# THE INVESTIGATION OF ELECTROCHEMICAL EFFECT OF DIOL COMPOUNDS IN NICKEL ELECTROPLATING BATH

**USTAMEHMETOĞLU BELKIS, SEZER ESMA
and KATIRCI RAMAZAN**

Department of Chemistry
Istanbul Technical University
Maslak, Istanbul
Turkey
e-mail: belkis@itu.edu.tr

## Abstract

In this study, the effect of functional groups of 1,4 butynediol (BOZ), 2-butyne-monopropoxylate (BMP), and butynediol ethoxylate (BEO) molecules in nickel electroplating bath was investigated by using electrochemical and computational methods (RHF, $6 - 31 + G(D)$) and compared. The initial potential of nickel electroplating shifts the negative area in the presence of organic additive according to the oxygen number in the structure. The shift increased in the order of BOZ, BMP, and BEO. Dipol moment and HOMO-LUMO energies obtained from theoretical calculations explained the reason of the negative area shift of BEO molecule, which consequently led to more bright surface even at lower concentrations and supports the experimental results.

## 1. Introduction

Obtaining a bright and commercially acceptable nickel electroplating requires adding some organic additives into Watts nickel plating bath together [1, 2]. Many articles were published on the electrochemical

behaviour of saccharin and three kind of diol compounds and hindering effect of those kinds of organics and their effect on the surface morphology and structure of nickel plated materials was reported [3-5, 7]. They reported that the smooth and tight nickel electroplatings could be obtained in the presence of saccharin and diols. The effects of the functional group of the organic additive is significant on the structure of platings. The effect of increasing bond number in compounds was investigated in another article [5]. As the number of bond number increase, $\pi$ electrons increase, and adsorbtion on the cathode surface becomes easier. Since butynediol has $4\pi$ electrons, it is the compound better adsorbed on the cathode surface and consequently increase the polarization of the nickel electroplating the most [5, 6].

The goal of this study is to investigate the effects of the functional group $(Y, Z)$, in the main skeleton $(Z–C–C{\equiv}C–C–Y)$ on nickel electroplating baths. To this end, the molecules which have $= Z = –OH$ (BOZ); $Y = –OH$, $Z = –OCH_2–CH_2–CH_2–OH$ (BMP); and $Y = Z = –OCH_2–CH_2–OH$ (BEO) functional groups and with the structure given in Scheme 1 are chosen and investigated with electrochemical methods.
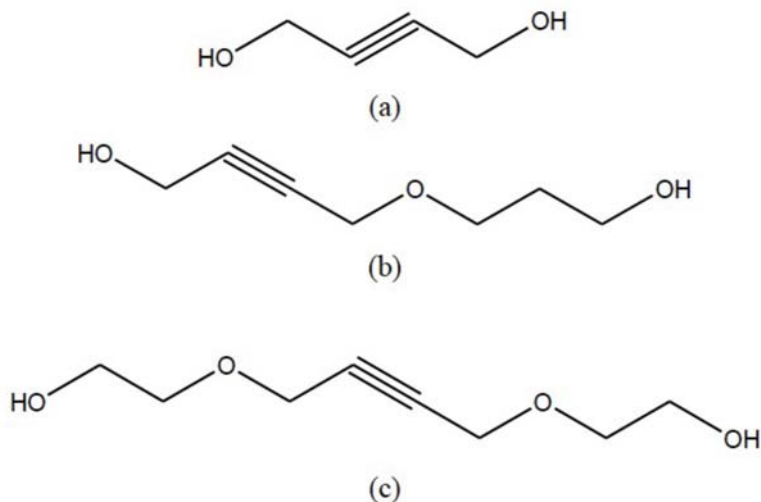


**Scheme 1.** The structure of organic additives used in nickel bath (a) BOZ; (b) BMP; and (c) BEO.

## 2. Experiment

### 2.1. Methods and equipments

Electrochemical measurements were performed with a PAR Versa STAT 4 model potentiostat/galvanostat. In all measurements and depositions, Watts nickel bath (A) was kept on the values of Table 1. To make internal stress lower, 2gr/l saccharine was added to the A bath and this bath called as B bath.

**Table 1.** Bath composition

| Base nickel bath (A) | |
| --- | --- |
| Chemicals | Quantity |
| $NiSO_4 \cdot 6H_2O$ | 200gr/l |
| $NiCl_2 \cdot 6H_2O$ | 100gr/l |
| $H_3BO_3$ | 45gr/l |
| EHS (Ethylhexyl sulphate) | 1 ml/l |

The cells which are used for electrochemical measurements have 10ml volume. As working electrode, copper cathode with $0.5cm^2$ surface and as an auxiliary electrode platinum wire was used. As a reference electrode, Ag/AgCl electrode was used.

Linear scanning voltammetry measurements were obtained in 0-(−1.5)V interval with a speed of 20mV/s. Chronoamperometric study was carried out between 0-20 seconds at 0.0V; 20-50 seconds at −1.0V; and 50-80 seconds at 0.0V. In the same way, for the chronopotentiometric study, between 0-20 seconds 0.0A; 20-50 seconds −10mA; and 50-80 seconds 0.0A were applied.

The SW voltammograms were recorded over the potential range from 0.05 to −1.0V. The altitude of step and pulse was 5mV and 25mV, respectively.

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

Nickelplatings were carried out in Hull-cell and, the thickness and brightness of platings were measured with Fisherscope XDL-B model X-ray flouresence (XRF) and Novo-Goss Trio model glossmeter, respectively.

The GC measurements were performed with Clarus 600GCMS model instrument. Column length is 30m and the internal diameter of column is 0.25mm.

## 2.2. Chemicals

Nickel sulphate $(NiSO_4 \cdot 6H_2O)$, nickel chloride $(NiCl_2 \cdot 6H_2O)$, boric acid $(H_3BO_3)$, ethylhexyl sulphate (EHS), chemicals were used as analytical grade. As organic additive, saccharine, butynediol ethoxylate (BEO), butynediol propoxylate (BMP), 2-butyne-1,4-diol (BOZ), chemicals were obtained from BASF company and all chemicals were used without further purification.

## 2.3. Cleaning process

During cleaning process, cathode material was exposed to $6A/dm^2$ fixed current application in alkali solution (Surtec Co., No.195, $100gr/dm^3$) for 60 seconds. After washing with distillate water, activation process was conducted in %5 $H_2SO_4$ (Merck) solution and again washed with distillate water.

## 3. Results and Discussion

### 3.1. Linear voltammetry measurements

For electrochemical measurements, B1, B2, and B3 baths were prepared adding 1gr/l BOZ, 1gr/l BMP, and 1gr/l BEO organic additives to B bath, respectively (Table 2).

**Table 2.** The composition of plating baths with organic additives

| Baths | BOZ (ml/l) | BMP (ml/l) | BEO (ml/l) |
|:-----:|:----------:|:----------:|:----------:|
| B  | 0 | 0 | 0 |
| B1 | 1 | 0 | 0 |
| B2 | 0 | 1 | 0 |
| B3 | 0 | 0 | 1 |

Linear voltammograms of the plating baths in the absence of (B) and presence of organic additives (B1, B2, and B3) were given in Figure 1. Onset of reduction potential $(E_{onset})$, peak potential $(E_p)$, and peak current $(I_p)$ values were obtained from these voltammograms and results were summarized in Table 3. There was a negative shift in $E_{onset}$ of Ni reduction potential in the presence of organic additives and the maximum shift was observed in the case of BEO molecule. Nakamura et al. [5] reported this type of behaviour for similar organic molecules. As the organic molecules adsorbed on the cathode surface, it inhibites the reduction of Ni ion and $E_{onset}$ shifts to more negative value, which depends on the adsorption ability that related to the functional groups of organic molecules.
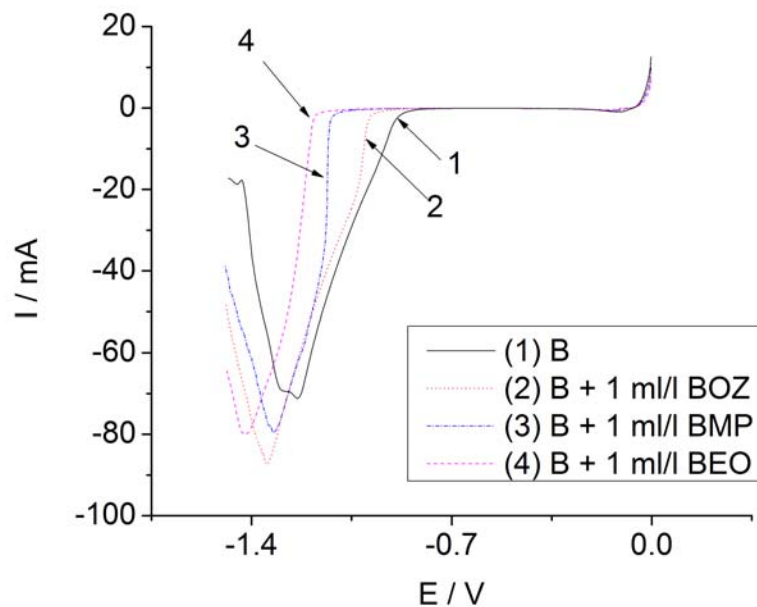
**Figure 1.** Linear voltammograms obtained in B, B1, B2, and B3 baths. Scan rate $= 20\text{mVs}^{-1}$.

**Table 3.** Onset of reduction potential $(E_{onset})$, peak potential $(E_p)$, and peak current $(I_p)$ values obtained from the voltammograms of B, B1, B2, and B3 baths

| Baths | $E_{onset}(V)$ | $I_p$ (mA) | $E_p(V)$ |
|:-----:|:------:|:------:|:------:|
| B | − 0.87 | − 70.88 | − 1.24 |
| B1 | − 0.97 | − 87.45 | − 1.35 |
| B2 | − 1.11 | − 79.43 | − 1.33 |
| B3 | −1.18 | − 79.85 | − 1.43 |

In this study, BEO seems the molecule that interact with the electrode surface the most and led to the highest shift in $E_{onset}$ (Table 3). In the presence of organic additives (B1, B2, B3), $I_p$ values were increased and the highest peak current was observed in the case of BOZ molecule (B1). As the potential shift to negative direction, $H_2$ gas

evaluation also starts in addition to Ni reduction and this is the one of the reason that cause the increase in current peak. As the organic molecule adsorbed on the surface, it results a resistive layer that cause to diminish the current flow. BOZ is the molecule that results the smallest shift in $E_{onset}$ and this shows that it is the least adsorbed molecule and results the thinnest adsorbed layer, which is the second reason of observing higher peak current.

### 3.2. Chronoamperometric and chronopotentiometric measurements

Current-time, potential-time curves obtained in the absence of (B) and presence of organic additives (B1, B2, and B3) were given in Figure 2A and 2B, respectively. For chronoamperometric measurements, while the maximum current was observed in the case of BOZ molecule at –1.0V constant potential, in the presence of BEO, minimum current was observed (Figure 2A). When BOZ was added, the reduction potential of Ni ion shifted to the more negative value by about 0.11V, which is lower than the value observed in the case of BEO (0.19V) (Table 3). This result suggests that adsorbability on the electrode surface of the organic additives increase in the order of BOZ, BMP, and BEO, which is the same order with decrease in current in chronoamperometric measurements and shift in the $E_{onset}$ of Ni reduction (Figure 1). In the previous studies, it is suggested that increase in degree of unsaturated linkage in organic additive led to increase in adsorbability and to inhibitory effect on the reduction of Ni ion [4-6]. In this study, investigated organic molecules have the same unsaturated bond, the only difference is the oxygen number and the length of the chain between triple bond and –OH groups. As the chain length and oxygen number increase, adherence of molecule on the surface become more favorable, this might be due to presence of oxygen and due to the longer chain that makes the molecule cover the surface better.

When –10mA was applied as constant current, the highest potential was required in the case of BEO, which is in agreement with chronopotentiometric results.
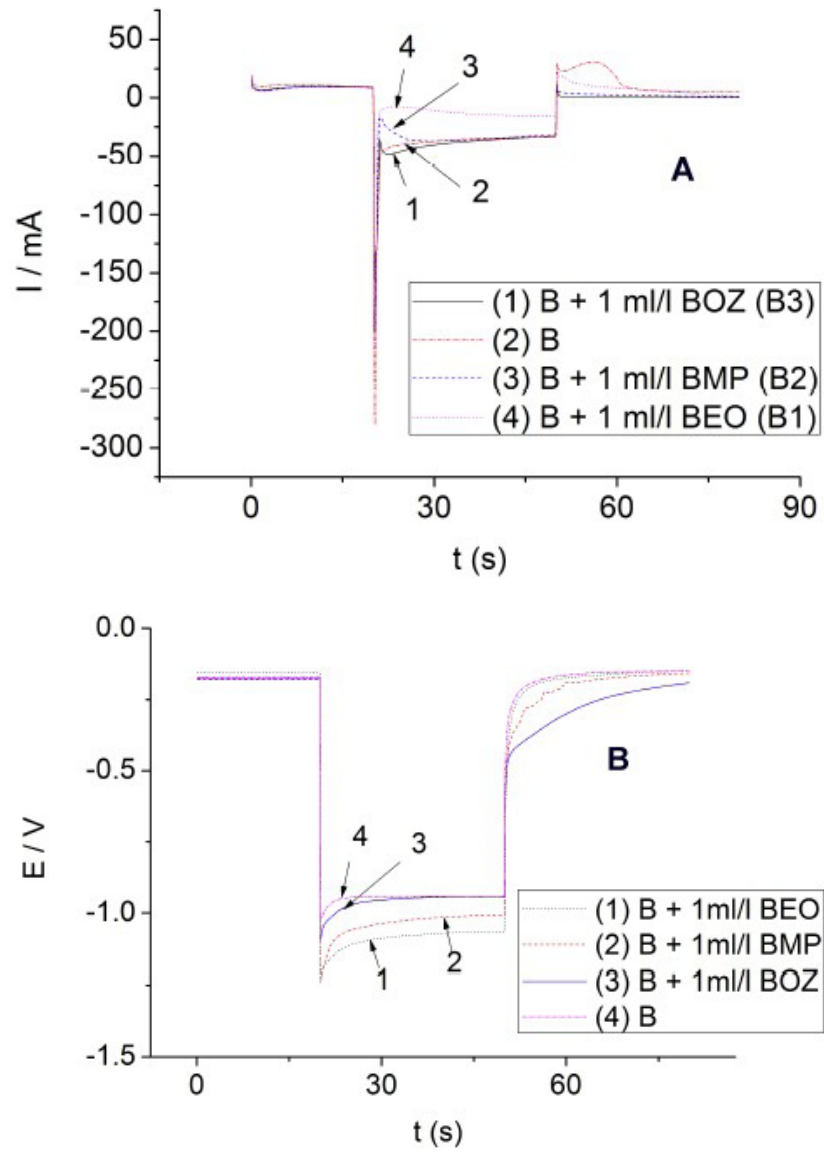
**Figure 2. A.** Chronoamperometric **B.** Chronopotentiometric results obtained in the absence of (B) and presence of organic additives (B1, B2, and B3).

### 3.3. Square wave voltametric measurements

SWV measurements in the plating baths in presence of organic additives were performed and results were given in Figure 3. The peak potentials were observed at – 0.95V, – 1.08V, and – 1.12V in the case of BOZ, BMP, and BEO, respectively. Shifts in the reduction potential of Ni ion are in agreement with linear voltammetric results. Since the BEO molecule has the better adsorbability than the other, it results more compact nickel electrodeposition that makes the surface more bright.
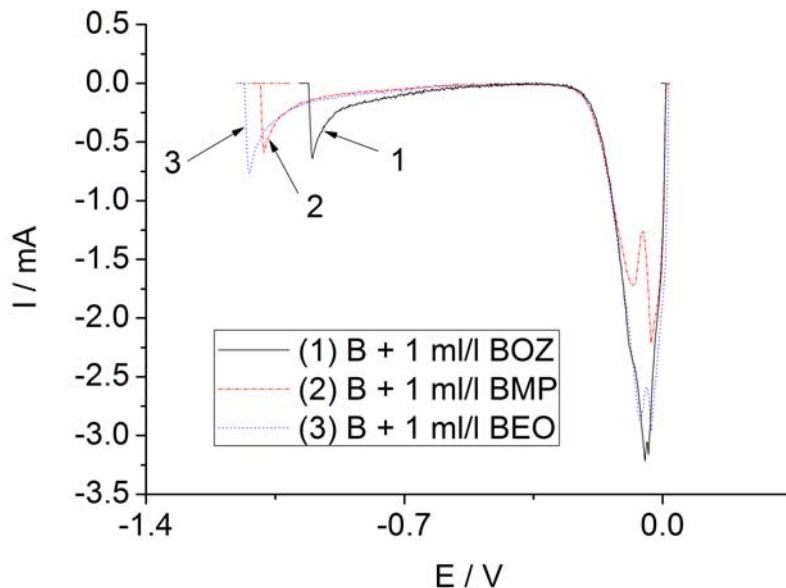


**Figure 3.** SWV results obtained in the presence of organic additives (B1, B2, and B3).

### 3.4. Theoretical calculations

Theoretical calculations were performed by using RHF method and $6-31+G(D)$ basis set and results were summarized in Table 4. Results show that although HOMO energies are close to each other, LUMO energy of BEO is higher than the others, and BOZ has the highest dipol moment. According to experimental results, BEO has the most shift in $E_{onset}$ of Ni reduction and it is more effective at low concentration, while

BOZ is effective at higher concentrations. In conclusion, higher LUMO energy and lower dipol moment seems led to BEO molecule to give electrons easily and less interaction with the environment and better adsorption to the surface.

**Table 4.** The results of theoretical calculation of BOZ, BMP, and BEO

| Chemicals | Dipol (D) | HOMO (Hartrees) | LUMO (Hartrees) |
|:---:|:---:|:---:|:---:|
| BOZ | 3.76 | − 0.388 | 0.060 |
| BMP | 4.00 | − 0.384 | 0.069 |
| BEO | 1.94 | − 0.383 | 0.073 |

## 3.5. Effects of BOZ, BMP, and BEO additives on brightness and thickness

Hull-cell experiments were carried out and the thickness of Ni in the absence and presence of BOZ, BMP, and BEO was determined by X-ray fluorescence measurements and were summarized in Table 5. The thickness of the coating in the presence of BEO is thinnest and the brightest. This result supports that BEO hinders the Ni reduction the most, which is agree with linear voltammetry results.

SEM images of nickel platings carried out in B bath and BEO added B bath (B3) are presented in Figure 4. As the additive adsorbed on surface, it prevents homogeneous distribution of nickel as shown in Figure 4. These results are in agree with linear voltammetry results.

**Table 5.** The thickness and brightness of nickel electroplating in Watts bath (B) and organic added baths (B1, B2, B3) and elution times of BOZ, BMP, BEO obtained from GC measurements in methanol

| Baths | Thickness $(\mu m)$ | Brightness (gloss) | Elution time (min) |
|:---:|:---:|:---:|:---:|
| B | 3.38 | 950 | − |
| B1 | 3.21 | 1050 | 4.19(BOZ) |
| B2 | 2.89 | 1160 | 6.71(BMP) |
| B3 | 2.55 | 1269 | 10.32(BEO) |
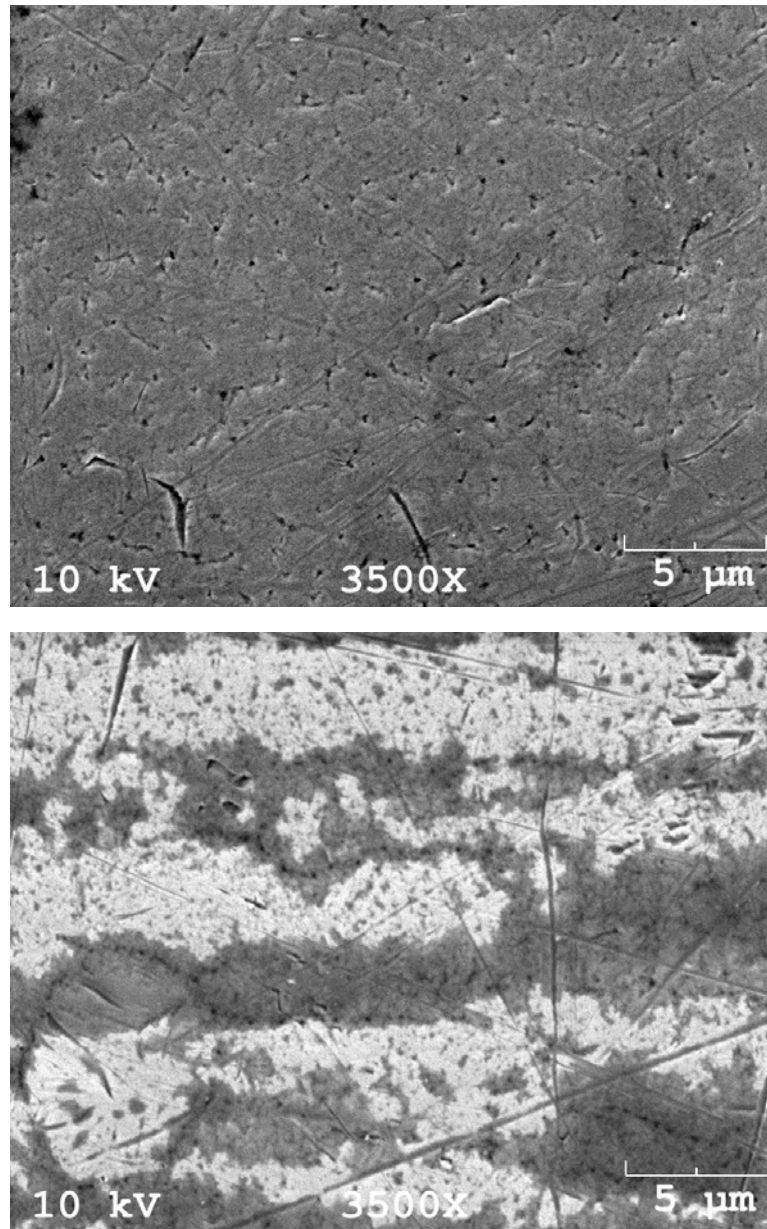
**Figure 4.** SEM images of nickel plating obtained in B bath (a) and 0.05ml/l BEO added B bath (b).

In our previous study [8], we investigated the effects of the surfactant N,N-dimethyl-N-2-propenyl-2-propene-1-ammonium chloride-2-propenamide (polyquaternium-7, PQ7), which is used for the first time in nickel bath, on plating rate, particle dimension and leveling effect were studied with electrochemical methods (linear voltammetry and impedance) surface analysis methods (scanning electron microscopy (SEM) and X-ray diffractometer (XRD)) compared to propargyl alcohol (PA), pyridinium propyl sulphobetaine (PPS), and butynediol ethoxylate (BEO). In our unpublished studies, the effects of triple bonds (propargyl alcohol (PA), propynol ethoxylat (PME), propargyl sulphonate (PS), diethylamino-propyne (DEP)) and pyridine (pyridinium propyl sulphobetaine (PPS), pyridinium hydroxyl propyl sulphobetaine (PPSOH), and 1-benzyl-3-carboxypyridinium (BPC)) containing molecules, on nickel electroplating was investigated systematically. In all these studies, results suggest that better adsorption results higher shift in reduction potential of Ni and smaller particle size and brighter plating. In the light of these results, we assume that the smallest particle should be in case of BEO.

In order to gain idea about individual adsorption behaviour of additives gas chromatography measurements of BOZ, BMP, BEO in water were performed (Figure 5). Elution times obtained from spectra were summarized in Table 5. As it can be seen the longest time was observed for BEO, which is adsorbed on substrate surface better and cause the highest shift in Ni reduction potential. This result support our conclusion that BEO has better adsorption ability than others and give the brightest Ni coating. According to the test results, the order of adsorption ability of molecules is BEO>BMP>BOZ.
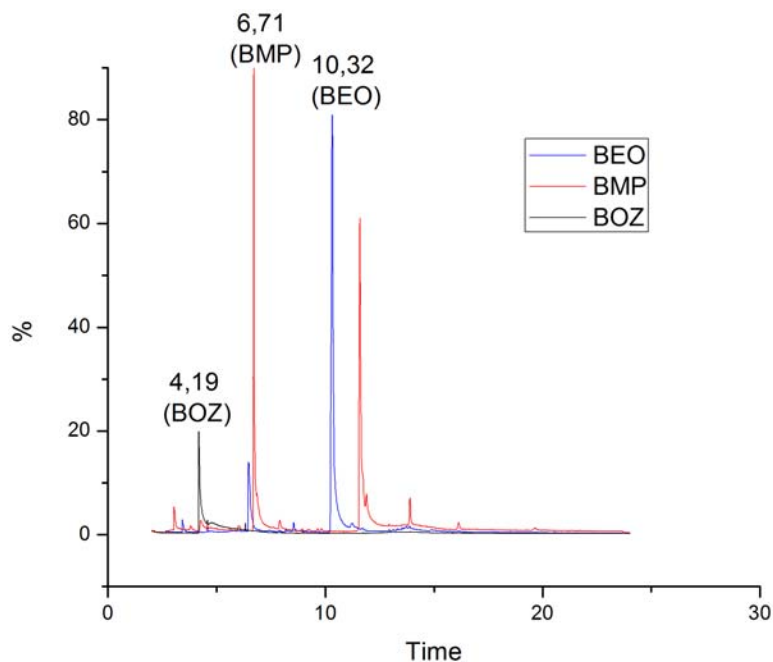
**Figure 5.** Gas chromatography results of BOZ, BMP, and BEO.

## 4. Conclusion

In this study, the effect of three kinds of aliphatic alcohols (BOZ, BMP, and BEO) as organic additives in the Ni electroplating bath were investigated. When we compare the molecules according to the shift of the cathodic onset potential of Ni ion, it was found that the higher shift led the smoothness of surface, increase in brightness and decrease in thickness (Table 5). BEO shifted the initial deposition potential the most and seems it is the most effective one in this group. When the structure of molecules considered, as the chain length and oxygen number increase shift in $E_{onset}$ of Ni reduction potential more and this explaines why the BEO has better effect on the properties of plating than the others.

In conclusion, theoretical and experimental results show that the more negative $E_{onset}$ of Ni reduction, the more bright surface are obtained and this results suggested that in order to obtain more bright and smooth Ni platings, one must use BEO molecule as organic additive at low concentration in nickel electroplating bath.

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