



Investigation of Calix[4]arene Molecule on Electroless Ni-P Alloy on Carbon Steel Substrate and Evaluation of its Corrosion Resistance in 3% NaCl

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The autocatalytic nickel bath uses sodium hypophosphite as a reducing agent, sodium citrate as a complexing agent and sodium acetate as an accelerator. The effect of calix[4]arene molecule type H₄L named (dicarboxylic acid *p*-*tert*-butylcalix[4]arene) was studied and used at various concentrations of 10⁻³ to 10⁻⁶ M to improve the microstructure, the microhardness and properties of nickel deposit obtained. The effect of varying the concentration of H₄L, on the deposition rate, the composition, the microstructure and morphology of chemical deposition was studied. The results showed that depending on the concentration of calix[4]arene, the deposition rate decreases from 11, to 7.75 μm/h. The microstructure and microhardness improves significantly at a concentration of 10⁻⁶ M of additive. It was also shown that the coating obtained is adherent and compact and the chemical bath has become more stable in the presence of calix[4]arene additives. Indeed, in both cases, the nickel content decreased with the addition of concentration. This decrease of nickel content might be related to the increase of deposition rate depending on the concentration. The X-ray diffraction analysis revealed peak intensification in the {111} orientation of plane in the presence of a concentration of 10⁻⁶ M; this may be in agreement with the results of metallographic study which showed that the coatings are adherent and have a good resistance. Hence, the Vickers microhardness of deposited coatings has a better value (376 HV) at the concentration 10⁻⁶ M. The corrosion resistance in 3% NaCl solution has been proven at the same concentration as found. Finally, the cyclic voltammetry and electrochemical impedance spectroscopic studies revealed that the additive strongly influences the cathodic process and affects slightly oxidation of hypophosphite.

Keywords: Electroless nickel, Calix[4]arene, Sodium hypophosphite, Cyclic voltammetry, Corrosion, Vickers microhardness.

INTRODUCTION

The Ni-P autocatalytic coatings have been often studied and used in industry due to its corrosion resistance, excellent wear resistance and weldability [1,2]. The properties of this coating (chemical and mechanical) strongly linked to its phosphorus content and its microstructure. The contents of deposited Ni-P layer will determine the structure of the coating which is nanocrystalline, microcrystalline, polycrystalline or amorphous [3-6].

The technique of autocatalytic deposition of Ni-P alloy coatings [7-9] is a well known commercial process, which has used in many fields due to its high corrosion resistance, good lubrication, high wear resistance, acceptable ductility and high

hardness [10,11]. The coatings with a low percentage of phosphorus (1 to 3% of P) are crystalline and have good wear resistance, but in a chloride environment the corrosion resistance is low. When the phosphorus content is medium (5 to 8% of P), the coating has crystalline particles of small size and tend to be semi-amorphous, concerning the high phosphorus contents (> 10%) and the particles are in the form of metallic glass. Generally, the deposition rate is improved when the phosphorus content is medium. Deposits with a high phosphorus content generally have the best corrosion resistance, but the deposition rates is very slow [12]. In addition, in order to enhance the important properties of electroless nickel coatings, many composite electroless nickel coatings are reported [13].

The characteristics of deposits of binary alloys of auto-catalytic Ni and P linked to the chemical balance of metallization solution, in particular of the type of stabilizer and pH of bath [14]. The morphology, phosphorus content and the phosphorus distribution of the coating can affect the degradation behaviour in aggressive environments, in particular which contains the chloride ions [14]. To stabilize the bath or accelerate the deposition rate, different additives are added. But these are influenced by several parameters such as pH, temperature, concentration, the presence of foreign matter and reducing agents [15]. The most critical parameter among these elements is the concentration [16] because these additives can act as accelerators [17] or deposition inhibitors in the coating bath [18,19].

Indeed, since calix[4]arene is in the form of a vase because hydrogen bonds produced by the protons of OH groups present at *ortho*-position [20-23]. Attraction of the OH groups between them creates an inclination of the phenols [24,25]. In addition, a vase shape of calix[4]arene has the possibility of stapling molecules and the strong negative bias of oxygen allows it to attract cations in the empty space at the center of the macrocycle, which makes it possible to obtain a very stable complex. The complex properties calix[4]arene, produced directly from the particular structure of macrocyclic nucleus. The production of molecules can be modulated by varying the substituents grafted at the top and bottom of calix[4]arene. The richness of calix[4]arene is that they have many functionalized sites, giving access to real bouquets of ligands arranged around a single central unit [26,27]. In recent years, we found calix[4]arene applications in several industries such as cosmetology, environmental technologies, *etc.* [28,29].

In this article, the effect of calix[4]arene molecule on the stability of the Ni-P coating bath was studied and also the effects of deposit composition, rate of deposition, structure and morphology of electroless nickel deposit in the hypophosphite-containing bath were evaluated. In this context, the gravimetric method was used to optimize the concentration of additive added in the bath. The SEM/EDAX and X-ray diffraction analysis were performed to determine the morphology, the composition and the microstructure of obtained deposit. In addition, to study the kinetics of chemical process, the electrochemical methods *viz.* cyclic voltammetry and electrochemical impedance spectroscopy were also conducted. Finally, a corrosion study of obtained deposits Ni-P in a very aggressive solution (3% NaCl) using electrochemical techniques was investigated.

EXPERIMENTAL

All solutions used through these experiments were freshly prepared from analytical grade reagents and distilled water. The electroless nickel-phosphorus alloy deposition was carried out using the generic bath composition. It was composed from nickel sulfate as ion source, sodium hypophosphite as a reducing agent, sodium citrate as a complexing agent and sodium acetate as an accelerator agent. The iron sample with dimension 2 cm × 2 cm × 0.1 cm as working electrode, Pt plate as the counter electrode while SCES as the reference electrode to which potentials will be referred. Prior to immersion test, the substrate was abraded using emery paper up to 1200 grade, cleaned with ethanol, etched in 10% dilute H₂SO₄, washed with distilled

water and finally dried. The additives used in this work were synthesized according to the literature [29]. This additive was dissolved in dichloromethane solvent (5 mL) and added in small concentration in the basic bath volume of 50 mL. Calix-[4]arene concentrations were varied ranging from 10⁻³ to 10⁻⁶ M to test the optimal concentration which can provide the highest deposition rate.

The electrochemical measurements were carried out using Potentiostat/Galvanostat/Voltalab PGZ 100 monitored by a personal computer. The voltammetric measurements were performed in the potential range between -1.0 and 1.0 V with a scan rate of 5 mV/s and impedance studies in a frequency range of 100 kHz to 10 MHz with the amplitude of ±10 mV. The determination of electrochemical parameters, potential corrosion E_{corr} and current corrosion I_{corr} from the polarization curve was performed using non-linear regression by original 6.0 software. The chemical composition of electroless Ni-P coating bath is given in Table-1. A scanning electron microscope (SEM, JEOL Model JSM- 5400) was used for the observations of Ni-P alloy coating and an EDAX attachment was used for qualitative elemental chemical analysis and crystallographic structure of the sample was studied by X-ray diffractometer (XRD). The corrosion resistance of elaborated deposits was measured by using computerized auto lab system PG state 30 (potentiostat galvanostat) electrochemical tests in 3% sodium chloride electrolyte. The working electrode was electroless nickel Ni-P deposited on carbon steel with 4 cm² surface area with an area of 4 cm². The auxiliary electrode was a platinum electrode and a saturated calomel electrode (SCE) used as a reference electrode.

TABLE-1
CHEMICAL COMPOSITION OF THE ELECTROLESS
NICKEL PLATING BATH AND ITS OPERATING
CONDITIONS (pH 5.5 ± 0.1 AND T = 85 ± 2 °C)

Chemical composition	Concentration
Nickel sulfate (NiSO ₄ ·6H ₂ O)	25 g L ⁻¹ (0.09 M)
Sodium hypophosphite (NaH ₂ PO ₂ ·H ₂ O)	23 g L ⁻¹ (0.21 M)
Sodium citrate (C ₆ H ₅ Na ₃ O ₇ ·2H ₂ O)	12.6 g L ⁻¹ (0.05 M)
Sodium acetate (CH ₃ COONa)	10 g L ⁻¹ (0.12 M)
Operating conditions	
pH	5,5
Temperature	85 ± 2 °C
Plating duration	30 min
Plating rate	11 μm h ⁻¹

RESULTS AND DISCUSSION

Effect of varying the additive concentration on the deposition rate: The deposition rate *versus* the concentration on additive is presented in Fig. 1. It was noted that deposition rate of electroless plating in the absence of calix[4]arene was higher with a value of 11 μm/h, but reduced to 2.86 μm/h at 10⁻³ M concentration, then it increases in function of the variation of the concentration until the value of 7.73 μm/h to 10⁻⁶ M.

In this study, it is possible that a decrease in deposition rate with the addition of calix[4]arene additive resulted in adsorption or weak transfer or nucleation of electrons at the electrode surface, but the deposition rate increases when the concentration of the additive reaches a maximum value at an optimal

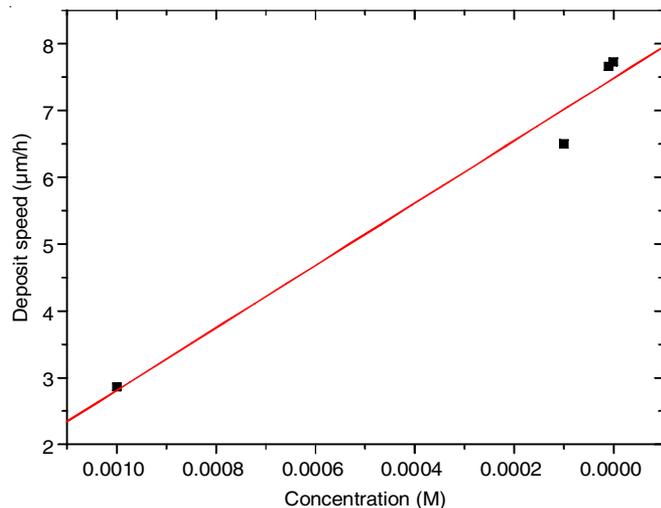


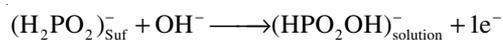
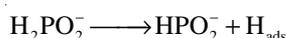
Fig. 1. Deposition rate of nickel deposit as function of calix[4]arene type H₄L. Based electrolyte: NiSO₄·6H₂O 0.09 M; NaH₂PO₂·H₂O 0.21 M; C₆H₅Na₃O₇·2H₂O 0.05 M; CH₃COONa 0.12 M; (pH = 5.5 ± 0.1 and T = 85 ± 2 °C)

concentration of 10⁻⁶ M. The adhesion and appearance of the deposit are improved as long as the bath was stable.

Effect of pH electrolyte on the deposition rate: The most important parameter in the filling of Ni-P alloy was pH, whatever the type of bath used. According to several researchers [30–34] different baths containing H₃PO₃ or sodium hypophosphite, the pH recommendation is different. Machizaud [32] and Poudroux [31] found a decrease in the phosphorus content with a pH increase. The same trend was also observed by Harris and Dang [35]. Generally, these researchers noted that if the pH is too basic with respect to the optimum value, the deposit would be blackish, which corresponds to the nickel hydroxide formation [33]. If the pH is less than optimum yield, loss is observed.

The nickel-plating using sodium hypophosphite as a reducing agent is a binary alloy of nickel and phosphorous. This is a well-established phenomenon [34]. Most of the properties of coatings are structure-dependent and the structure depends on phosphorous content. Among all these parameters, pH is one of the most dominant factors, which controls phosphorous content in the deposits [36].

Effect of pH: The pH effect of the solution on the deposition rate is shown in Fig. 2. It is observed that the deposition rate increases remarkably from 5.4 to 7.73 µm h⁻¹ with the increase of solution pH from 3.5 to 5.0. This behaviour can be justified by the effect of pH on the anodic reaction [37]. In present studies on the deposit of alloy Ni-P alloy in ammoniacal medium [38], in anodic range, a chemical reaction precedes charge transfer. This is a deprotonation reaction, which can be written as:



An increase of pH solution enhances reaction 1, which supports the anodic process. In addition, anodic oxidation of hypophosphite is the dominant factor in electroless deposition [37,39], when the pH is above 5.5, a decrease in the deposition rate is observed.

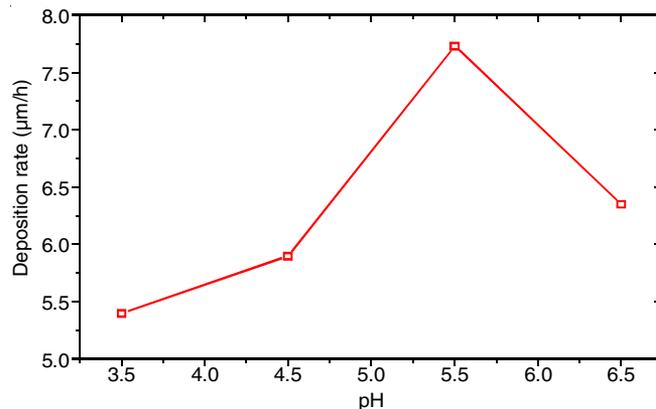


Fig. 2. Deposition rate of nickel deposit as function of solution pH. Based electrolyte: NiSO₄·6H₂O 0.09 M; NaH₂PO₂·H₂O 0.21 M; C₆H₅Na₃O₇·2H₂O 0.05 M; CH₃COONa 0.12 M; (T = 85 ± 2 °C)

Voltammetric analysis: It is well known that autocatalytic deposition of metals or alloys usually result from two half reactions: anodic oxidation of the reducing agent (sodium hypophosphite) and the cathodic discharge of the metals. However, interactions often occur between these reactions [40,41]. Cyclic voltammetry was carried out to characterize the various oxido-reduction processes. Fig. 3 shows the different voltammograms obtained from the bath at different concentrations of H₄L additive. These obtained voltammograms have the same results in the basal medium [42] and they revealed the existence of (a) a cathodic peak K representing the reaction of reduction of Ni²⁺, H₂PO₂⁻ and H₃O⁺ ions; (b) a small anodic peak located at -646 mV/s relating to the oxidation of H₂PO₂⁻ ions and hydrogen atoms adsorbed at the electrode surface; (c) peak B appeared (at -300 mV/s) of dissolution of deposit Ni-P. According to literature, the first peak represents the dissolution of crystalline phase of alloy [42].

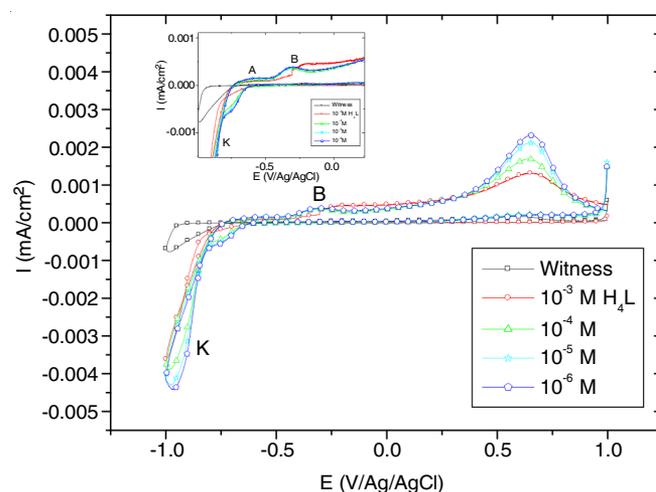


Fig. 3. Cyclic voltammograms of the electroless nickel deposits at different concentrations of calix[4]arene H₄L (v = 10 mV/s). Based electrolyte: NiSO₄·6H₂O 0.09 M; NaH₂PO₂·H₂O 0.21 M; C₆H₅Na₃O₇·2H₂O 0.05 M; CH₃COONa 0.12 M; (pH = 5.5 ± 0.1 and T = 85 ± 2 °C)

By decreasing the H₄L concentration from 10⁻³ to 10⁻⁶ M, a remarkable fall is noticed in the current of peak K, and decrease in the current of peak A, thus confirmed the effect of additive concentration on the oxidation of hypophosphite, and

a small displacement of the potentials peaks related to alloy dissolution in the cathodic field. From these voltammograms, it is concluded that the additive concentrations strongly influence the cathodic process. In fact, intensities of current nickel diffusion current and peak K for the reduction of Ni^{2+} ions, $\text{H}_2\text{PO}_4^{2-}$ and H^+ vary due to the different concentrations of additive.

Impedance behaviour: The deposition potential is characterized by a net current equal to 0, resulting from two simultaneous anodic and cathodic processes. Fig. 4 shows the different impedance diagrams obtained from the base baths at different concentrations of H_4L additive. It is generally observed that the size of loops increases with the concentrations of additives. In Fig. 5, a high-frequency capacitive loop is attributed due to the relaxation of dual layer in parallel with R_1 , charge transfer resistance. Its size decreases with increasing additive concentration and aq medium frequency curve characterizes the adsorption of nickel into an infinite layer.

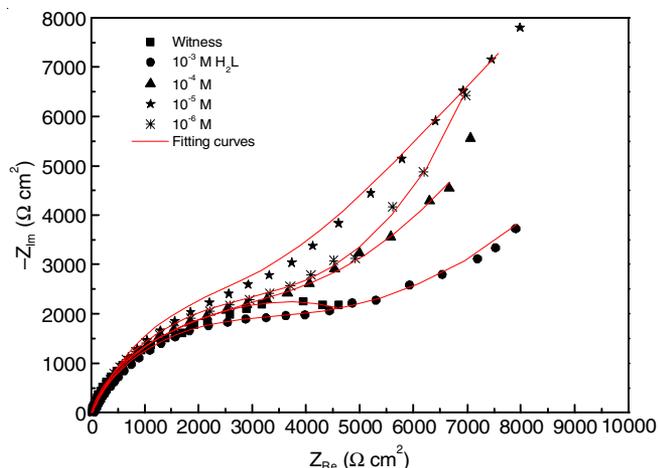


Fig. 4. Electrochemical impedance spectra obtained from based electrolyte at different concentrations of the additive H_4L . Based electrolyte: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 0.09 M; $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ 0.21 M; $\text{C}_6\text{H}_3\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ 0.05 M; CH_3COONa 0.12 M; (pH = 5.5 ± 0.1 and $T = 85 \pm 2^\circ\text{C}$)

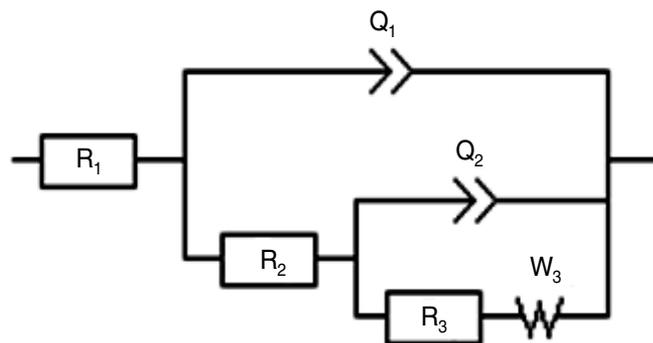


Fig. 5. Equivalent circuit model used to adjust the impedance for the chemical bath at different concentrations in calix[4]arene

The pace of diagrams was influenced by the addition of calix[4]arene additive at different concentrations. It is also noted that the charge transfer resistance is almost certainly increased, which indicates a decrease in the deposition rate. This is consistent with the results obtained by gravimetric analysis.

Characterization of obtained deposits

Surface morphology of deposits and microhardness of coatings: The surface morphology of the coatings obtained was investigated by SEM techniques for five coatings are shown in Fig. 6. The SEM examination shows that the coating has a nodular and relatively uniform appearance. It is noticed that the grain size decreases as the concentration of additive and appearance of the deposit becomes clearer and brighter. Indeed, the micrograph of concentration 10^{-6} M (Fig. 6e) presents a lighter and uniform as compared to the other. This is in agreement with the results obtained by gravimetry and electrochemistry that at 10^{-6} M concentration is the best one obtained. This bright appearance of the deposits usually indicates better mechanical and electrical properties. Metallographic images (Fig. 7) showed that the coatings obtained in the presence of additives and different concentrations were adherent and exhibited good high Vickers microhardness deposits reaching a maximum at 10^{-6} M. The results of hardness are listed in Table-2.

Concentrations (M)	HV average	P (%)
0	296	7.58
10^{-3}	216	5.64
10^{-4}	269	6.81
10^{-5}	316	7.71
10^{-6}	376	8.04

The results (Fig. 7) also indicated that the hardness increases as P content increases in the coating and with the concentration H_4L additive. The addition of P to Ni bath has an advantage of increasing the hardness coating by forming an alloy with Ni as reported earlier [43], where a maximum value of 650 HV could be reached for the coat containing more than 10 wt.% P in the as-coated deposit on steel substrate. In previous works [44-46], a wide range of hardness values were found, depending on bath composition, plating parameters, concentration of additives, as well as with different phosphorus content.

The analysis of the composition of deposits in the presence of four different concentrations of additive, EDX generally shows that an addition of additive weakly influences the composition. In fact, in both cases, nickel content increased according to the decrease in additive concentration. So, it is found that the deposits with fine grains have relatively high resistivity [47]. During the variation of additive concentration, it was found that the deposition morphology obtained has spherical nodules. This observation is similar to previous work [48], and the grain size decreases with increasing P content in the Ni-P coating. However, the concentration of 10^{-6} M shows that the decreasing grain size and nodule structure of nickel-phosphorus deposits decreased with increasing phosphorus content from other concentrations, which is in total agreement with the work of Lu and Zangari [48].

Composition and microstructure of deposits: An addition of calix[4]arene additive, depending on the concentration, does not have a marked effect on the morphology of the deposit. The four concentrations of the deposits analyzed by EDX generally showed that indeed in both cases, the nickel content

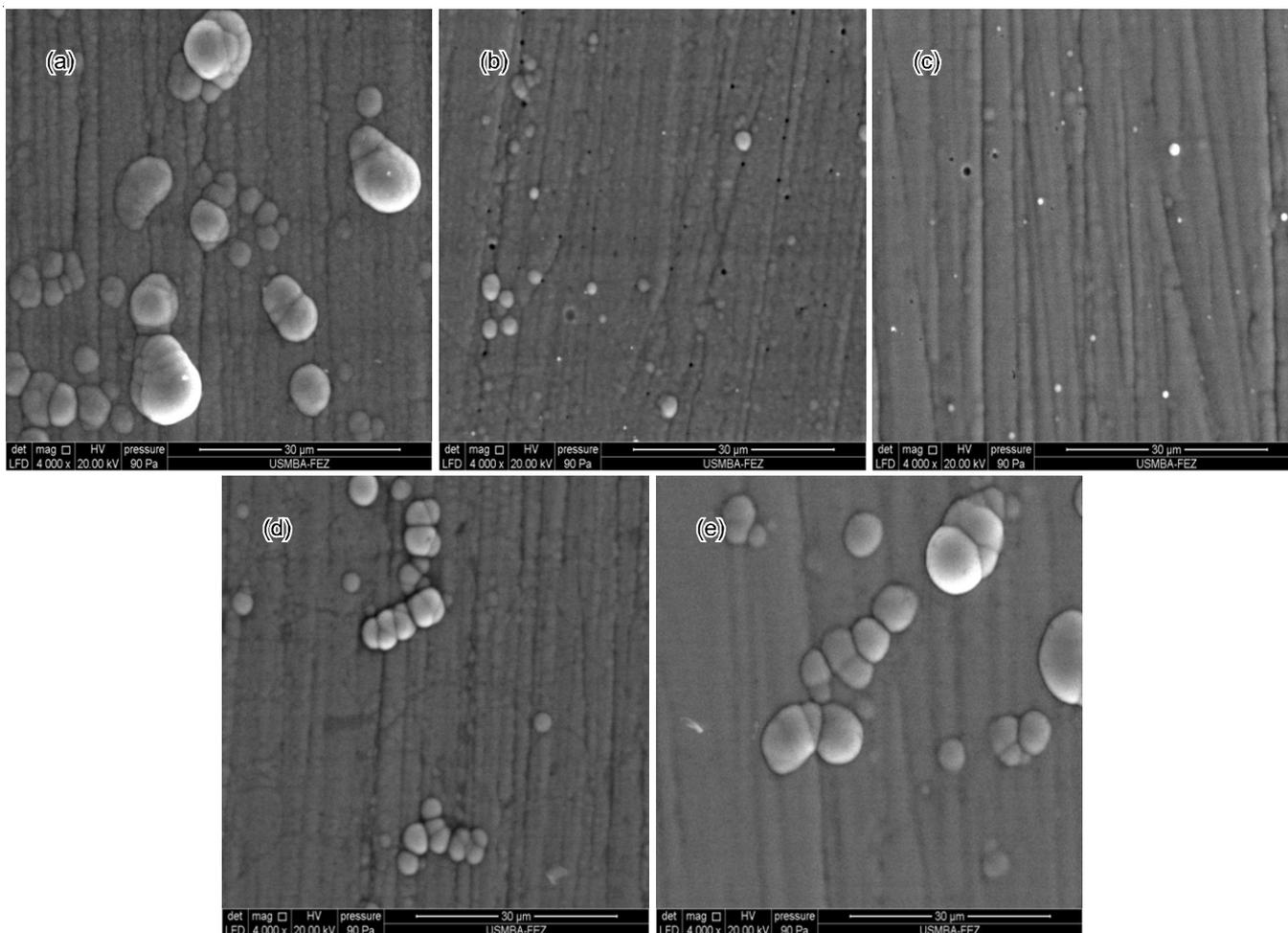


Fig. 6. SEM photographs of the electroless nickel deposits obtained from based electrolyte at different concentrations of H_4L : (a) 0 M; (b) 10^{-3} M; (c) 10^{-4} M; (d) 10^{-5} M and (e) 10^{-6} M. Based electrolyte: $NiSO_4 \cdot 6H_2O$ 0.09 M; $NaH_2PO_2 \cdot H_2O$ 0.21 M; $C_6H_5Na_3O_7 \cdot 2H_2O$ 0.05 M; CH_3COONa 0.12 M; (pH = 5.5 ± 0.1 and $T = 85 \pm 2$ °C)

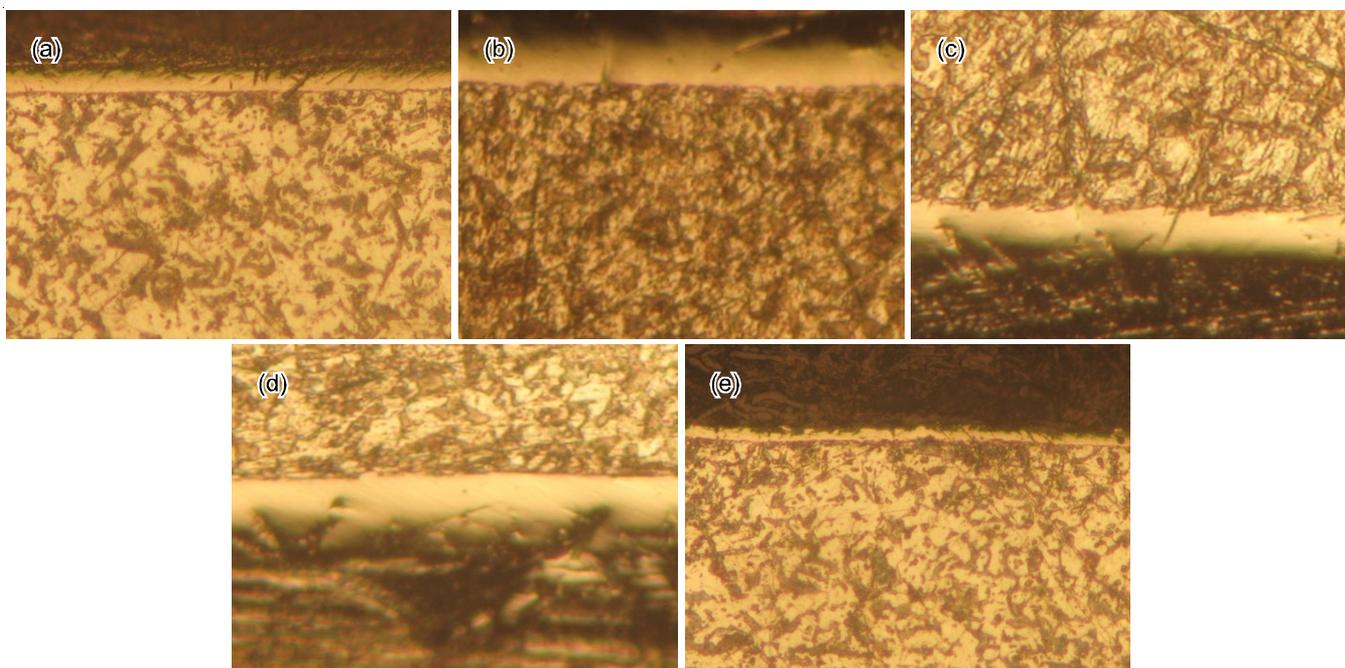


Fig. 7. Metallographic images of composite coating profile obtained from based electrolyte, (A) Without additive, (B) 10^{-3} M, (C) 10^{-4} M, (D) 10^{-5} M and (E) 10^{-6} M of additive H_4L . Based electrolyte: $NiSO_4 \cdot 6H_2O$ 0.09 M; $NaH_2PO_2 \cdot H_2O$ 0.21 M; $C_6H_5Na_3O_7 \cdot 2H_2O$ 0.05 M; CH_3COONa 0.12 M; (pH = 5.5 ± 0.1 and $T = 85 \pm 2$ °C)

decreases with the addition of concentration as indicated in Table-3 (Fig. 8). This decrease of the nickel content may be related to the increase of the deposition rate depending on the concentration [49].

Concentrations (M)	Ni (%)	P (%)
0	92.42	7.58
10^{-3}	94.36	5.64
10^{-4}	93.19	6.81
10^{-5}	92.29	7.71
10^{-6}	91.96	8.04

XRD analysis: The diffraction patterns of X-ray of deposits of electroless nickel obtained at different concentrations are shown in Fig. 9. In all the diffraction patterns, the reflections corresponding to the {111} plane of a face centered cubic (fcc) phase of nickel could be observed. It is evident from Fig. 9a and Table-4 that as deposited Ni-P coating for witness had only a single broad peak at 44.59° with a grain size of 12.8 nm. The literature has shown that Ni-P deposits containing more than 7% by weight of P have an amorphous structure [50]. In present case, it can be seen that the coating is crystalline with a P content of 8.04% at the concentration of 10^{-6} M. With a decrease of P content, the structure has changed. In addition, the total width at half height (FWHM) of the diffraction peaks

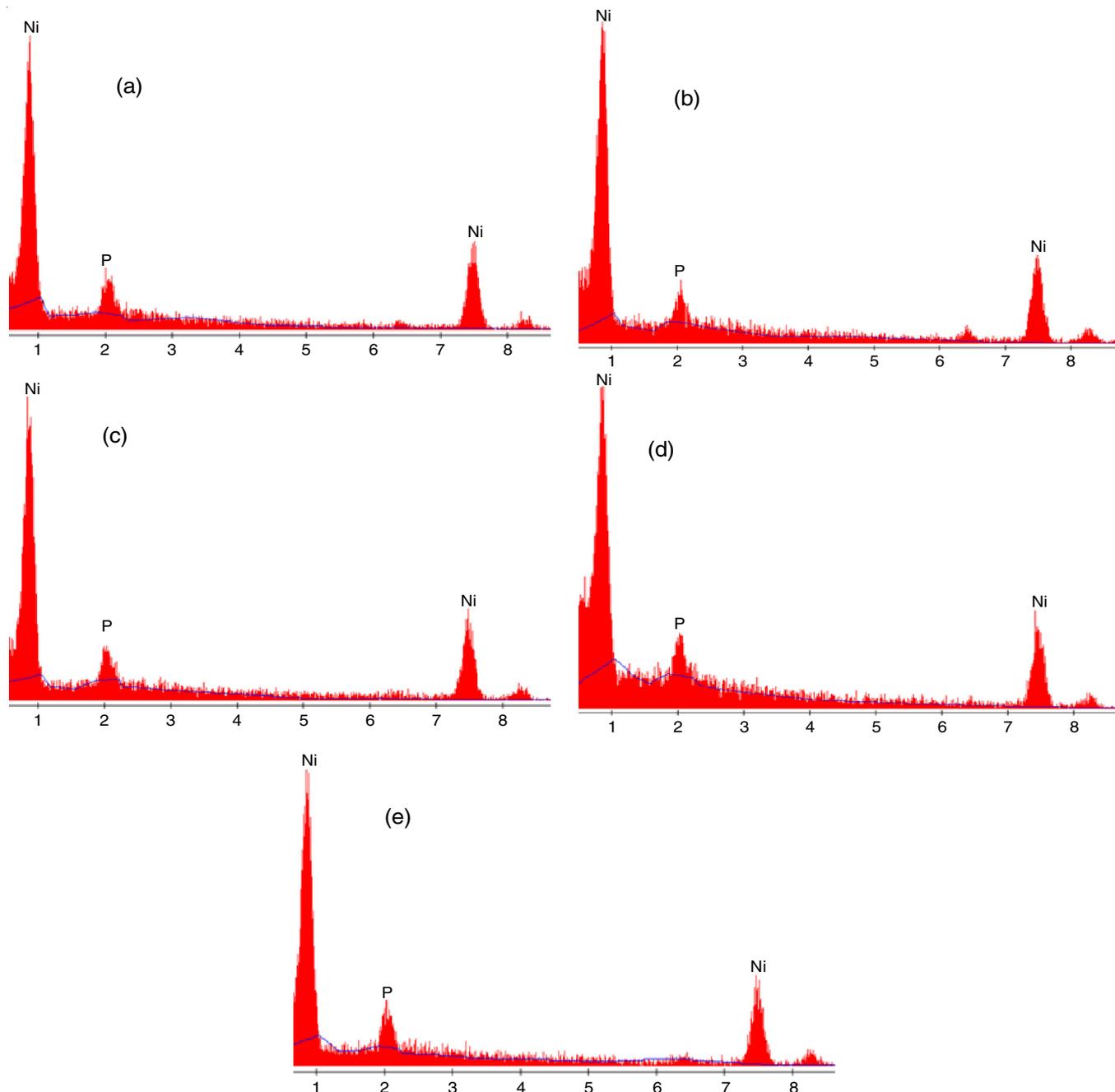


Fig. 8. EDAX Profil for the electroless nickel deposits obtained from based electrolyte at different concentrations of H₂L: (a) 0 M; (b) 10^{-3} M; (c) 10^{-4} M; (d) 10^{-5} M (e) and 10^{-6} M. Based electrolyte: NiSO₄·6H₂O 0.09 M; NaH₂PO₂·H₂O 0.21 M; C₆H₅Na₃O₇·2H₂O 0.05 M; CH₃COONa 0.12 M; (pH = 5.5 ± 0.1 and T = 85 ± 2 °C)

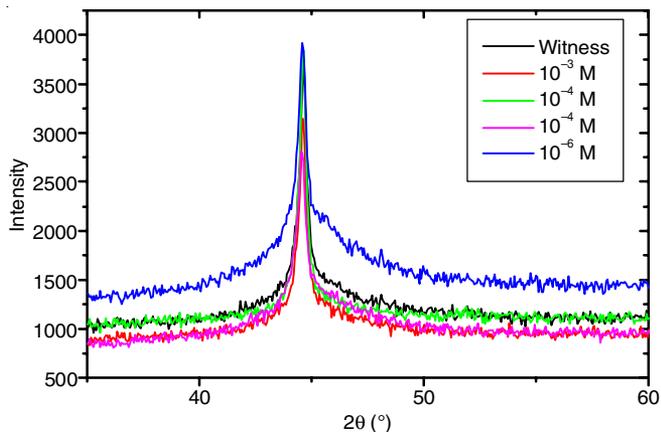


Fig. 9. X-ray diffraction patterns of electroless nickel deposits obtained from based electrolyte at different concentrations of H₄L: (a) 0 M; (b) 10⁻³ M; (c) 10⁻⁴ M; (d) 10⁻⁵ M (e) and 10⁻⁶ M. Based electrolyte: NiSO₄·6H₂O 0.09 M; NaH₂PO₄·H₂O 0.21 M; C₆H₅Na₃O₇·2H₂O 0.05 M; CH₃COONa 0.12 M; (pH = 5.5 ± 0.1 and T = 85 ± 2 °C)

TABLE-4

PEAK POSITION (2θ), FULL WIDTH AT HALF MAXIMUM AND GRAIN SIZE OF THE NICKEL DEPOSITS OBTAINED FROM THE BATH AT DIFFERENT H₄L CONCENTRATION (pH 5.5 ± 0.1 AND T = 85 ± 2 °C)

Concentration (M)	Peak position	FWHM	Grain size (nm)
0	44.59	0.44	12.8
10 ⁻³	44.57	0.47	12.1
10 ⁻⁴	44.58	0.35	17.4
10 ⁻⁵	44.54	0.42	13.8
10 ⁻⁶	44.52	0.52	10.4

decreased with the decrease of P content, indicating that the grain size was increased. Similar observations have also been reported by other authors [51]. In addition, the 10⁻⁶ M concentration has a very high peak intensity (111) relative to the other concentrations and to the control; this can give good electrical deposition properties.

Corrosion studies

Potentiodynamic polarization studies: Electrochemical potentiodynamic polarization experiments were applied in 3% NaCl solution to measure the corrosion resistances of low carbon steel alloy and as-deposited Ni-P at concentration 10⁻⁶ M in additive coating. For comparison, the corrosion properties of low carbon steel alloy coated by Ni-P without additive, deposited from basic bath and containing the same content of Ni and P have been studied. The electrochemical parameters obtained from the polarization curves (Fig. 10) for uncoated low carbon steel and the coated alloy by Ni-P with additive and Ni-P (blank) are shown in Table-5.

TABLE-5

CORROSION CHARACTERISTICS OF AS-PLATED ELECTROLESS NICKEL AND ADDITIVE COATINGS IN 3% SODIUM CHLORIDE SOLUTION BY POTENTIODYNAMIC POLARIZATION TECHNIQUE (pH 5.5 ± 0.1 AND T = 85 ± 2 °C)

	E _{corr} (mV)	I _{corr} (μA/cm ²)	E (%)
Black	-560	120	-
Without additive	-318	1.65	98.62
10 ⁻⁶ M H ₄ L	-393	1.26	98.95

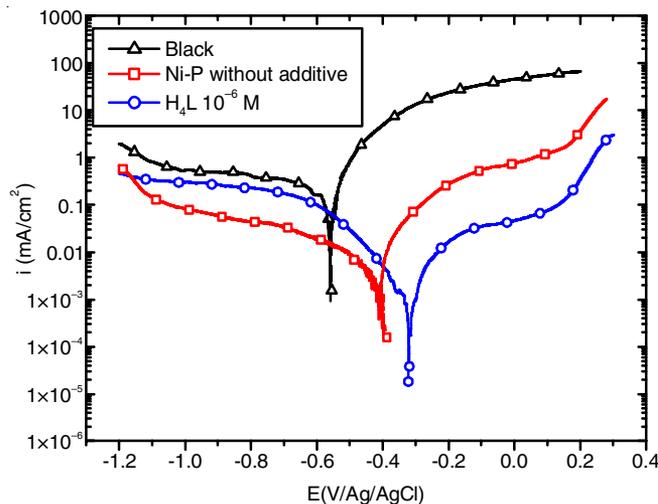


Fig. 10. Potentiodynamic polarization curves of electroless Ni-P composite coating obtained from based electrolyte in 3% NaCl solution obtained with blank (carbon steel), in the absence and presence of additive substrate

The polarization curves show that the behaviour of alloys in saline aggressive environment is generally governed by an activation mechanism. Thus, the potential E_{corr} and the current density i_{corr} at the neighborhood of ± 100 mV were measured from Tafel plot of the straight curves to which the anodic and cathodic curves show that the chemical reaction is controlled by a pure charge transfer kinetics. The anodic zone can be divided into two parts: (a) first part of the corrosion potential between -359 and 150 mV or the appearance of a pseudo-bearing in case of coatings suggests the formation of a barrier layer, which slows the dissolution of alloy; (b) second part of the potential 150 and 300 mV means an increase of the course of corrosion indicates the dissolution or the rupture of barrier layer.

Extrapolation of Tafel straight lines makes it possible to determine the rate of corrosion. The values of i_{corr} of the coating obtained are reported in Table-5. It is clear that corrosion current density values for the coating in 3% NaCl solution is around 1.26 μA/cm². Higher corrosion current density values are obtained for carbon steel substrate. The application of alloy significantly changes the shape of the polarization curves compared to only steel substrate. It is noted that the additives have an anodic character. In general, the corrosion resistance of any alloy depends on the speed of formation of a surface protective film.

Electrochemical impedance spectroscopy studies: The impedance measurement technique has been applied to the study of pitting corrosion and other localized corrosion [52-55]. The impedance technique has marked advantages in the study of interfacial reactions and other interfacial phenomena. The impedance information obtained has time-resolved and surface-averaged characteristics [55]. Fig. 11 shows the Nyquist representations electrochemical impedance obtained for ordinary steel substrate coating and uncoating by electroless Ni-P in the presence of additive H₄L coatings in 3% NaCl solution at their respective open circuit potentials. All curves appear to be similar (Nyquist curves) and consist of a single semi-circle in the high frequency region indicating that the reaction is

TABLE-6
ELECTROCHEMICAL PARAMETERS OF CORROSION OF Ni-P CHEMICAL DEPOSITION
IN THE PRESENCE OF ADDITIVE IN 3% NaCl (pH 5.5 ± 0.1 AND T = 85 ± 2 °C)

	R_s (k Ω cm ²)	Q_{ct} (μ F/cm ²)	α_{ct}	R_{ct} (k Ω cm ²)	Q_{dif} (μ F/cm ²)	α_{dif}	R_{dif} (k Ω cm ²)	R_p (k Ω cm ²)
Carbon steel	0.010	201	–	175	–	–	–	0.165
Without	0.011	35	0.86	3.468	11	0.63	21.922	25.38
10 ⁻⁶ M of H ₄ L	1.716	0.1	1	10.5	0.03	0.83	24.000	32.784

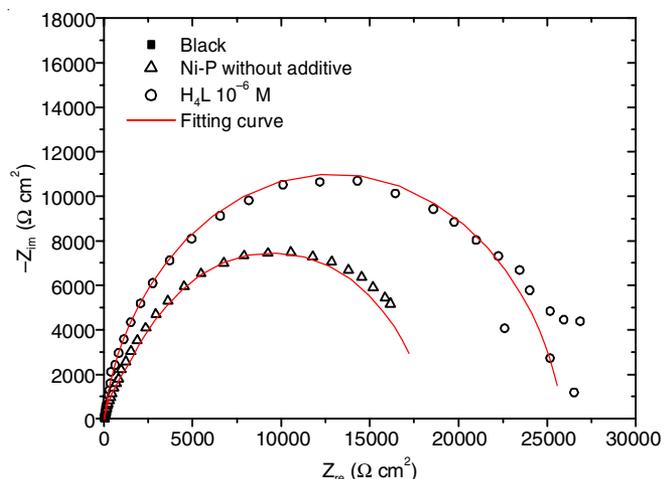


Fig. 11. Electrochemical impedance spectra of electroless Ni-P composite coating obtained from based electrolyte in 3% NaCl solution obtained with blank (carbon steel), in absence and presence of additive substrate. Based electrolyte: NiSO₄·6H₂O 0.09 M; NaH₂PO₂·H₂O 0.21 M; C₆H₅Na₃O₇·2H₂O 0.05 M; CH₃COONa 0.12 M; (pH = 5.5 ± 0.1 and T = 85 ± 2 °C)

governed by charge transfer. The electrochemical parameters obtained from the diagrams are listed in Table-6. Moreover, even if the corrosion current density values obtained for all the coatings are lower than those of the carbon steel, the addition of additive to our formulation has increased the polarization resistance R_p thus that an effectiveness of corrosion inhibition of these coatings is achieved.

Conclusion

The effect of calix[4]arene as an additive on the formation and characteristics of electroless Ni-P deposits obtained from an acidic hypophosphite reduced electroless nickel bath was investigated. The study shows that the variation of the additive concentration influences the composition of the deposits. The deposition rate increases with the increase of additive, as well as the appearance, adhesion and also the stability of the bath chemical have been improved. Indeed, at the concentration 10⁻⁶ M of additive, a spherical nodular structure becomes more homogeneous and more compact. The microhardness deposits improve and increases as a function of the additive concentration to achieve to a maximum value of 376 HV at the same concentration. The XRD revealed peaks corresponding to the deposits have an intensified orientation plane with calix[4]arene addition at 10⁻⁶ M. Electrochemical measurements showed that kinetic parameters depend on the variation of the concentration of additive. The electrochemical and gravimetric measurements were in total agreement. The anti-corrosion properties of Ni-P coatings were investigated in 3% NaCl solution by the potentiodynamic polarization techniques, where it was found that Ni-P coating obtained using the concentration of

the additive at 10⁻⁶ M has very good resistance in the corrosive solution.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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