Potentiodynamic polarization

The electrochemical behaviour of the substrate and the coatings in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 3% NaCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -1200 to 100 mV versus corrosion potential at a scan rate of 1 mV s⁻¹. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}). From the polarization curves obtained, the corrosion current (I_{corr}) was calculated by curve fitting using the equation:

$$I = I_{corr} \left[\exp\left(\frac{2.3\Delta E}{\beta_a}\right) - \exp\left(\frac{2.3\Delta E}{\beta_c}\right) \right] \quad (2)$$

β_a and β_c are the anodic and cathodic Tafel slopes and ΔE is $E - E_{corr}$.

The inhibition efficiency was evaluated from the measured I_{corr} values using the relationship:

$$\eta_{Tafel} \% = \frac{I_{corr}^{\circ} - I_{corr}^i}{I_{corr}^{\circ}} \times 100 \quad (3)$$

where, I_{corr}° and I_{corr}^i are the corrosion current density in absence and presence of inhibitor, respectively.

RESULTS AND DISCUSSION*Stationary Curves voltage-time*

Figure 1 summarizes the voltage-time curves obtained without (Fig.1a) and with (Fig.1b) additive at different current density. The results show that the additives shift the reduction potential to more cathodic potential at a given current density. This is due to the adsorption of the additive on the surface of the electrode [18-20]. The apparent increase in voltage (decrease in absolute cell voltage) over time is at first attributed to the furthered activation of the anode and the covering of the steel cathode with tin and later the result of a reduction of current density at the surface which gets rougher with time as the plated layer grows with time [21].

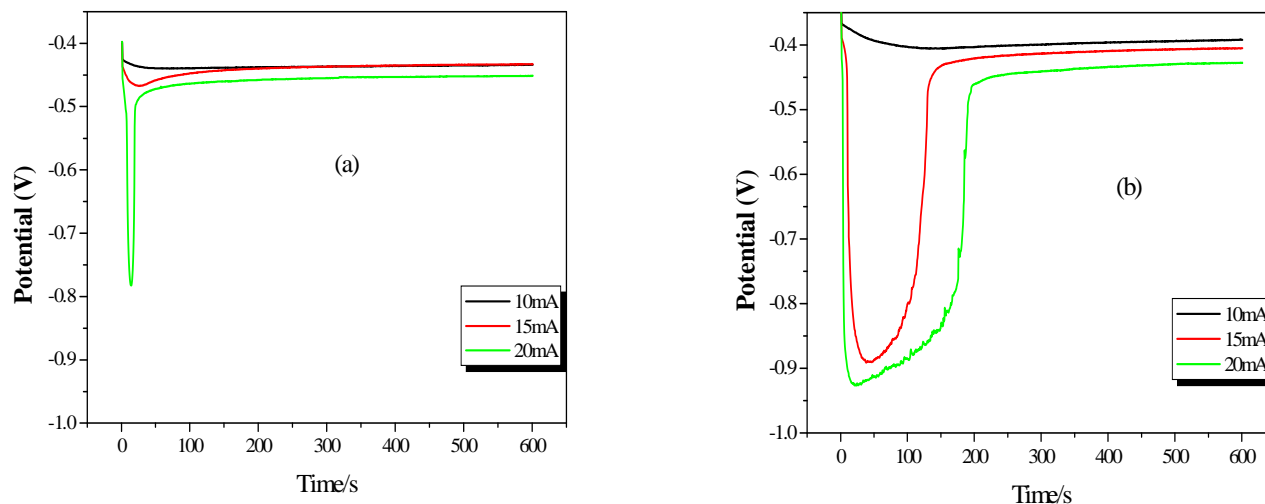


Figure 1. Chronopotentiometric curves without (a) and in the presence (b) of linseed oil additive

Cyclic voltammetry analysis

The cyclic voltammetry curve of the additive-free tin and in the presence of additive solution with a scan rate of 25 mV/s is shown in Fig. 2. It could be seen that LSO show lower than that observed in additive-free tin alone. The depolarization caused by them offsets the effect of LSO in modifying the nature of deposits. These additives show cross over in the reverse scan indicating the presence of three dimensional nucleation which is required for producing coherent, compact deposits unlike the tin additive-free tin [22].

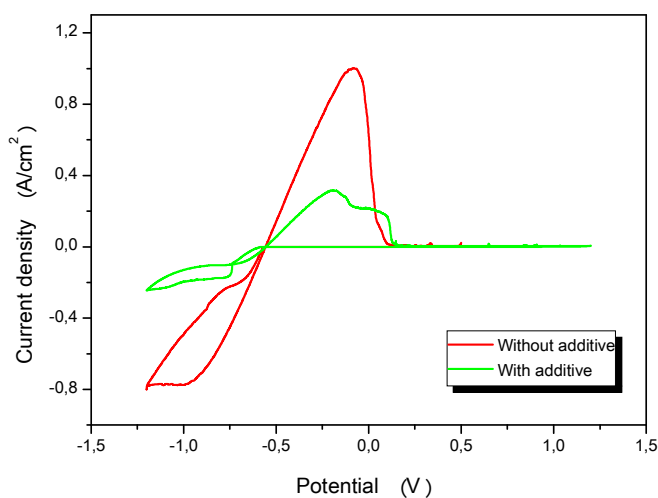


Figure 2. Voltammetry cyclic with and without linseed oil additive at 25mv/s

On the other hand, It can be seen that the stannous reduction process is a single two-electron step from the stannous ion to metallic tin:



The tin electrodeposition starts at a nucleation potential of -0.55 V approximately, via an abrupt increase in current density, as the deposition potential moves negatively away from the equilibrium potential. Upon reversing the potential sweep from -1.2 to 1.2 V, a single oxidation peak is observed at -1 V. This confirms a single two-electron oxidation step from metallic tin to the stannous ion according to the reverse of reaction (1).

The result show that ,the presence of linseed oil additive has an appreciably positive effect in hindering the tin oxidation process, and hydrogen gas evolution , As well as stripping peak is much sharper [23,24]. Therefore, a

bright and smooth tin deposit, with fine crystallites, can be obtained by adding an appropriate amount of additive [25].

LSO concentration effect on stannous reduction

The cathode polarizations were measured in the basic solution (Table 2) with various linseed oil concentrations with a scan rate of 5mV/s (Fig. 3). The results show that the effect of the additive appeared only from 0.3mL and when the LSO concentration is increased more there is shift of the curve, so the additive significantly decreases the reduction current at a given potential. This is due to the adsorption of the additive on the surface of the electrode [7,12,13]. On the other hand, the hydrogen gas evolution is more hindered with increasing of linseed oil concentration. It appears that parts of the surface become shut down to tin deposition, presumably due to the high concentration of adsorbed blocking additive, as well as the formation of whiskers became very limited.

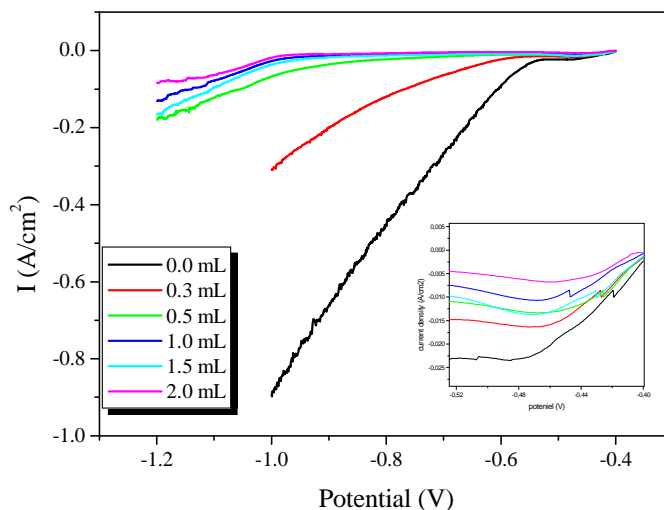


Figure 3. Cathodic polarization curves of the basic solution with various concentrations of linseed oil

To determine the effect of linseed oil on the coating rate, varying the current density applied by the chronopotentiometry method for 10min, and calculating the ratio of the electrodeposition of tin with and without linseed oil. The results are showing in figure 4.

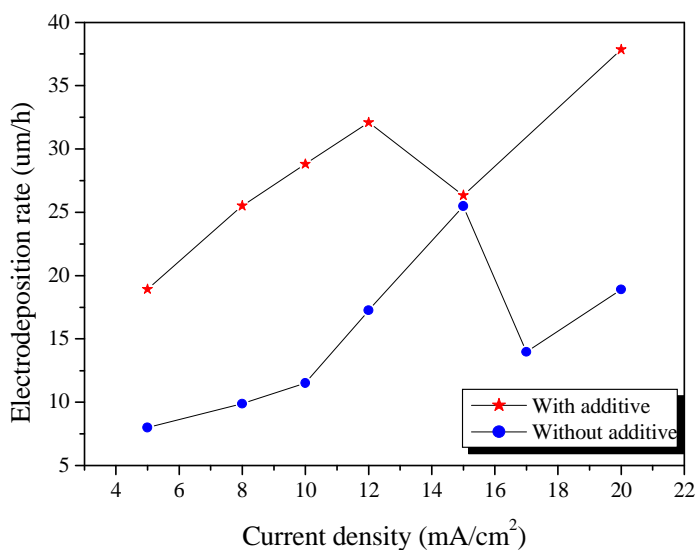


Figure 4. Current density effect in electrodeposition rate with and without additive

The results show that the presence of additives influences the rate of deposition [25]. Thus, it's clear that an enormous difference and an improvement of the electrodeposition rate in the presence of linseed oil additive comparing with the case without additive, and that the electroplating rate generally increases with increasing of current density (Fig.5). This result can be explained by the adsorption of additive at the electrode surface and blocking mechanism [26].

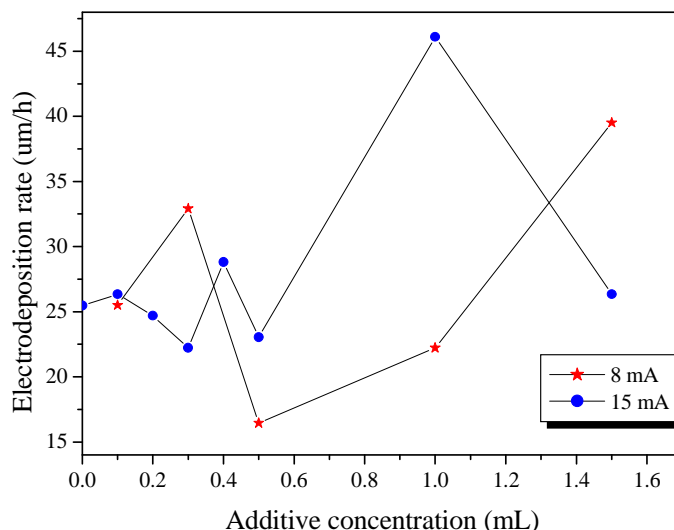


Figure 5 .Additive concentration effect on electrodeposition rate

Polarization measurements

The polarization curves of ordinary steel substrate coated and uncoated tin electrodeposited with and without additive in 3% NaCl after one hours of immersion are presented in Fig. 6. The examined deposit coating shifted the corrosion potential (E_{corr}) towards more anodic potentials. This shift is about 45mV/ E_{corr} and 85mv/ E_{corr} respectively for without and with additive. As shown in the Table, E_{corr} shifts toward slightly more positive values this due to the possible formation of a thin passive film on the metallic surface, which may enhance protective characteristics. In the cathodic and anodic range, the Tafel slopes were changed by the coating. These results further confirmed that these coatings can be used for corrosion protection application in salty environments. No passivity tendency was observed in the measurement range, which is consistent with the work of Mimani and Mayanna [27]. Various corrosion parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel slopes (β_a and β_c), efficiencies ($\eta_{\text{Tafel}}\%$) are given in Table 3. The results showed that I_{corr} values in presence of additive decreased compared with blank solution and electrode coated.

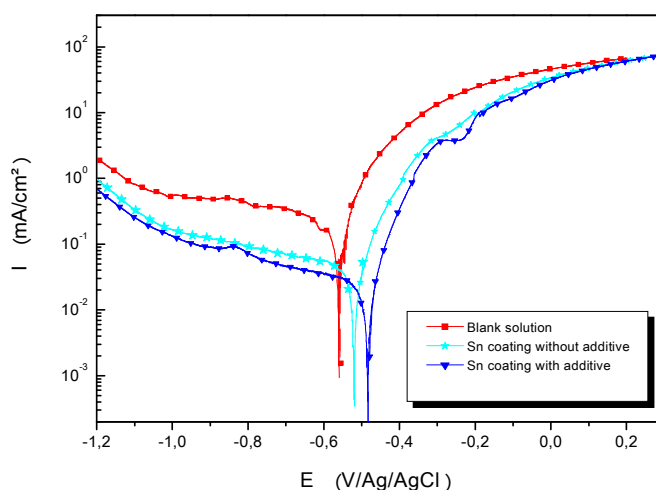


Figure 6. Polarization curves obtained in 3% NaCl for the Blank substrate and for electrodeposited Sn coating without and with additive

Table 3. Corrosion parameters obtained from polarization measurements for mild steel in NaCl 3% at 303 K

	E_{corr} (mV/Ag/AgCl)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	η_{Tafel} (%)
Blank	-559	280	121	121	--
Sn coating without additif	-518	28.7	72	274	89
Sn coating with additif	-482	23.01	164	560	92

Electrochemical impedance measurements

Impedance measurements were performed in the frequency range 100MHz to 10 mHz with a.c. amplitude of 10 mV. Various impedance parameters like polarization resistance (R_p), solution resistance (R_s), double layer capacitance (C_{dl}) are determined. Figure 7 shows the experimental data of Nyquist diagrams, which are obtained after one hour of immersion in neutral media for ordinary steel substrate coating and uncoating tin electrodeposition with and without additive.

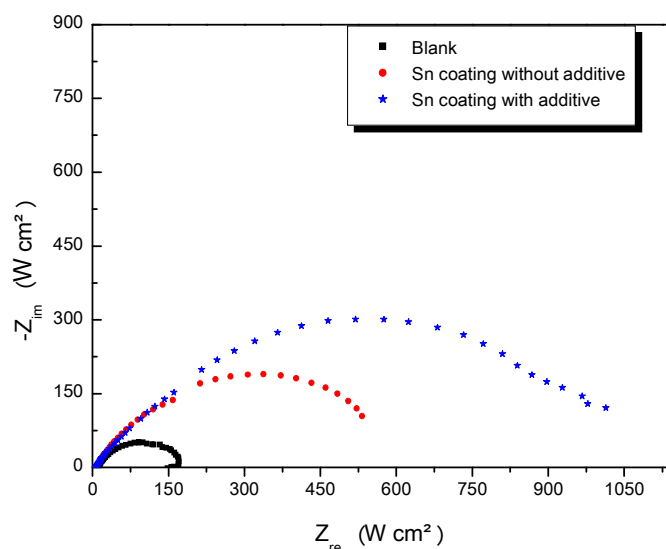


Figure 7. Nyquist diagrams for blank solution, tin coated with and without linseed oil additive in NaCl 3%

In the absence of tin coating, the plots consist of one semicircle which may be devoted to the response of a combination of resistance transfer (R_{ct}) and capacitance (C_{ct}). In the presence of tin coatings with additive, the plots consist of two semicircles: the first which is located between 100 kHz and 100 Hz (at high frequency) may be attributed to the adsorbed film, but the second one is the response of charge transfer resistance R_{ct} . This resistance increases in the presence of additive. These comments were reported in the study of the Ni-P alloy in acid media by other authors [28]. They attributed the first loop to the capacity of an adsorbed film which is due to the oxide layer formation. From the Table 4, we can say that the electrodeposition of tin coatings with additive improve the corrosion resistance of mild steel in neutral media.

Table 4. Polarization resistance, capacitance and inhibitor efficiencies for mild steel in NaCl 3% at 303 K, obtained using electrochemical impedance method

	R_s ($\Omega \text{ cm}^2$)	R_f ($\Omega \text{ cm}^2$)	C_f ($\mu\text{F}/\text{cm}^2$)	C_{ct} ($\mu\text{F}/\text{cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	R_p ($\Omega \text{ cm}^2$)	η_{EIS} (%)
Blank	10	---	---	201	175	165	---
Sn coating without additive	6	---	---	696	571	565	71
Sn coating with additive	7	368	73	521	775	1143	86

The equivalent circuit proposed to fit the experimental data is shown in Fig. 8. It consists of electrolytic solution resistance R_s connected with two time constants. The model is based on the circuits mostly used in the literature for simulation of the kinetics of alloy corrosion process and the protective properties of surface corrosion product layer [29-32].

The Bode plots of the coating show two phase maxima, which indicate the presence of two time constants representing the electrode processes. The impedance data were analyzed using the Volta Master 4 software provided with the impedance system where the dispersion formula was used. For a simple equivalent circuit model consisting

of a parallel combination of a capacitor, C_{dl} , and a resistor, R_{ct} , in series with a resistor, R_s , representing the solution resistance, the electrode impedance, Z , is represented by the mathematical formulation:

$$Z = R_s + \left[\frac{R_p}{1 + (2\pi f R_p C_{dl})^\alpha} \right]$$

Where α denotes an empirical parameter ($0 \leq \alpha \leq 1$) and f is the frequency in Hz [33,34]. To account for the presence of a passive film, the impedance data were analyzed using the equivalent circuit model shown in Fig. 8 where R_s = solution resistance, R_{ct} = charge-transfer resistance, C_{dl} = double layer capacitance, R_{pf} = passive film resistance, and C_{pf} = passive film capacitance.

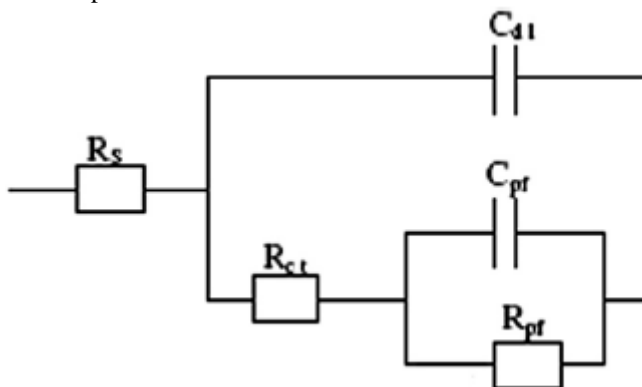


Figure 8. Equivalent circuit used to simulate the electrodeposited Sn impedance spectrum in 3% NaCl

CONCLUSION

The electrochemical behaviour of Sn(II) was studied in sulphuric bath with linseed oil as additive at 298 K using mild steel working electrode. The effect of process variables such as electrodeposition rate, current density, and additive concentration, were investigated. The results show that the electrodeposition rate increased with increasing current density. The best value is 20mA/cm². The use of additive improves the quality of tin deposition and good result is registered at 1mL. The characteristic pic of tin reduction is observed at 0.14M tin concentration. The cyclic voltammetry results show that the reduction of Sn (II) to Sn is irreversible and it proceeds via a one-step two electrons transfer process. The testing of corrosion resistance with polarization curves, electrochemical impedance spectroscopy confirmation that the electrodeposited Sn obtained with linseed oil presented a better corrosion resistance. The improvement in corrosion resistance is caused by the compact microstructure and the presence of linseed oil additive in the coatings incorporated during the electrodeposition process. This additive could favor the formation of a passive film that is more resistant to chloride attack and therefore increases the corrosion resistance.

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