Tin electrodeposition in the presence of *Linseed* essential oil

A. Benabida*, M. Cherkaoui

Laboratory of Materials, Electrochemistry and Environment, Faculty of Science, Ibn Tofail University, PB 133-14050 Kénitra, Morocco

In the present study, a tin deposit was elaborated electrolytically at different temperatures on an ordinary steel substrate in an H_2SO_4 based electrolyte for different linseed essential oil (LSEO) concentrations. The effect of this additive on the electrochemical properties of the coating was investigated using both the stationary and chronopotentiometry method. Thermodynamic parameters such as Ea, $\Delta*G$, $\Delta*H$ and $\Delta*S$ have been evaluated in accordance with the Arrhenius theory and it has been found that the sorption process is non-spontaneous and endothermic in nature. The surface state of the deposit obtained was characterized by electron microscopy (SEM). The results have shown an approving surface quality of the deposit involved with the addition of an optimum concentration of LSEO in the electrolyte.

Keywords: Electrodeposition, Thermodynamic parameters, additive, kinetic, linseed essential oil, Tin, chronopotentiometry.

INTRODUCTION

Tin and its alloys are utilized in a large range of industrial applications pertaining to light engineering and electronics. An increasing interest of their investigation has been manifest in recent years because of the health and environmental concerns, particularly in the electronics industry, likewise in the automotive industry and in decorative plating,where the coatings types are mentioned as ecological alternatives to replace lead based soldering or nickel-chromium decorative coatings [1-3].

In tin plating baths including no organic additives, the tin is massively deposited under a low polarization. The deposit obtained is then porous, less adherent and dendritic with the formation of tin whiskers that spontaneously extend on the tin surface, which may cause a short circuit between the anode and the cathode [4-6].

To remedy or minimize this problem, it is essential to modify the kinetics of deposition. Several authors have proposed the addition of an organic compound into the bath, which can slow the deposition rate. First of all, marked efforts have been made in order to promote adequate additives and then to determine their intervention modes in both the mechanism and the kinetics of the deposit and hence their effect on the coating structure [7, 8]. The advantage in using natural organic compounds is due to theiraccessibility, cost and effect on the environment [9-12]. They pose no detrimental effects on the environment or risk to human health. A number of natural organic compounds have been recognized as good brightening actors in tin electroplating. A sample of these substances is *linseed* essential oil (LSEO). These classes of organic compounds are biodegradable and non-toxic.

Linseed oil is yellowish oil,also known as flax seed oil,extracted from the dried ripe seeds of the flax plant (Linumusitatissimum, Linaceae). As a renewable resource for agriculture, the application knowledge of the *linseed* essential oil as an industrial product has acquired much consideration. In 1965, the triglyceride composition of *linseed* essential oil was assured by a combination of several chromatographic techniques [13]. After that, the oxidation of *linseed* essential oil was reported by different groups [14,15]. Then, the drying operation was investigated with different methods and influencing factors [16-19]. More complex systems of *linseed* essential oil were also applied in concrete penetration [20], characterized by spectroscopy [21]. The recent interest in materials science, focusing on producing environmentally friendly products that substitute the oleo-chemical derived ones, point out a new way to the area of technical significance for *linseed* essential oil [22].

EXPERIMENTAL METHODS

Linseed oil is pressed from the seeds of the flax plant, Linumusitatissum, grown in temperate and cold climates such as Morocco. The essential oil was acquired by hydrodistillation and analyzed by Gas chromatography (GC) and Gas

* To whom all correspondence should be sent:
E-mail: benabida2000@hotmail.com

chromatography mass spectrometry (GC-MS) techniques as described in our earlier work [23, 24]. The chemical structure of the linseed essential oil is presented in Fig. 1. The major constituents of linseed essential oil are α-linolenic acid (60%), linoleic acid (29%), and oleic acid (27%). Linseed oil, which contains 60% α-linolenic acid, is an example of non-conjugated oil and it is rich in polyunsaturated fatty acids [23]. Oxygen atoms are present in their molecular structures and in addition, linolenic and linoleic acids include double bonds, which form potential adsorption sites on the mild steel surface by the donation of electrons to the empty d-orbital of Iron.
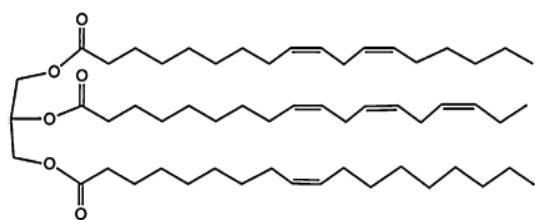
Fig. 1. The chemical structure of *linseed* essential oil additive.

The solution of tin sulfate and sulfuric acid were prepared using analytical grade chemicals. The pH is around 1 as in industrial applications and the temperature was varied as (25, 35, 45, and 55)°C using a hotplate stirrer. Table 1 contains the electrolytes used.

Table 1. Compositionofthestudiedbaths.

| Electrolytes	$SnSO_4$ (M)	H_2SO_4 (M)	LSEO (ppm)
a	0	0.56	0
b	0	0	20
c	0	0.56	20
d	0.14	0.56	0
e	0.14	0.56	10
f	0.14	0.56	20
g	0.14	0.56	30

A 200ml cell was used. The gravimetric method is used to evaluate the electrodeposition efficiency, in the basic solutions without and with an *LSEO* additive, using rectangular mild steel coupons having the same purity as for mild steel rods. The substrates were iron plates (1cm^2), mechanically polished down to 1200by SiC paper, degreased in ethanol, etched in dilute sulfuric acid and rinsed with distilled water prior experiment initiation. The electrochemical measurements were executed with

a potentiostat (VoltaLab model PGZ100). A platinum electrode was used as the counter electrode and a silver/silver chloride (Ag/AgCl) as the reference electrode with all potentials referred. The surface of the deposits was examined by scanning electron microscopy (SEM) to confirm the results obtained.

RESULTS AND DISCUSSIONS

Cathodic Polarization curves

This study was carried out for the first time to explore the effect of LSEO on the cathodic polarization without tin in a cathodic polarization sweepin the potential range from -0.35V to -1.2V. The results foundfrom the three basic solutions (table 1) are shown in Fig.2.
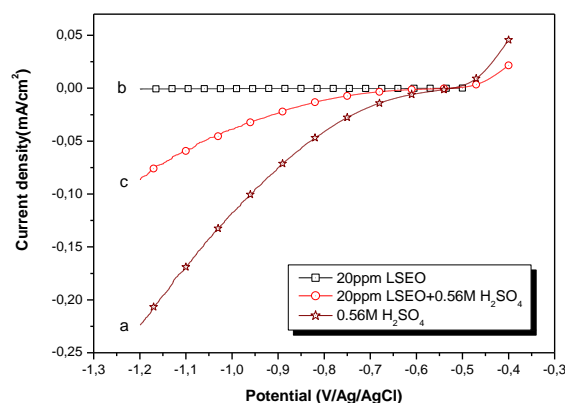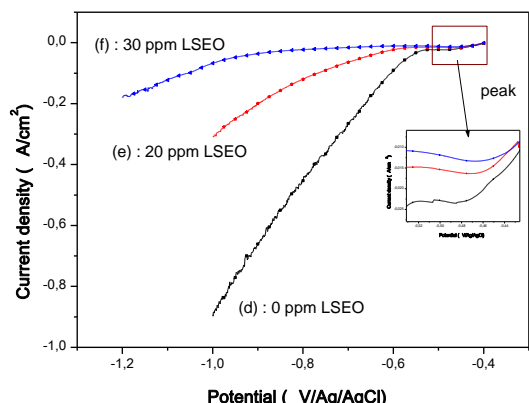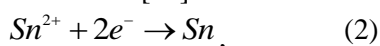

Fig. 2. Linear sweep polarizations in the tin-free electrolyte. (a) 0.56M H2SO4. (b) 10 ppm LSEO. (c) 0.56M H2SO4 + 10 ppm LSEO. at 25∘C andscanrateof 10 mv.s^{-1}

When the cathodic sweep takes place in the sulfuric acid electrolyte alone, there is a high hydrogen evolution reaction (HER) that appears rapidly when LSEO is added to the electrolyte. The process reduction changes concretely, such that the HER reaction is delayed until a higher potential is reached. Increasing the LSEO concentration in the electrolyte inhibits the HER more. On the other hand it can be inferred that this electrolyte is not electroactivein the zone of the potential studied:

$$2H^+ + 2é = H_2, \qquad (1)$$

The cathode polarizations were measured in the basic solution (Table 1) in the presence of the tin electrolyte, at different *LSEO* concentrationsand under the scan rate of 5mV/s presented in Fig. 3. The results show that this additive significantly decreases simultaneously with the current densities and the peak of tin reduction (2) at a disposed potential. This can be explained by the adsorption of the additive on the surface of the electrode [25, 26]. On the other hand, the hydrogen gas evolution

(1) is more impeded whenever the LSEO concentrations increase[27].

$$Sn^{2+} + 2e^- \rightarrow Sn, \qquad (2)$$

Fig. 3. Linear sweep polarizations in the presence of tin in the electrolyte. (d) 0.14M $SnSO_4$ + 0.56M H_2SO_4. (e) 0.14M $SnSO_4$ + 0.56M H_2SO_4 + 10 ppm LSEO. (f) 00.14M $SnSO_4$ + 0.56M H_2SO_4 + 20 ppm LSEO. at $25°C$ and a scan rate of 10 mv.s^{-1}

Chronopotentiometry

The transitory curves E=f(t) plot, for different current densities in baths from (d) to (g) (Fig. 4) show that the potential of stabilization is affected by the presence of *linseed* essential oil for different chosen current densities, as well as there is an overvoltage occurs when increasing the current density due 10 mA/cm^2 to 20 mA/cm^2, for all baths studied. These results show that the additive studied has a considerable effect on tin electrodeposition on the substrate. This potential drop after the addition of *LSEO* may be attributed to a partial blockage of the surface by adsorption of the additive [28]. Furthermore, the cathodic overvoltage increases as the concentration of the additive rises, as may be expected if the inert film behaves as a physical barrier [29].

In view of the galvanostatic curves shown above (Fig.4), the lowest overpotential is obtained in the absence of an LSEO additive,when the voltage increases gradually as a function of the LSEO concentration.Therefore, it is obvious that the increase in the concentration of LSEO would significantly affect the electrochemical properties of Sn. The highest overpotential is obtained as the structure becomes more compact and uniform (Fig.10).
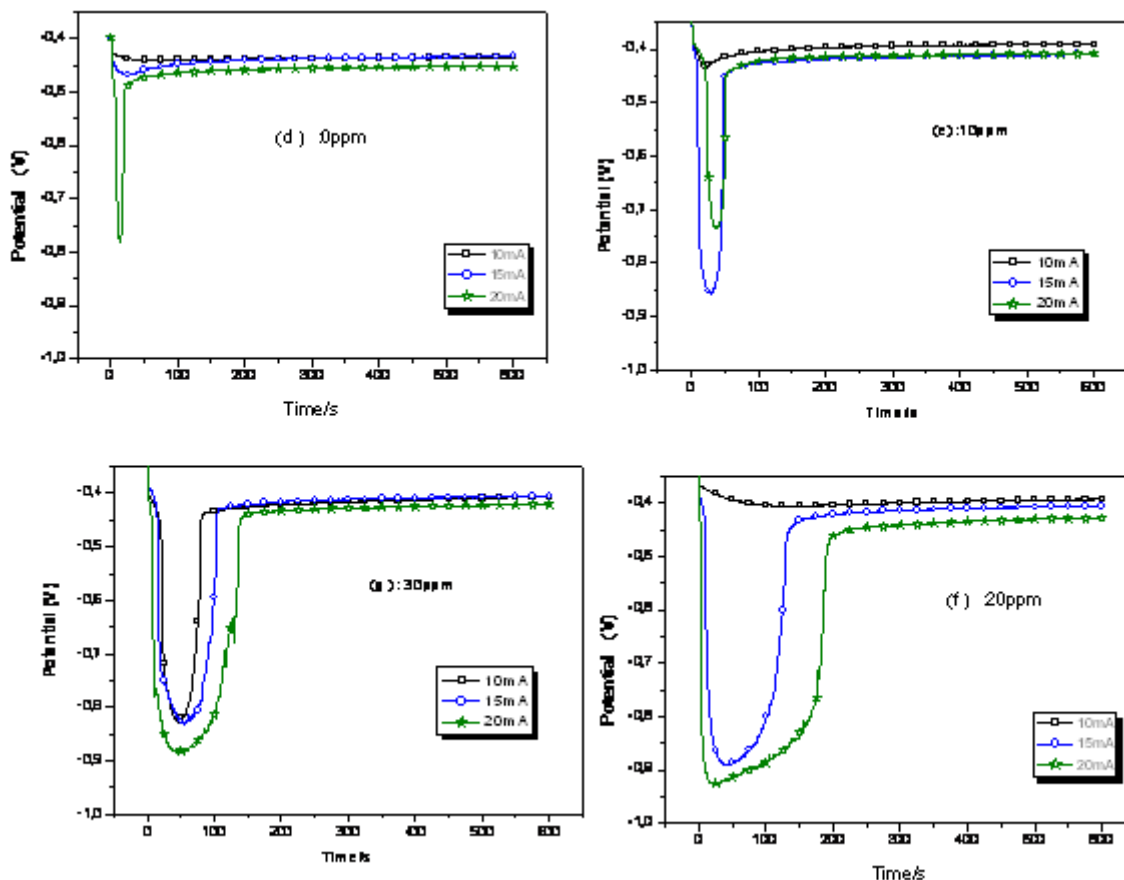
Fig. 4. Potentiostatic current-time transients during tin deposition in the absence and in the presence of different LSEO concentrations (d):0ppm; (e): 10ppm; (f): 20ppm; (g): 30ppm.

700

Electrodeposition efficiency

The amount of tin deposited at the working electrode surface can be expressed using the electrodeposition efficiency (CE) that may be calculated from the Faraday's law (3) :

$$CE = \frac{m_{\exp}}{m_{theor}} x100, \qquad (3)$$

Where $m_{\exp}$ is the weight of the deposit obtained experimentally and m_{theor} the theoretical mass m_{theor} of the deposit calculated theoretically according to Faraday's law[30].

Fig. 5 presents the electrodeposition efficiency with different LSEO concentrations as a function of various current densities. It is noticeable that the CE increases in general with an elevation of the current density.
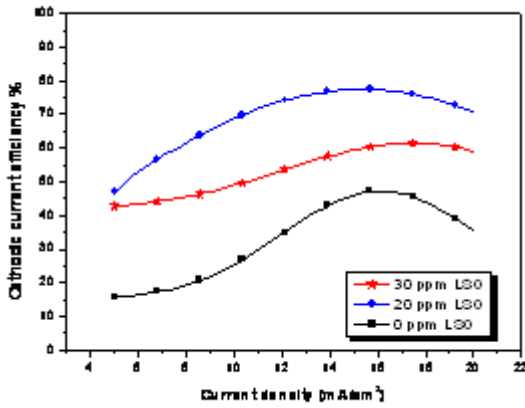
Fig. 5. Effect of the current density on the cathodic electrodeposition efficiency for various LSEO concentrations at 25°C.
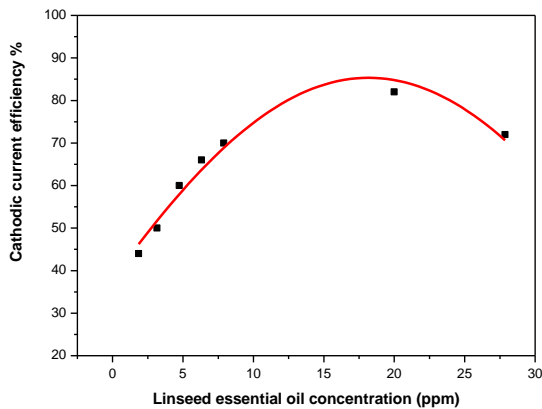
Fig. 6. Effect of the LSEO concentration on the cathodic electrodeposition efficiency at 25°C and 15mA/cm².

Furthermore, the presence of the LSEO significantly improves the electrodeposition efficiency, which may be explained by the fact that the stannous ions when they arrived on the substrate they attach themselves better than in the case of the absence of an additive, which results in the absence of whiskers during electrodeposition [27]. On the other hand, it is noticeable that the obtained results (Fig. 6) show that the CE varies in accordance with the different concentrations and the highest value is obtained when we choose a concentration of 20ppm. This result is confirmed in the curve of Fig.4f by the drop of the voltage for this value of the concentration. The decrease in the CE at a high concentration may lead to a decrease in the number of catalytic sites on the metal surface because of the formation of a thin film of adsorbed LSEO on top of the active surface [31].

Thermodynamic parameters

A thermochemical study of the temperature effects on the tin electrodeposition system by means of potential–current density is presented in Fig.7 to understand the effect of temperature on the deposition mechanism. These studies have been completed by activation parameters calculation at different temperatures between room temperature and 55°C.

The Arrhenius equation provides a mathematical dependency between the reaction rates (the time limiting current density) and temperature as follows:

$$\log I_\ell = \log A - E_a / 2.3R.T \quad (4)$$

Where I_ℓ is the limiting current density. A is the Arrhenius pre-exponential constant. R is the molar gas constant and T is the absolute temperature. A plot of log I versus 1/T produces straight lines (fig. 8) with a slope as $(-E_a/2.3R)$ and an intercept at log A. The activation parameters calculated from the plot are displayed in table 2. The transition state equation (18) afforded thermodynamic parameters (table 2) such as the enthalpy change $\Delta*H$ and entropy change $\Delta*S$ from a plot of log I_ℓ/T versus 1/T as shown in Fig. 9.

$$I_\ell = \frac{RT}{Nh}\exp\left(\frac{\Delta*S}{R}\right)\exp-\left(\frac{\Delta*H}{RT}\right)$$

where N is Avogadro's number and h is Plank's constant. The enthalpy was calculated from the slope $(-\Delta*H/2.3R)$ while the entropy was calculated from the intercept $\{ \ln(R/Nh)+ (\Delta*S/2.3R)$ of the plot. Therefore $\Delta*G$ is calculated from equation (4):

$$\Delta*G = \Delta*H - T\Delta*S \ , \qquad (4)$$

The activation energies of the tin deposition with and without LSEO are calculated in accordance with the Arrhenius equation (4). The results obtained (Table 2) reveal that the higher

values of Ea obtained for the deposition of tin containing LSEO may be attributed to the blockage of the surface of the working electrode by molecules of the additive [32].
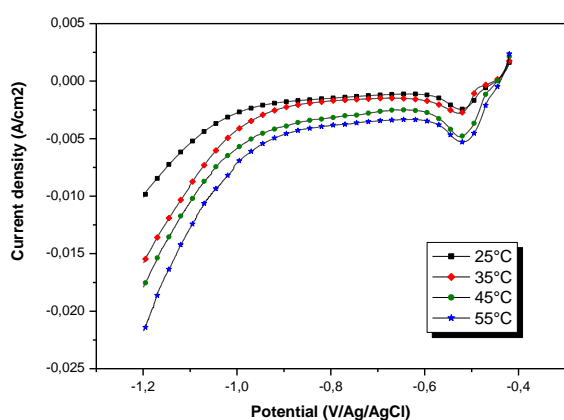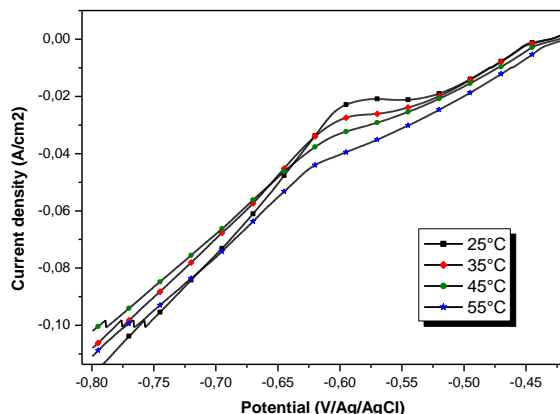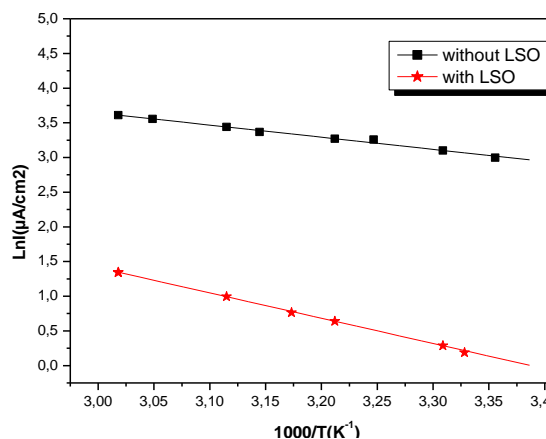

Fig. 7. Linear sweep polarizations recorded at various temperatures and a scan rate of 10 mV.s^{-1}for the electrolyte ; (a) without an additive, (b) with 20 ppm of LSEO.

Like Ea, the $\Delta*H$ increases in the presence of the additive. The positive values of $\Delta*G$ are a sign of the non-spontaneous process as expected. The process was endothermic due to the positive values of $\Delta*H$. Therefore, the entropy $\Delta*S$ was negative and decreased gradually with the presence of the LSEO compared to that of the LSEO - free solution, meaning that the formation of the new tin layer with LSEO is less disordered[33].
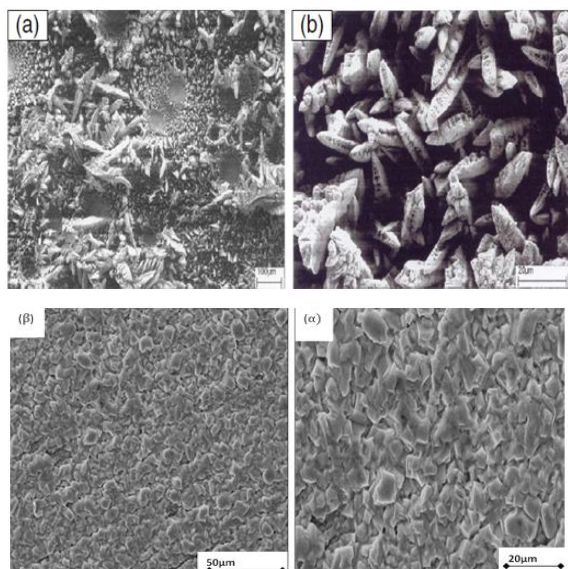

Fig. 8. Thelogarithmofthe currentdensityversus T^{-1}forthelinearsweeppolarizationsat a potentialof −570 mV ;(a) 0.14M SnSO$_4$ + 0.56M H$_2$SO$_4$, (b) 0.14M SnSO$_4$ + 0.56M H$_2$SO$_4$ + 20 ppm LSEO. Data takenfromFig. 7.
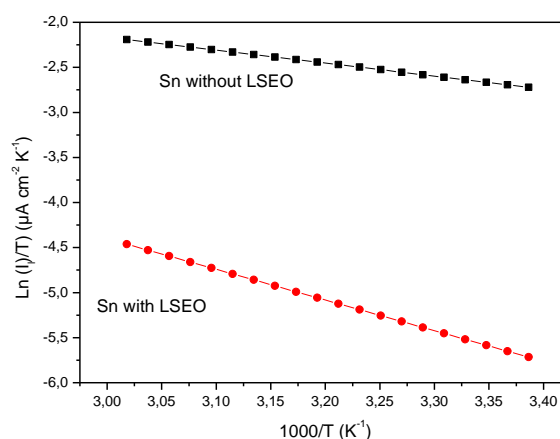
Fig. 9. Transition state plots for tin reduction on mild steel;(a) 0.14M SnSO$_4$ + 0.56M H$_2$SO$_4$. (b) 0.14M SnSO$_4$ + 0.56M H$_2$SO$_4$ + 20 ppm LSEO.

Surface morphology of deposits

The surface morphology of tin deposits was studied in the absence and in the presence of LSEO using scanning electron microscopy (SEM) and is given in Fig.10a and Fig.10b. It is remarked that the tin deposit in the absence of LSEO was rough and porous.

Table 2. The thermodynamic parameters for tin electrodeposition in 0.56 M H$_2$SO$_4$, in the absence and presence of 20 ppm LSEO.

Surfactant	Linear regression coefficient (r)	E$_a$ (kJ/mol)	$\Delta*H$ (kJ/mol)	$\Delta*S$ (J/mol)	$\Delta*G$ (kJ/mol)
Without additive	0.99964	14.54	11.957	-122.29	48.399
In the presence of LSEO	0.99877	30.92	28.315	-185.34	86.153

Fig. 10. (a and b) SEM images of tin deposits obtained at 25°C from the additive-free bath under the current density of 15 mA/cm^2. (α and β) SEM images of tin deposits obtained at 25°C at 20 ppm of LSEO under the current density of 15 mA/cm^2.

However, the tin deposit became compact and the roughness was decreased in the presence of LSEO as shown in Fig.10α and Fig.10β. It is noted that the grain size was clearly decreased with LSEO addition. Thus, it is found that the deposits with fine grains have a relatively large resistivity [34]. Also, the color of the deposits is modified from dark brown to bright with the presence of LSEO. This bright appearance of the deposits generally manifests better mechanical and electrical properties.

CONCLUSION

The electrochemical behavior of Sn (II) was studied in the sulphuric acid bath where *linseed* essential oil is an additive at different temperatures between room temperature and 55°C, using a mild steel working electrode. The insertion of *LSEO* into the base electrolyte of a tin deposit containing SnSO$_4$ and sulfuric acid leads to an improvement of the coating quality. Thus, the coating is more homogeneous more regular and less burnt than the one obtained from the base bath. This improvement may be attributed to a slowdown in the process of tin reduction by adsorption of this additive on the surface blocking a part of the actives sites. The thermodynamic parameters (Ea. Δ*G. Δ*H and Δ*S) showed that the adsorption process is non-spontaneous and endothermic in nature. In addition,*linseed* essential oil can be efficiently used as a low-cost and eco-friendly alternative as an organic compound in the bath.

REFERENCES

1. C.Han, Q.Liu, D. G. Ivey., *Electrochim. Acta,* **54**, 3419 (2009).
2. J.A. Jaen, M.I. Varsanyi, H. Csontos, A. Vertes, *Hyperfine Interact*, **66**, 101 (1991).
3. M.S. Jellesen, P. Miller., *Plat. Surf. Finish,* **92**, 36 (2005).
4. E. Chason, N. Jadhav, F. Pei, E. Buchovecky, A. Bower., *Progress in Surf. Sci*, **88**, 103 (2013).
5. S. Bakkali, T. Jazouli, M. Cherkaoui, M.E. Touhami, N. El-Hajjaji, E. Chassaing, *Plat. Surf. Finish*, **90**, 46 (2003).
6. G.S. Tzeng, S.H. Lin, Y.Y. Wang, C.C. Wan, *J. of Electroanal. Chem*, **26**, 419 (1996).
7. A. Aragon, M.G. Figueroa, R.E. Gana, J.J.H. Zagal, *Appl.Electrochem*, **22**, 558.
8. C.T.J. Low, F.C. Walsh., *J. Electroanal. Chem*, **615**, 2 (2008).
9. B.C. Tripathy, P. Singh, D.M. Muir, S.C. Das, *J. Appl. Electrochem*, **31**, 301 (2001).
10. A.Loto, I. Olefjord., *Corros. Prevent. Contr*, **39**, 149 (1992).
11. C. A.Loto, *Discov. Innovat*, **5**, 253 (1993).
12. C.A. Loto , I. Olefjord, H. Mattson., *Corros. Prevent. Contr*, **39**, 885 (1991).
13. A.G. Vereshchagin, G.V. Novitskaya., *Journal of the American Oil Chemists' Society,* **42**, 970 (1965).
14. P.S. Hess, *Industrial and Engineering Chemistry*, **42**, 1424 (1950).
15. C. Nunn, A.I. Smedley-Maclean, *Biochemical Journal,* **32**, 1974 (1938).
16. S.Tuman, J.Chamberlain, D. Scholsky, K.M. Soucek, M.D, *Progress in Organic Coatings, 28*, 251 (1996).
17. M.Lazzar, O.Chiantore, *Polymer Degradation and Stability,* **65**, 303 (1999).
18. J. Mallégol, J. Lemaire, J.L. Gardette, *Progress in Organic Coatings,* **39**, 107 (2000).
19. C. Stenberg, M. Svensson, M. Johansson, *Industrial Crops and Products*, **21**, 263(2005).
20. P. Blankenhorn, R. Barnes, D. Gowen, W. Kline, P. D.D.E. Cady, *Cement and Concrete Research*, **9**, 353 (1979).
21. V. Sharma, J.S. Banait, P.P. Kundu, *Polymer Testing,* **27**, 916 (2008).
22. Y.Xiaohong, L. Jing., *Industrial Crops and Products*, **41**, 437 (2013).
23. D. Rashmita, B. Sudip, R. Bandyopadhyay, P. Panchanan, *Sensors and Actuators B: Chemical*, **185**, 293 (2013).
24. D.M. Kasote, Y. S. Badhe, M. V. Hegde, *Industrial Crops and Products,* **42**, 10 (2013)
25. E.Rudnik., *Ionics,* **19**, 1047 (2013).
26. F.J. Barry, V.J. Cunnane, *J. Electroanal. Chem,* **537**, 151 (2002).
27. A. Benabida, M. Galai, A. Zarrouk, *Der Pharma Chemica,* **6**, 285 (2014).
28. S. Cherrouf, Y. Salhi, A. Benabida, H. Elgrini, M. Cherkaoui, L. Lakhrissi, B. Lakhrissi., *J. Chem.,* **2**, 175 (2014).

29. M. Moussa, A. El-Far., A. El-Shafei., *Materials chemistry and physics,* **105**, 105 (2007).
30. N.V. Sotskaya, O.V. Dolgikh, *Protection of Metals*, **44**, 479 (2008).
31. J. Huh, *Corros. Sci. Soc. Korea*, **29**, 46 (2000).
32. M. Charrouf, S. Bakkali, M. Cherkaoui, M. Amrani, *Journal of the Serbian Chemical Society,* **71**, 661 (2006).
33. A.I. Rasheed, *J. For Pure & Appl. Sci.,* **24,** 10 (2011).
34. W. Sha, X. Wu, K.G. Keong, Electroless copper and nickel–phosphorus plating, processing, characterization and modeling, first ed., Woodhead Publishing Limited, New Delhi, 2011.

ЕЛЕКТРООТГАЛАНЕ НА КАЛАЙ В ПРИСЪСТВИЕ НА ЕСЕНЦИАЛНО МАСЛО ОТ ЛЕНЕНО СЕМЕ

А. Бенабида*, М. Черкауи

Лаборатория по материалознание, електрохимия и околна среда, Научен факултет, Университет Ибн Тофайл, Кенитра, Мароко

(Резюме)

В настоящата работа електролитное отлаган калай при различни температури на обикновен стоманен субстратв H_2SO_4 базирани електролит за различни концентрациина ленено етерично масло (LSEO). Изследван е ефекта на тази добавка върху електрохимичните свойства на покритието,както при стационарни, така и при хроно-потенциометрични методи. Определени се термодинамични параметри, като Ea, Δ*G, Δ*H и Δ*S в съгласие на теорията на Арениус и е установено, че адсорбцията е ендотермичен и неспонтанен процес. Повърхностното състояние на отлагането е охарактеризирано с електронна микроскопия. Резултатите показват, че подобрените повърхностни качества на покритието се дължат на оптималната концентрация на LSEO в електролита.