Effects of functional groups of triple bonds containing molecules on nickel electroplating

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Abstract: The effects of propargyl alcohol (PA), propynol ethoxylate (PME), propargyl sulfonate (PS), and diethylamino-propyne (DEP) compounds as additives in a Watts bath on coating brightness, thickness, and efficiency were investigated and compared using electrochemical methods such as linear and square wave voltammetry (SWV), chronoamperometry, chronopotentiometry, electrochemical impedance (EIS), and X-ray fluorescence (XRF) spectroscopy. The charge transfer resistance values obtained in the presence of PA and PME were similar and higher than the other values obtained; this result suggests that PA and PME have better adsorption. The optic and XRF measurements revealed that for the PS molecule the plating is the brightest, and its leveling effect is the highest at the high current density, while the PA molecule has the same effect at low current density. The surface coverage (θ) values of the PS and PA molecules were determined from adsorption isotherms and the results show that PA has higher % θ. In addition, the optimization of PA, PME, PS, and DEP molecules was performed using a RHF basis set, and the results agreed with the experimental results. The SEM results obtained in the presence of additives revealed that brighter and smoother surfaces were obtained at low concentrations.

Key words: Nickel electroplating, brightener, leveler, propiolic alcohol, propynol ethoxylate, propiolic sulfonate, diethylaminopropyne

1. Introduction

To achieve bright and commercially acceptable nickel plating it has been found that a combination of several organic additives must be added to Watts baths. These organic additives are adsorbed on the cathode surface and make the crystal size smaller. Brighteners are classified into first class (characterized by the group $=SO_2$ group in the molecule) and second class (characterized by the presence of an unsaturated group C=O, C=C, C≡C, C=N, and C≡N in the molecule); these 2 types of brighteners are used together.[1−5] Many researchers have published articles on the effect of these organic additives on the surface morphology and crystal structure of electroplated nickel.[6−9] In one of these studies, the electrochemical behavior of saccharine and 3 types of diol compounds (butanediol, butenediol, butynediol) added to a Watts bath and the repressive effect of such organic additives on the electrocrystallization of nickel were reported. With the addition of saccharine and butynediol, smooth and compact electroplating was achieved.[6] In another study, Nakamura investigated the electrochemical characteristics of 3 types of aliphatic alcohols (n-propyl alcohol, allyl alcohol, propargyl alcohol) and their effects on the surface morphology of nickel electroplated material and the crystal direction when used

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concomitantly with saccharine.[1] According to these results, for higher bond counts in the molecule, a greater tendency to shift to the negative area was observed; propargyl alcohol shifts the nickel reduction potential to the negative area the most.

Organic additives affect the surface of the cathode by acting as adsorbents by which physical and chemical adsorption occur. It is known that the adsorption isotherms are very important for understanding the mechanism of adsorption. The most frequently used isotherms are Langmuir,[10−12] Freundlich, Temkin, and Frumkin equations. Many approaches explain the adsorption–desorption properties of these additives. The most important of these approaches is the Langmuir isotherm (Eq. (1)).

$$\theta = \frac{\alpha \cdot P}{1 + \alpha \cdot P}, \tag{1}$$

where θ is the fractional coverage of the surface, P is the gas pressure or concentration, and α is a constant. In the literature this equation was adapted to electrochemical impedance measurements and arranged.[13,14]

When compared with other methods, electrochemical impedance spectroscopy (EIS) has important advantages that are obtained without damaging the material in the assessment of metal interfaces related to plating, corrosion inhibitors, and materials, including anodizing materials, and it is possible to obtain detailed information about electrochemical mechanisms and reaction kinetics using this technique.[15] Square wave voltammetry is a complex but powerful pulse technique that enables one to determine changes in the voltammetric response with time nondestructively and the peak-shape voltammogram obtained displays excellent sensitivity and rejection of background current, via the help of the fast-scan capability.[16,17] It is also possible to analyze organic and inorganic materials in a solution using a square wave voltammogram.[18,19]

The goal of the present study was to investigate the effects of change in the functional group (Y) in the main skeleton (C≡C–C–Y) of organic additives used in nickel electroplating baths on the resulting coatings. Molecules that have Y= –OH (PA), –OCH$_2$–CH$_2$–OH (PME), –N(CH$_2$CH$_3$)$_2$ (DEP), and –SO$_3^-$ (PS) as the functional groups are illustrated in Scheme 1.
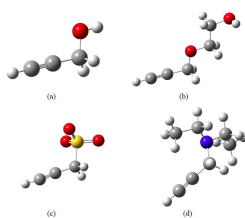
Scheme 1. The structure of organic additives used in nickel bath; a) propargyl alcohol (PA), b) propynol ethoxylate (PME), c) propargyl sulfonate (PS), d) diethylaminopropyne (DEP).

2. Results and discussion

2.1. Linear sweep voltammetry

The linear voltammograms obtained in bath A and in the baths with organic additives (A1, A2, A3, and A4) in the range of 0.0 to –1.5 V with a scanning rate of 20 mV/s are presented in Figure 1. The peak current (I_p) values and the initial potentials of deposition ($E_{initial}$) obtained from these voltammograms are summarized in Table 1.
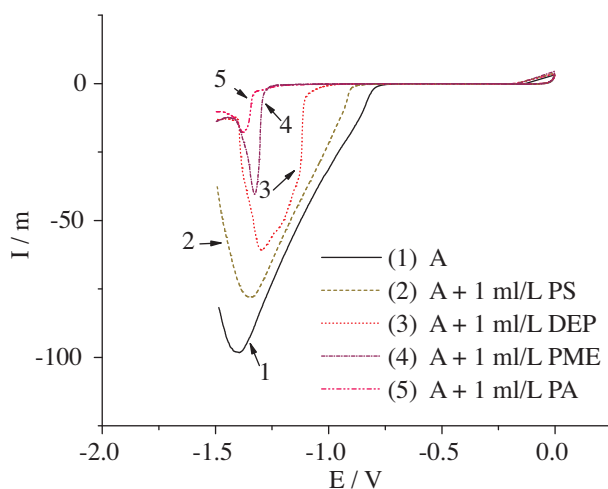
Figure 1. The current–potential graphs of Watts bath (A) and in the presence of organic additives (A1, A2, A3, A4).

Table 1. The parameters obtained from current–potential graphs of Watts bath (A) without and with organic additives (A1, A2, A3, A4).

Baths	$E_{initial}$ (V)	I_p (mA)	E_p (V)
A	−0.79	98.30	−1.39
A1	−1.32	17.91	−1.38
A2	−1.28	40.41	−1.33
A3	−0.88	77.04	−1.35
A4	−1.08	60.82	−1.29

Unsaturated linkage in the molecule causes the deposition potential to shift to the negative area.[1] The additives hinder the reduction of nickel, causing the crystal size to shrink. PA is the molecule that causes the highest negative shift in Ni reduction, and PME behaves similarly to PA because they have very similar structures.

2.2. Effects of organic additives on brightness, thickness, and efficiency

The thickness, efficiency, and brightness values of nickel-electroplated plates in a basic Watts bath (A) and organics-added baths (A1, A2, A3, A4) were determined by XRF measurements and glossmeter and are presented in Figures 2a–2c, respectively. As observed in Figure 2a, with the addition of organic additives, the thickness value decreased for all cases compared with bath A. This result might be due to the adsorption of organic additives on the surface. The surface brightness value decreased only for DEP, while other additions resulted in brighter surfaces. Although the thickness order is A > A3 > A4 > A2 > A1 (Figure 2a), the order of the brightness values of the molecules is A3 > A1 > A2 > A > A4 (Figure 2b).

The efficiency was calculated from the experimental and theoretical values of deposition using Faraday's law. The plates that were used as cathodes were weighed before and after plating. All of the nickel plating was achieved after 5 A for 5 min. The highest efficiency was obtained for bath A, and the lowest was obtained for bath A1 because the PA molecule in bath A1 shifts the Ni reduction potential to the negative area the most. The order of the plating efficiencies of the baths was A > A3 > A4 > A2 > A1, which is the same order as for the thickness, as expected.
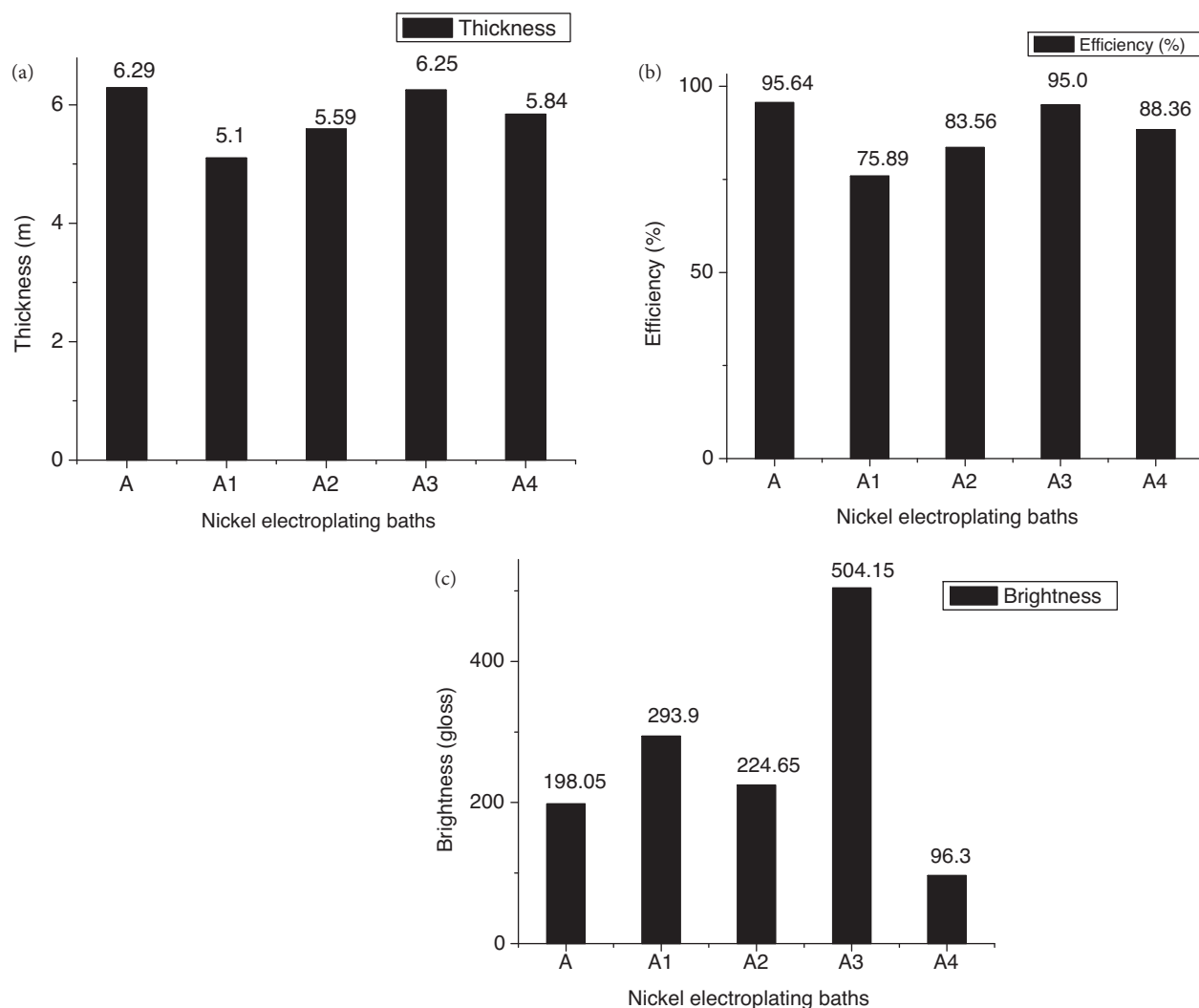
Figure 2. The thickness (a), efficiency (b), and brightness (c) measurements of nickel electroplated plates in Watts baths (A) with and without organic additives.

It appears that the decrease in thickness is correlated with an increase in brightness because the decrease in thickness is also related to the shift of nickel reduction potential to the negative area. Organic additions hinder the reduction of nickel, causing the crystal size to shrink.[1] The molecule PA causes the highest negative shift in Ni reduction. When the baths are sorted according to the shifts in the nickel reduction potential, the order is A1 > A2 > A4 > A3 > A.

It is expected that the molecule whose thickness decreases the most will achieve the brightest surface. However, this did not occur in our study. Thus, it is better to examine other parameters. The measuring principle of the glossmeter might be one of the reasons for this discrepancy. When there is a roughening in the macro size, the brightness value obtained from the glossmeter is low even if the surface is bright, as reported in the literature.[6] When the baths are ordered according to their macro roughness, as examined visually, the order is A4 > A2 > A1 > A3 > A. The difference in brightness determined from the glossmeter measurements from the observations with the naked eye originates from the different surface roughness, which affects the reflection of light and makes the comparison unreliable. To support this idea, the effect of the concentration of organic

additives on the brightness and thickness was examined when PA was added to this B bath in concentrations of 0.005 mL/L, 0.010 mL/L, and 0.020 mL/L. Low concentrations were selected as much as possible to keep the internal stress and decomposition products low and to increase the durability of the bath. In the absence of PA, for the plate surface with current density of 0.1 A/dm^2, the brightness value is 673.1 gloss, and this value increases up to 1004 gloss with the addition of 0.020 mL/L PA (Figure 3). At the same current density, the thicknesses were observed to be 0.831 μm and 0.584 μm in the absence and in the presence of 0.020 mL/L PA, respectively. When the plates have similar roughness, using the additives at low concentrations makes the comparison more reliable, and the expected relationship between thickness and brightness can be determined. Increases in brightness together with the decrease in plating thickness with the increase in PA concentration support the idea that the adsorption of PA slows the reduction of Ni ions on the cathode surface and leads to fine-grained, compact, and smooth Ni electrodeposits, as reported in the literature (Figure 3).[1]
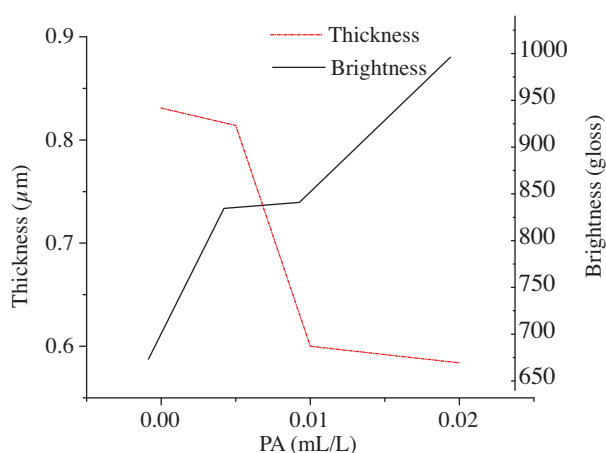

Figure 3. The value of brightness and thickness in 0.1 A/dm^2 current density areas in the presence of PA in B bath.

2.3. Chronoamperometric and chronopotentiometric study

Potential-controlled current-time and current-controlled potential-time graphs were obtained for bath A and baths A1, A2, A3, and A4 and are presented in Figures 4a and 4b, respectively. In the chronoamperometric study, when –1.0 V was applied, the highest current was observed in bath A; for the organic additives, the current intensity decreased in the following order: PS > DEP > PME ≈ PA. For PA and PME, this decrease was more significant, and the current values were very similar.

In the chronopotentiometric study, for PA, the highest voltage should be applied to obtain the desired constant current (–10 mA) (Figure 4c). A higher hydrogen evaluation rate caused some distortion in the curve. Chronoamperometric and chronopotentiometric studies suggest that PA addition results in a decrease in the current and an increase in the potential with the aid of better adsorption than the other additives. These results are consistent with the linear voltammetry results.

2.4. The effect of the concentration of PA and PME molecules

Because the PA and PME molecules were observed to be the most effective for brightening and leveling in nickel electroplating baths, many baths with different PA and PME concentrations and PA and PME mixtures were prepared. Linear voltammograms were obtained for these baths, and the results are provided in Figures 5a–5c.
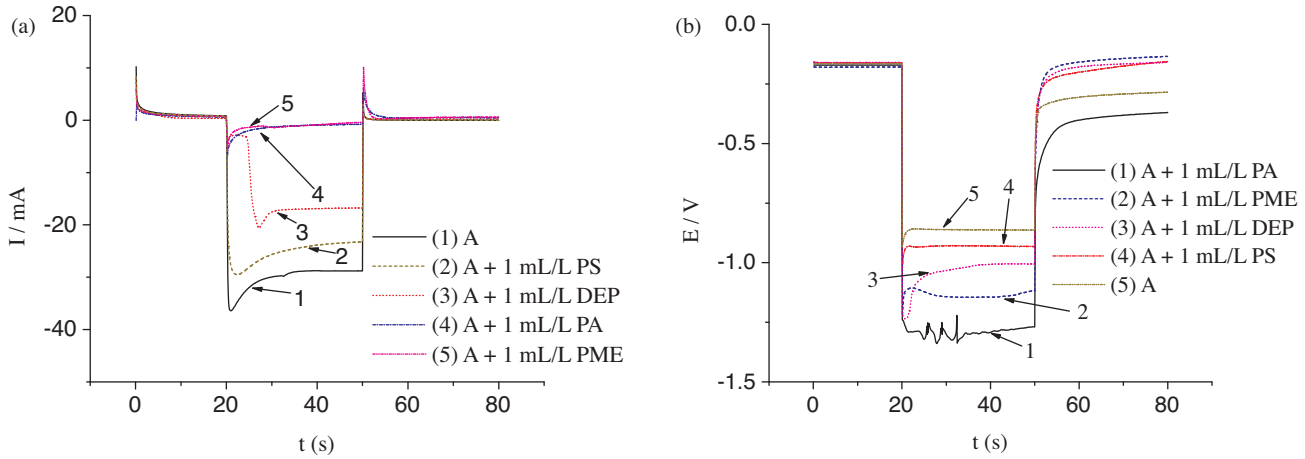
Figure 4. (a) Chronoamperometric, (b) Chronopotentiometric study without and with organic additives (A1, A2, A3, A4) in Watts nickel electroplating baths.
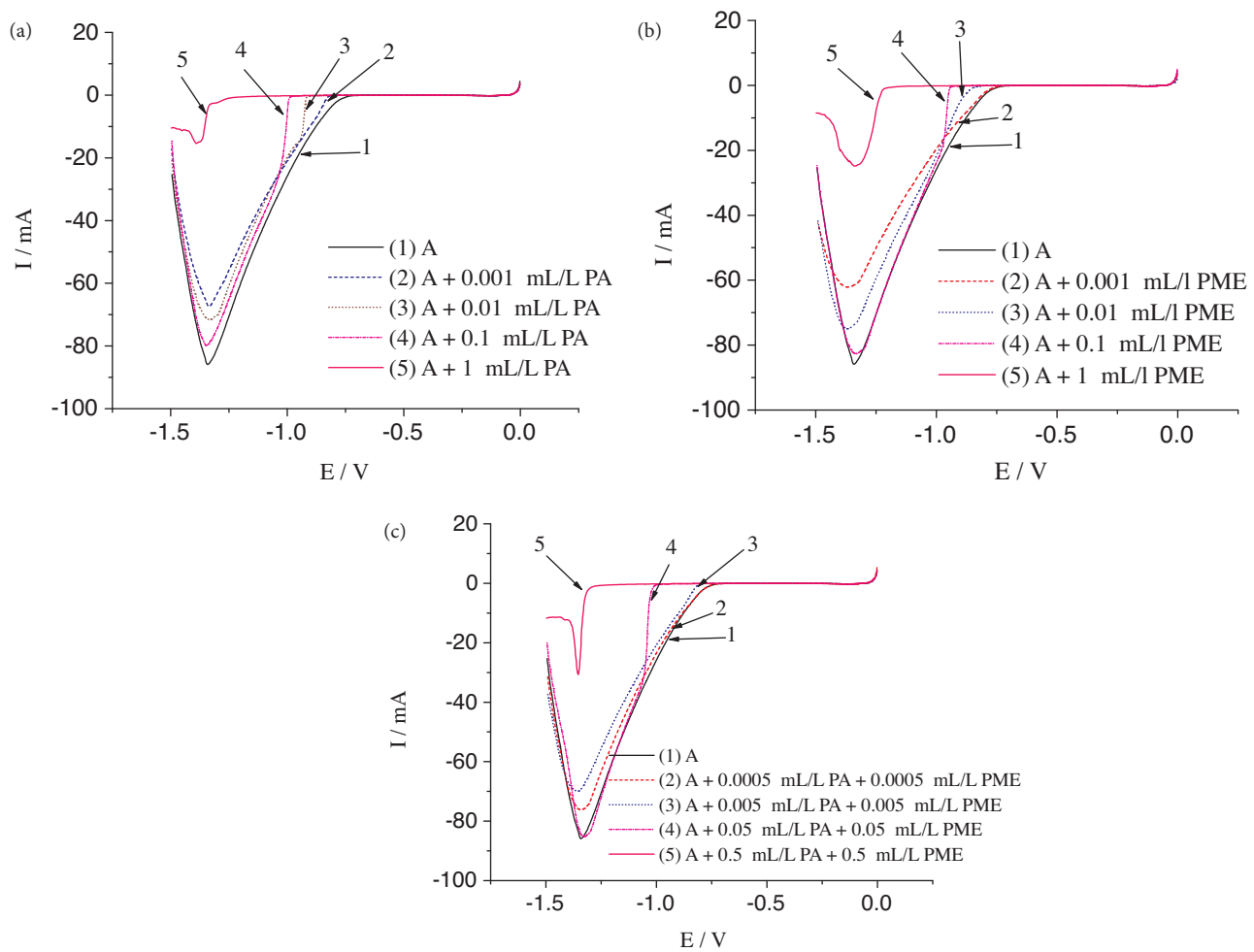

Figure 5. Potential–current curves obtained from (a) PA (b) PME (c) PA and PME molecules added to nickel electroplating baths in different concentrations.

At lower concentration levels, PA is more active than the PME molecule. When PA and PME molecules were added separately to bath A, the PA molecule (Figure 5a) shifted the nickel reduction potential to a negative potential to a greater extent than did the PME molecule (Figure 5b). When the concentration is increased, the current intensities decrease in both cases. At a higher concentration of additives, the amount of the shift in the reduction potential of Ni becomes too high, which causes H_2 evolution and a decrease in the deposition efficiency. Therefore, to overcome this disadvantage, PA and PME should be added at the minimum concentrations that yield the optimum plating properties.

To understand the effect of a mixture of additives, PA and PME were added together, and the results indicate that these additives behave similarly to a single compound (Figure 5c).

2.5. EIS studies

EIS measurements were also performed in baths A, A1, A2, A3, and A4. Before the measurements, the electrodes were left for 1 h to balance the cathode surface, and then impedance measurements were performed. The Nyquist diagrams obtained from baths A, A1, A2, A3, and A4 are presented in Figures 6a and 6b. The impedance data were analyzed graphically with the use of Z Simp-Win software. The conventional equivalent circuit consists of a series of a resistor and capacitor, $R_s(C_{dl}(R_p \text{ or } R_{ct}))$, where R_s is the uncompensated ohmic resistance between the working electrode and the reference electrode, R_p is the polarization resistance, and C_{dl} is the differential double layer capacitance, which represents the total capacitance at the metal/electrolyte interface. The fit was considered to be good if the χ^2 parameter was below 10^{-4}. The impedance parameters obtained from these measurements are summarized in Table 2.
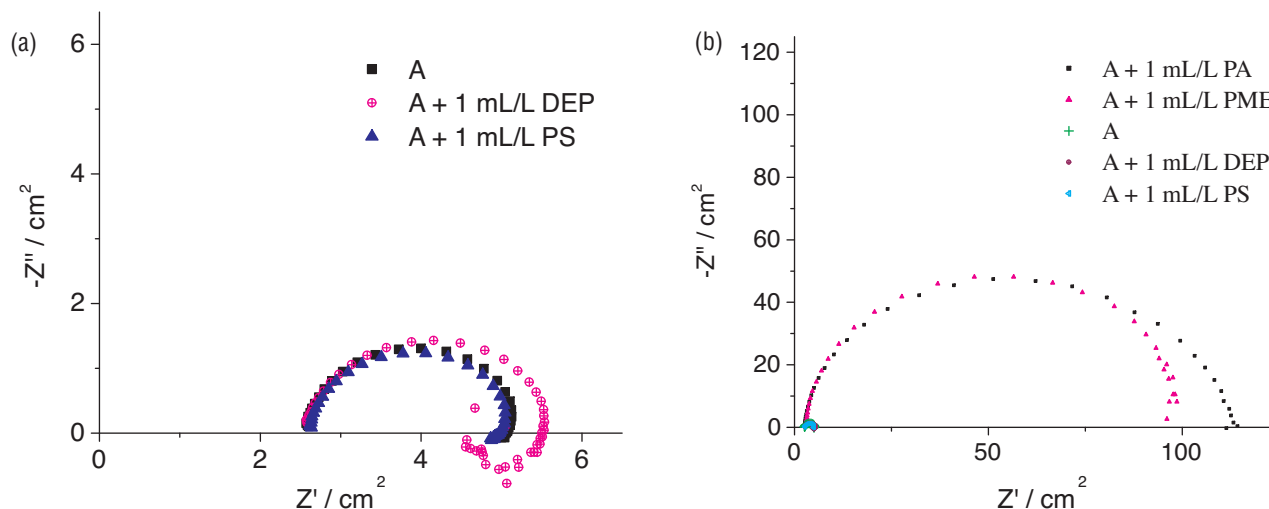

Figure 6. Electrochemical impedance spectroscopy from (a) A, A3, A4 (b) A1, A2 nickel plating baths.

Table 2. The impedance parameters obtained from different nickel baths.

Baths	R_s (ohms cm)	C_{dl} (μF/cm^2)	R_{ct} (ohms cm)
A	1.3	53.8	1.25
A1	1.4	7.8	52.25
A2	1.5	6.8	48.15
A3	1.25	53	1.2
A4	1.45	47	1.35

The solution resistance values are very similar, as expected. The lowest charge transfer resistance was obtained when the nickel plating was performed in the presence of PS (26.5 ohms) (Table 2), which facilitated the reduction of nickel ions. This result provides an explanation for the high efficiency of PS. For PA and PME, high R_{ct} values result in a decrease in the efficiency of the nickel plating and explain why the reduction of nickel is hindered (Figure 6). The impedance parameters obtained in baths A3 and A4 are very similar to the impedance parameters of bath A. However, the charge transfer values of baths A1 and A2 increase when the capacitance values decrease.[23] The change in Cdl values was caused by the gradual replacement of water molecules by the adsorption of the organic molecules on the metal surface.[24] This result indicates that the PA and PME molecules are better adsorbed to the electrode surface compared with the DEP and PS molecules.

The voltammetry and EIS results are consistent with each other and suggest that PA- and PME-added baths hinder nickel reduction due to better adsorption.

2.6. Square wave voltammetry

For SWV measurements, different concentrations of the PA, PME, and PA–PME mixtures were added to bath A, and voltammograms were obtained (Figure 7).

When 0.001 mL/L DEP was added to bath A, the maximum peak potential was observed at –854 mV, and, at higher concentrations, this peak potential disappeared (Figure 7a). For PS, at all the concentrations, only a small shift to the negative value in the nickel reduction potential is observed (Figure 7b). For the PA and PME addition, while at lower concentrations only small shifts to the negative area were observed, as the PA concentration increased the adsorbed molecules covered the surface to a greater extent. As a result, the net current diminished until finally the value became zero. When the concentrations were increased to 0.1 mL/L, this peak disappeared (Figures 7c and 7d), which is related to the change in the plating mechanism from being kinetic controlled to being diffusion controlled. When the PA and PME molecules were used together, the same behavior was observed as for the individual addition of PA and PME (Figure 7e).

2.7. Langmuir isotherms for PA and PS adsorption

Electrochemical impedance spectroscopy is a useful method to characterize the cathode surface by using R_{ct} values. The literature indicates that adsorption on the cathode surface is not only based on the structure of the organic additives but also depends on the concentration of the adsorbent and immersion time.[4,7] Additives that are adsorbed on the cathode surface hinder the reduction of nickel. The voltammetry results suggest that PA hinders the reduction of nickel the most and that PS hinders the reduction the least. In order to gain information about the relationship between adsorption ability and voltammetric behavior of organic additives, the solutions were prepared by separately adding PA and PS molecules in various concentrations to bath A, and impedance measurements were performed by applying –1.0 V DC voltages. The Nyquist diagrams are presented in Figures 8a and 8b, and the charge transfer resistances (R_{ct}) obtained from these measurements are summarized in Tables 3 and 4. It has been reported[13,14] that the adsorption mechanism on the cathode surface obeys the Langmuir isotherm. Therefore, the degree of surface coverage (θ) for different concentrations of organic additives has been evaluated from impedance measurements from Rct values by using Eq. (2):

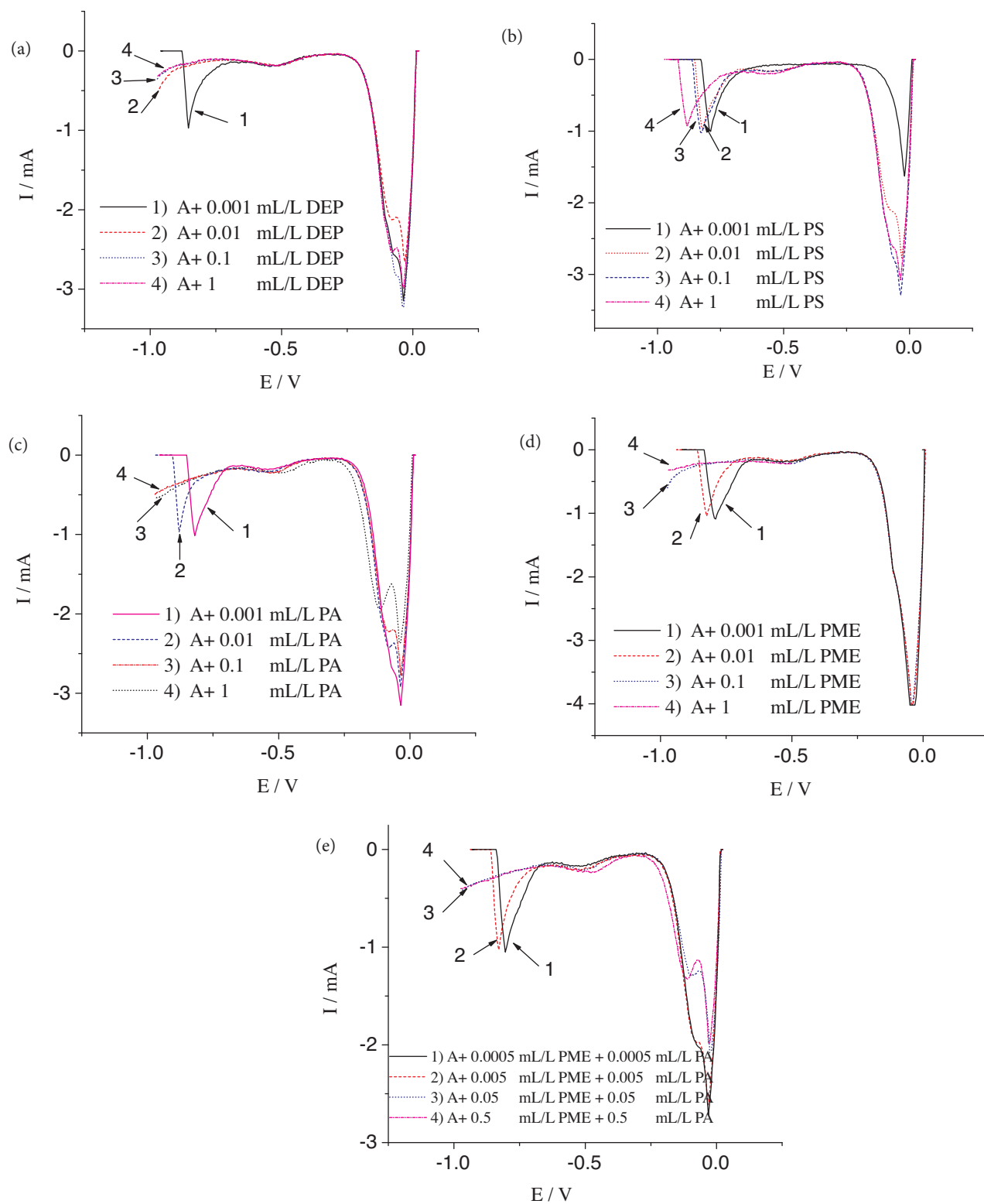$$\theta = \frac{Rct(ads) - Rct}{Rct(ads)} \tag{2}$$

Figure 7. SWV curves obtained from nickel plating baths including (a) DEP, (b) PS, (c) PA, (d) PME, (e) PA and PME molecules.
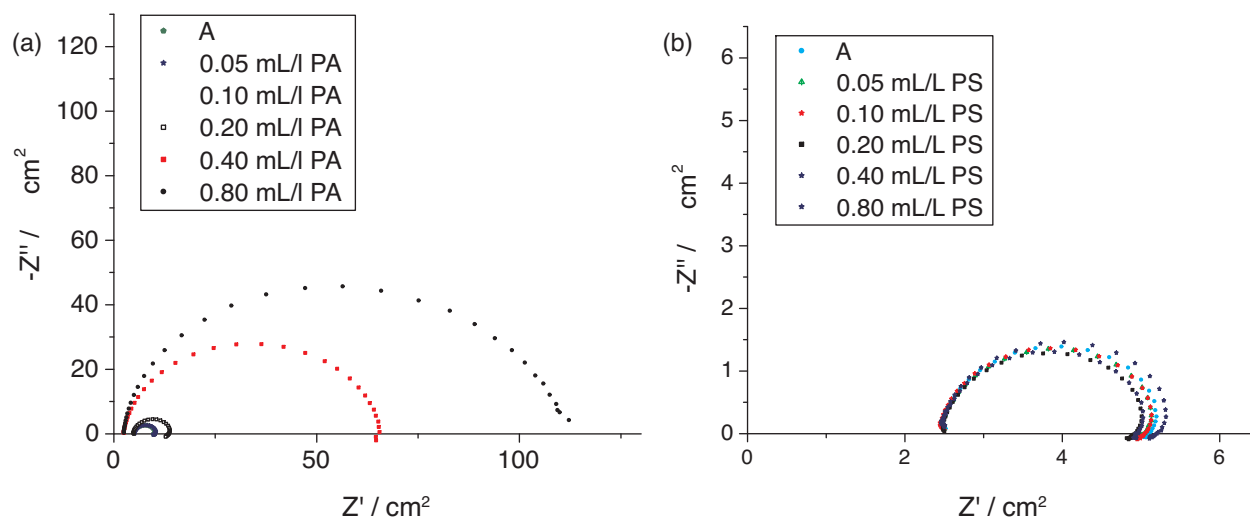
Figure 8. Impedance measurements of (a) PA and (b) PS molecules at various concentration in nickel electroplating bath.

Table 3. Impedance parameters of PA molecule.

PA (mL/L)	R_{ct} (ohms)	θ	θ %
A	2.5		
A + 0.05	2.5	0.0051	0.5
A + 0.1	2.6	0.0152	1.5
A + 0.2	4.3	0.4191	41.9

Table 4. Impedance parameters of PS molecule.

PS (mL/L)	R_{ct} (ohms)	θ	θ %
A	2.5		
A + 0.05	2.8	0.0945	9.5
A + 0.1	2.7	0.0597	5.9
A + 0.2	2.6	0.0307	3.1

where the θ and *Rct(ads)* and *Rct* parameters represent the surface coverage, and charge transfer resistance with and without an organic additive, respectively.

When the PS concentrations increased, R_{ct} remained almost constant. In addition, almost the same θ values were obtained (Table 4). The R_{ct} values obtained from bath A increased from 2.5 to 4.3 ohms in the presence of 0.2 mL/L PA, and the surface coverage percentages (θ%) increased to 42%. Because the percentage of surface coverage of PA is high, as observed previously in voltammetry and impedance results, in the presence of PA, the reduction of nickel ion was hindered on the cathode surface. The low surface coverage of the PS molecule may result because the molecule dissolves ionically in solution. The anionic character of PS caused the molecule to move toward the high current density region, where positive nickel ions are very dense and where interaction with these ions is more favorable, instead of adsorbing on the negatively charged cathode surface.
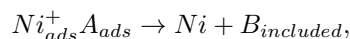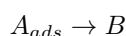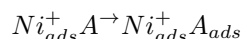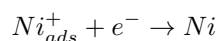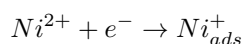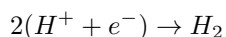
By using surface coverage values, the Langmuir adsorption isotherm model can also be described by the following equation:

$$\theta/(1 - \theta) = K_{ads}c, \tag{3}$$

where K_{ads} is the equilibrium constant of the adsorption process and c is the additive concentration. The data were tested graphically by fitting to various isotherms. A best fitting straight line is obtained for the plot of c/θ vs. c with slopes close to 1 for all additives. Strong correlations were found for the compound PA, $R^2 = 0.99$, and for PS, $R^2 = 0.98$. This suggests that the adsorption of additives on the metal surface for PA and PS obeys Langmuir's adsorption isotherm.[13]

2.8. Computational study on PA, PME, PS, and DEP molecules

The mechanism of Ni^{2+} reduction from acid sulfate solutions has been extensively studied by Epelboin et al., using Watts electrolytes. It is generally acknowledged that the electrocrystallization of the Ni^{2+} ion will occur in several steps. It was suggested that there were 2 successive faradic reactions, the first involving the formation of Ni_{ads} followed by subsequent reduction to Ni. However, organic additives in the presence of freshly deposited nickel strongly bond to the electrode surface and inhibit reduction. Most of the studies conducted to date point to a complex relationship between the nature and presence of inhibiting species and the reduction of nickel and hydrogen.

$$2(H^+ + e^-) \rightarrow H_2$$

$$Ni^{2+} + e^- \rightarrow Ni^+_{ads}$$

$$Ni^+_{ads} + e^- \rightarrow Ni$$

$$Ni^+_{ads} A \rightarrow Ni^+_{ads} A_{ads}$$

$$A_{ads} \rightarrow B$$

$$Ni^+_{ads} A_{ads} \rightarrow Ni + B_{included},$$

where A represents organic additive (PA, PS, DEP) and B shows the decomposed organic additives.

To understand the adsorption–plating property relationship, the geometries of PA, PME, DEP, and PS molecules were optimized using the RHF method and 6-31+G(d) basis, and the HOMO and LUMO energies of the geometries and dipole moments were calculated. The results are summarized in Table 5. The molecules have a singlet structure; thus, they have no unpaired electrons in the HOMO energy levels.

Table 5. The theoretical calculation results of PA, PME, DEP, and PS molecules.

Chemicals	Dipole (Depye)	E_{HOMO} (Hartree)	E_{LUMO} (Hartree)
PA	2.17	−0.391	0.061
PME	2.12	−0.393	0.077
DEP	1.27	−0.355	0.075
PS	5.87	−0.243	0.158

From experimental and theoretical evidence, it is clear that PA acts as an effective organic additive to brighteners for Ni plating baths. Molecules that contain triple bonds are known to show good adsorption ability to metal surfaces via the pi electron.[5,8] Although all molecules have triple bonds, functional groups such as alcohol (PA), ethoxylate (PME), sulfonate (PS) and dietylamino (DEP) seem to affect the adsorption ability of triple bonds. Because PA has the highest HOMO and the lowest LUMO energies, an electron from the HOMO is more favorable, and an electron that comes to the LUMO from the cathode surface is more stable; thus, adsorption becomes stronger than that of the others.[25,26] The high coverage obtained from the adsorption

isotherm supports this idea (Table 5). However, the better effect of the PA molecule on the brightness and leveling at low current density than at high current density results from the low dipole moment of this molecule, which causes the molecule to be less attractive to positively charged Ni ions in the bulk.

Because the LUMO energy of the PS molecule is very high, it does not obtain an electron from the cathode; thus, physical adsorption appears to be more favorable.

Although the dipole moment of the DEP molecule is the lowest because it has a larger structure than PA and PME, steric hindrance inhibits its interaction with the cathode surface, and its effectiveness becomes low.

Electrochemical measurements indicate that the PA molecule shifted the reduction potential of nickel the most, which led to an increase in the nucleation number and a decrease in the particle size. Computational studies are in agreement with the experimental results.

2.9. Surface morphology of nickel electroplated material with PME addition

To obtain further information about the effects of organic additives on surface morphology, SEM images of the nickel coatings obtained in the presence of different PME concentrations in bath B were taken (Figures 9a–9c). Random deep cracks and lines are observed in the plating obtained from B bath (Figure 9a). However, in the presence of 0.1 mL/L PME, the cracks disappear and lines are observed (Figure 9b), which confirms that the PME molecules have a very good leveling effect in low current densities on Ni electroplating. Further PME addition (0.3 mL/L) causes the formation of deep cracks (Figure 9c). As the additive adsorbs on the surface, it prevents a homogeneous distribution of nickel, and, as observed in Figure 9c, ordered deep lines containing nickel plating appear.

In conclusion, smooth and fine-grained Ni electrodeposits can be obtained as the concentration of the additives is increased to a certain extent, and these results are consistent with studies in the literature.[8] When we compared the SEM images with the images obtained by Nakamura for the PA molecule, the plating achieved in the presence of PA and PME was observed to have similar features.

3. Experimental studies

3.1. Equipment and methods

Using a OEM PRT 446 1617 direct current generator, nickel electroplating was performed in a 30-mL cell at 55 $\pm$ 1 °C with a 5 A/dm^2 fixed current for 5 min. The thicknesses of the coatings were measured using Fischerscope XDL-B X-ray fluorescence (XRF) instrument, and the brightness of the films was determined using a Novo-Gloss Trio Glossmeter. Brass plates (Jungdo Testing Instrument Co.) were used as the cathode and nickel panels were used as the anode. The surface area of each electrode was 10 cm^2. The electrochemical measurements were performed with a PAR VersaSTAT 4 Potentiostat/Galvanostat. For the voltammetric measurements, a copper cathode with a surface area of 0.5 cm^2 was used as the working electrode, and a platinum wire was used as the auxiliary electrode. A saturated Ag/AgCl electrode was used as the reference electrode. The cells that were used for the electrochemical measurements had a volume of 10 mL. Linear scanning voltammetry measurements were obtained in the range of 0 to –1.5 V with a speed of 20 mV/s. A chronoamperometric study was performed between 0 and 20 s at 0.0 V, between 20 and 50 s at –1.0 V, and between 50 and 80 s at 0.0 V. In the same manner, a chronopotentiometric study was performed between 0 and 20 s at 0.0 A, between 20 and 50 s at –10 mA, and between 50 and 80 s at 0.0 A. EIS measurements were carried out in the frequency range of 100 kHz–0.1 Hz, at 1 V potential, by applying 10 mV sine wave AC voltage. The impedance data were obtained using a Verstat 4 device. The impedance data were fitted using equivalent electrical circuits and
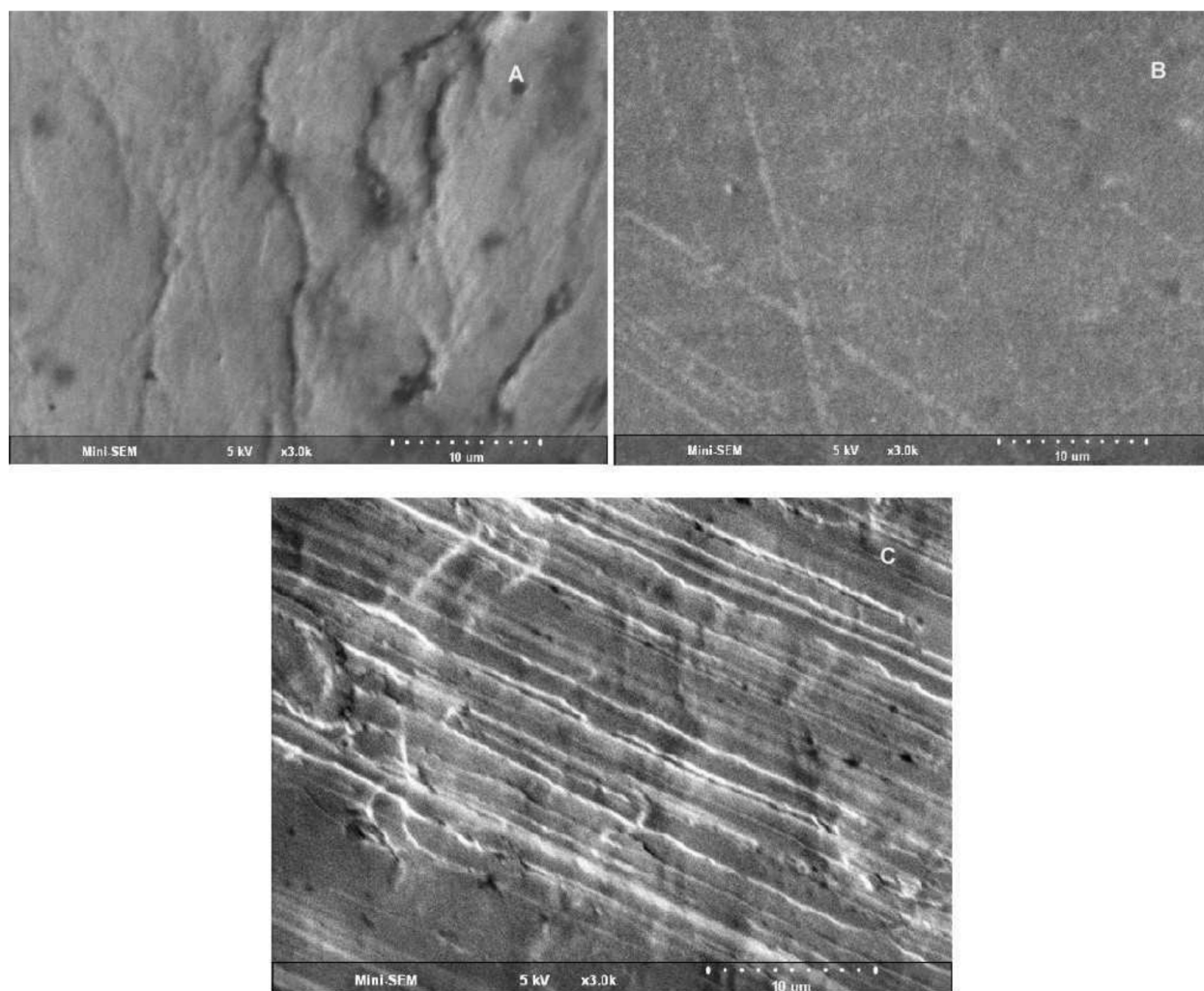
Figure 9. SEM images of nickel platings coated in (A) B bath (B) B+ 0.1 mL/L PME, C) 0.3 mL/L PME.

ZSimp-Win EIS data analysis software (EChem Software, USA). Good agreement between the experimental and the calculated results was obtained from the best fitting electrical equivalent circuit model by confirming the chi-squared (χ^2), which is defined as the sum of the squares of the residuals and was minimized below 10^{-4}.[20−22] The composition of the Watts bath (A) used in the electroplating is provided in Table 6.

Boric acid was used as a buffer to keep the pH of the bath in the range of 4.5–5.5. Ethylhexylsulfate (EHS) was used to decrease the surface tension and chloride effects such as nickel anode corrosion. Baths A1, A2, A3, and A4 were prepared from bath A by individually adding 1 mL/L PA, 1 mL/L PME, 1 mL/L PS, and 1 mL/L DEP organic molecules to each bath, respectively (Table 7). Bath B was prepared from bath A by adding 2 g/L saccharine.

The SW voltammograms were recorded by applying a negative-going scan over the potential range from 0.0 to –1.0 V. The altitudes of the step and the pulse were 5 mV and 25 mV, respectively.

To investigate the deposition efficiency of the Ni bath, the plates that were used as the cathode were weighed before and after plating at 5 A for 5 min. The efficiency was calculated from the experimental and theoretical values of the deposition using Faraday's law.

Table 6. Watts nickel bath (A).

Chemicals	Quantity
$NiSO_4.6H_2O$	200 g/L
$NiCl_2.6H_2O$	100 g/L
H_3BO_3	45 g/L
EHS	1 mL/L

Table 7. Watts nickel baths with and without organic additives.

	PA (mL/L)	PME (mL/L)	PS (mL/L)	DEP (mL/L)
A	0	0	0	0
A1	1	0	0	0
A2	0	1	0	0
A3	0	0	1	0
A4	0	0	0	1

Theoretical calculations were performed with Gaussian 98 programs using the RHF method and 6-31+G(D) basis set.

3.2. Materials

Nickel sulfate ($Ni_2SO_4.6H_2O$), nickel chloride ($NiCl_2.6H_2O$), boric acid (H_3BO_3) (Merck), and EHS, PA, PME, PS, and DEP (BASF Co.) were of analytic quality and were used without any purification process.

3.3. Cleaning process

For precleaning, the cathode plate was placed in a cathodic cleaning bath prepared with alkaline solution (Surtec Co., No. 195, 100 g/dm^3), and a fixed current of 6 A/dm^2 was applied for 60 s. After washing with distilled water, the activation process was executed in 5% H_2SO_4 (Merck) solution, and the plate was then washed again with distilled water.

4. Conclusion

In this study, the effects of PA, PME, DEP, and PS molecules added to nickel electroplating baths on brightness, efficiency, and thickness were investigated using optical, XRF, SEM, and electrochemical methods. All of these additives have the tendency to shift the Ni reduction potential to the negative area due to the presence of triple bonds in their structure, which facilitate their adsorption on the surface compared with single and/or double bonds. The PA and PME molecules, which have –OH functional groups in the main skeleton, have better adsorption ability, while the PS molecule, which contains $–SO_3^{-1}$ ionic group, has the least adsorption ability. Langmuir adsorption isotherms suggest that the surface coverage is much higher for PA than for PS, and these results agree well with the result above and support the conclusion.

The effect of the molecule also depends on whether it is ionic. If the molecule dissolves ionically in water, as is the case for PS, its adsorption at low concentration is low at lower current intensities. Thus, the additive should be used at higher concentration or at higher current intensities. However, for PA and PME, adsorption is enhanced, and the additives become effective even at low concentrations and at lower current intensities, which makes them favorable as organic additives. If these additives are used at high concentrations, the internal stress increases and the ability of the nickel plating is lowered dramatically.

The HOMO/LUMO energies and dipole moments obtained from theoretical calculations explained the better adsorption behavior of the PA molecule to the surface at low current density, which consequently led to a brighter surface even at lower concentrations and supports the experimental results. The SEM measurements suggest that the surface properties depend on the additive concentration, and at a certain critical concentration it is possible to obtain smooth and homogeneous plating.

Both the experimental and theoretical calculation results support the conclusion that to obtain the highest brightening and leveling effect in lower current areas one must add PA or PME to the nickel plating baths, whereas PS is more favorable at high current density.

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