

Article

Comparison between Electrooxidation of 1-Naphthol and 2-Naphthol in Different Non-Aqueous Solvents and Suppression of Layer Growth of Polymers

László Kiss^{1,2,*}, Péter Szabó³ and Sándor Kunsági-Máté^{1,2,*} 

¹ Department of Organic and Medicinal Chemistry, Faculty of Pharmacy, University of Pécs, Honvéd Street 1, H-7624 Pécs, Hungary

² Green Chemistry Research Group, János Szentágothai Research Center, Ifjúság Street 20, H-7624 Pécs, Hungary

³ Environmental Analytical and Geoanalytical Research Group, Szentágothai Research Center, Ifjúság Street 20, H-7624 Pécs, Hungary; sz.piiit01@gmail.com

* Correspondence: kissl@gamma.ttk.pte.hu (L.K.); sandor.kunsagi-mate@aok.pte.hu (S.K.-M.)

Abstract: The two naphthol isomers were investigated in different organic solvents by taking cyclic voltammograms, and fouling took place on a platinum electrode surface, except for dimethyl sulfoxide and dimethyl formamide. Studies in allyl alcohol rarely used in electrochemical investigations pointed to the importance of the carbon–carbon double bond as electrode deactivation was remarkably faster compared with its saturated analog solvent. Similarly, the use of the other unsaturated solvent mesityl oxide in the electropolymerization of naphthols resulted in different findings compared with methyl isobutyl ketone. As dimethyl formamide was the best choice concerning the solubility of products, it was successfully tested in electrode renewal after deactivation in an aqueous solution. The increase in dimethyl formamide content led to more and more improved reproducibility of the currents of the outlined aromatic compounds. Naphthol isomers were assessed in the suppression of layer growth originating from the electrooxidation of another monomer phloroglucinol. Its simultaneous electrooxidation with naphthol monomers had a dramatic effect on layer morphology and it was found that instead of a coherent organic layer originating from the homopolymerization of phloroglucinol, the copolymerization with naphthols led to the development of more porous and rougher deposits. The suppressed electropolymerization thus increased sensitivity towards a chosen redox active compound, 4-methoxyphenol.

Keywords: naphthols; non-aqueous solvent; electropolymerization; suppression



Citation: Kiss, L.; Szabó, P.; Kunsági-Máté, S. Comparison between Electrooxidation of 1-Naphthol and 2-Naphthol in Different Non-Aqueous Solvents and Suppression of Layer Growth of Polymers. *Surfaces* **2024**, *7*, 164–180. <https://doi.org/10.3390/surfaces7010011>

Received: 30 January 2024

Revised: 8 March 2024

Accepted: 13 March 2024

Published: 15 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Naphthols are a focus of interest in many organic syntheses, so they are widely applied not only in chemical but electrochemical preparations. The family of these compounds has similar electrochemical behavior as phenols, as the compounds undergo irreversible oxidation during the anodic polarization of electrodes, producing naphthoxyl radicals and leading to polymerization on their surfaces. It has been reported that in acetonitrile, a conducting polymer can be formed from 1-naphthol on glassy carbon [1]. This interesting finding usually observed in acetonitrile solvents can be attributed to the fact that the structural analyses of deposits demonstrated the presence of alternating furan and naphthoxyl moieties along the polymeric backbone connected by ether linkages. The related potentiostatic curves after the fast current drop by starting an experiment usually observed by each surface blocking the currents passed through a maximum and this indicated that an electronic polymer formed. Both the speed of reaching the maximum and their heights increased significantly by changing the deposition potential from 1.1 to 1.3 V due to the enhanced nucleation rate. As in the case of numerous other monomers, basically two layers

formed. One of them is a bottom layer adhering strongly to the electrode surface and an outer layer easily removable mechanically. An important property of the electronically conducting polymers is the stability towards the charging/discharging process when doping anions migrate into and from the deposit bearing the positive charges in the oxidized form. In that work, the cyclic voltammograms were repeated in acetonitrile containing a tetrabutylammonium perchlorate (TBAP) supporting electrolyte which was also used in the deposition experiments. The peak currents declined after a lot of cycling repeating to a steady value indicating that this is not a degradation, but rather that a polymer rearrangement takes place.

In contrast, in methanolic alkaline solutions poly(naphthalene oxide) can be produced without furan rings, but the polymers formed in aqueous alkaline solutions also have identical properties [2]. The polymer backbone also contains furan rings, as the deprotonated hydroxyl groups are able to act as a nucleophilic reactant as the FT-IR studies showed. Ketone groups could be also detected. As it was observed generally, C-C bonds formed in parallel to many ether linkages, and as a matter of fact, it made the development of ketone groups possible. For the linkages, the ortho and para positions were favored inside the ring bearing the hydroxyl group. Obviously, these linkages were responsible for the propagation of polymer growth. These structural characteristics were observed in the case of both poly(1-naphthol) and poly(2-naphthol).

Apart from solution pH, the dependence on the nature of presenting functional groups attached to the naphthalene ring in naphthol molecules can strongly influence electrochemical behavior [3]. For example, 5-amino-1-naphthol electropolymerized only through the -OH groups, while in acidic conditions this occurred through the amino groups exclusively, as no C-O-C coupling could be detected. The aniline part is present in this molecule; thus, it electropolymerizes with the same mechanism as aniline, leading to favorable conducting properties. On the other hand, the low anodic potential is enough for the oxidation of aromatic amino groups in acidic conditions. Organic layer adherence was higher in water than in acetonitrile. To demonstrate the popularity of 5-amino-1-naphthol in electropolymer preparation, its deposit was deeply investigated with resonance Raman spectroscopy [4] also verifying its conducting nature through the observation of imine groups. Its electropolymer also has an electrochromic character [5] and excellent reversible redox properties in acidic conditions [6]. With this monomer, electrodeposition experiments were carried out both in acidic aqueous and acetonitrile solutions, and the conductivity of film grown in acetonitrile was approximately three orders of magnitude lower, showing the importance of acidic conditions [7].

As another naphthol derivative naphthol, Green B is also widely investigated due to the favorable properties of its film and as the modifier of carbon paste electrode contributed to the simultaneous determination of dopamine and uric acid [8]. A similarly modified carbon paste electrode showed excellent capability for simultaneous quantification of paracetamol and norepinephrine [9] and catechol and hydroquinone [10]. A modified glassy carbon electrode with the polymer of naphthol Green B showed promising detection ability towards NADH [11]. The as-modified graphite pencil electrode proved its usefulness in the determination of dopamine in the presence of uric acid [12].

Conducting films were also formed from monomers 1,1'-binaphthyl and 1,1'-bi-2-naphthol in CH_2Cl_2 by adding boron trifluoride diethyl etherate, and the latter compound was highly responsible for the elevated electric conductivity [13]. The couplings formed at the α -positions of the naphthalene rings. Polymers deposited in those conditions showed favorable fluorescence properties attributable mainly to the naphthalene rings. Similarly advantageous fluorescence properties can also be attributed to the polymers formed from 2,2'-binaphthyl ether [14] by using boron trifluoride diethyl etherate as an additive in the sulfuric acid solution. The couplings were built in the α - and C_6 -positions. The polymer seemed to be a good candidate for use in optoelectronic devices.

In the majority of cases, low electronic conductivity polymers form from 1-naphthol and from their numerous derivatives, and this is always true for 2-naphthol [15,16]. Dif-

ferent modes of nucleation for phenol and 2-naphthol take place on gold electrodes in aqueous alkaline solutions [17].

The permselectivity of films originating from the electrooxidation of naphthols was utilized in enzyme immobilization, with high importance in biosensor applications. Poly(2-naphthol) was particularly useful in this respect [18]. It is usually observed that the latter polymer has high permselectivity [19]. The bilayer membrane consisting of polypyrrole and poly(2-naphthol) showed excellent anti-interference properties in the simultaneous determination of choline and acetylcholine [20]. The immobilization of a heteropolyacid anion was successful in acetonitrile [21], but the distribution of the anion was not homogeneous in poly(1-naphthol).

Copolymerization studies were also carried out with naphthols. For example, Rehan et al. found that 1-naphthol and methyl naphthyl ether presenting in the same methyl naphthyl ether solution had a suppression effect on the polymerization of 1-naphthol [22], but in parallel to this process copolymers also formed. However, poly(1-naphthol) has superior conductivity in the doped form with ClO_4^- ions which can be attained by oxidation, and incorporation of methyl naphthyl ether units in the polymer backbone does not destroy the electronic conductivity.

In this work, the electrochemical behavior of the two naphthol isomers is described in various non-aqueous solvents as their studies were carried out in a few organic solvents including acetonitrile which is the most common due to its wide potential window and chemical inertness. These studies aimed at the electrodeposition of poly(naphthols) and earlier investigations showed that the electrochemistry of a certain compound can be very different depending on the solvent. This offers further possibilities for applications. On the other hand, due to the analytical importance, the majority of studies of naphthols were carried out in aqueous systems, as at very low concentrations compounds susceptible to electrochemical polymerization cannot foul the electrode. The studies of aqueous systems are also extended herein to electrode regeneration studies and the usefulness of dimethyl sulfoxide as a solvent in the suppression of electrochemical polymerization of a typical phenolic compound phloroglucinol caused by naphthols. The resulting poly(naphthol) layers were also assessed in the voltammetric analysis of 4-methoxyphenol by comparing the peak heights obtained with a polymer-modified electrode with that measured with the bare electrode.

2. Results and Discussion

2.1. Studies with the Naphthol Isomers in Different Non-Aqueous Solvents

In earlier studies, we found that the electrochemical behavior of aromatic hydroxyl compounds differs depending on the solvent. Such a typical compound was pyrogallol, as its voltammograms were highly reproducible in some non-aqueous solvents, so they enabled the quantification of this compound in apolar real samples [23]. To elucidate the solvent-dependent electrochemical behavior, similar studies were also carried out with the naphthol isomers, taking the voltammograms between 0 and 2 V and inserting stirring between the scans by moving the working electrode by hand for restoration of concentration in the vicinity of the platinum surface (Figure 1). Where the peak appeared, the peak current was taken into account, but in several cases, the peak was embedded into the background current of the electrolyte, so in this case the shoulders were utilized for evaluation. Their behavior differed markedly in acetonitrile as the increase in current peaks in the case of 1-naphthol indicated the formation of a polymer with a conducting nature in accordance with the results of Abd El-Rahman [1]. The formed deposit from 1-naphthol was investigated in acetonitrile containing only TBAP, and similarly to that earlier work, the same rearrangement took place in the film, also presenting on a platinum electrode. An insulating polymer formed during the electrooxidation of 2-naphthol was shown by a decrease in peak currents. Acetone was only appropriate for the preparation of poor electronic conductivity polymers and the thickness was not high as almost nothing was

noticeable with the naked eye, in contrast to acetonitrile where a black deposit formed from 1-naphthol.

Dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) proved excellent concerning signal reproducibility, as due to the favorable solvation of the product oligomers, fouling could be avoided. In general, these two solvents are very appropriate for a huge number of organic compounds to dissolve them [24–28] and this is true also for naphthol polymers as the results here also confirm. The rate of deactivation could be only slightly decreased in 1-propanol, showing a high affinity of solvent molecules to solvate the formed oligomers, but it depends on the length of the aliphatic carbon chain (see Figure 1c for 1-pentanol solvent). This last observation suggests that increasing the alkyl chain length destroys the solvation properties of alcoholic solvents. Currents of 2-naphthol are higher as its anodic peaks appeared at more positive potentials by the involvement of higher background currents due to the solvent.

As allyl alcohol has received poor attention as a solvent in electrochemical studies, it came into focus for this applicability. However, this alcohol has versatile usefulness in other areas. The voltammograms are seen in Figure 2 to compare it with its saturated analog 1-propanol. There is a high difference in the shape of curves, as after the appearance of the peaks, currents drop remarkably in allyl alcohol, while in 1-propanol the elevated background currents are more clearly seen by enhancing the anodic potential. In the vicinity of the electrode surface, allyl alcohol molecules contribute to the development of a more coherent network due to their assistance in leading to copolymerization, and a part of them remains there. So, organic film growth runs with a different mechanism in allyl alcohol as its molecules can insert between the naphthoxyl units as demonstrated in [29]. As the oxidation potential of 1-naphthol is lower, some film rupture occurs, indicated by the second peak. It was very remarkable when allyl alcohol was the solvent as the fouling was accelerated by both naphthol isomers. On the other hand, the height of current peaks of the first measurements was obviously higher compared with 1-propanol. The viscosities of 1-propanol and allyl alcohol are practically the same, so in 1-propanol the diffusion-limited currents are not characteristic of the pure solvent which is the fastest mass transfer in unstirred solutions. These facts are more visible in the voltammograms than in Figure 1 where only peak currents are displayed, mainly due to the wider scale adjusting to currents measured in other solvents. It is suggested by the results in 1-propanol that the hindering effect of the forming polymer is reproduced with a slight decline due to some residual product arising from the previous scans. The difference observed in allyl alcohol arises from the carbon–carbon double bond being able to form a copolymer with the electrochemically generated radicals from the substrate and taking into account the voltammetric data this solvent contributed to the formation of deposits with a smaller network nature than in 1-propanol. This is the cause for the obtained higher peak currents in the first and second scans as it suggests the formation of a less compact layer in the time interval of peak appearance than in 1-propanol which immediately covers the surface of the electrode. In earlier work, the opposite was demonstrated by phenol as the speed of deactivation was approximately the same as in 1-propanol [29]. Optical images also demonstrated this fact.

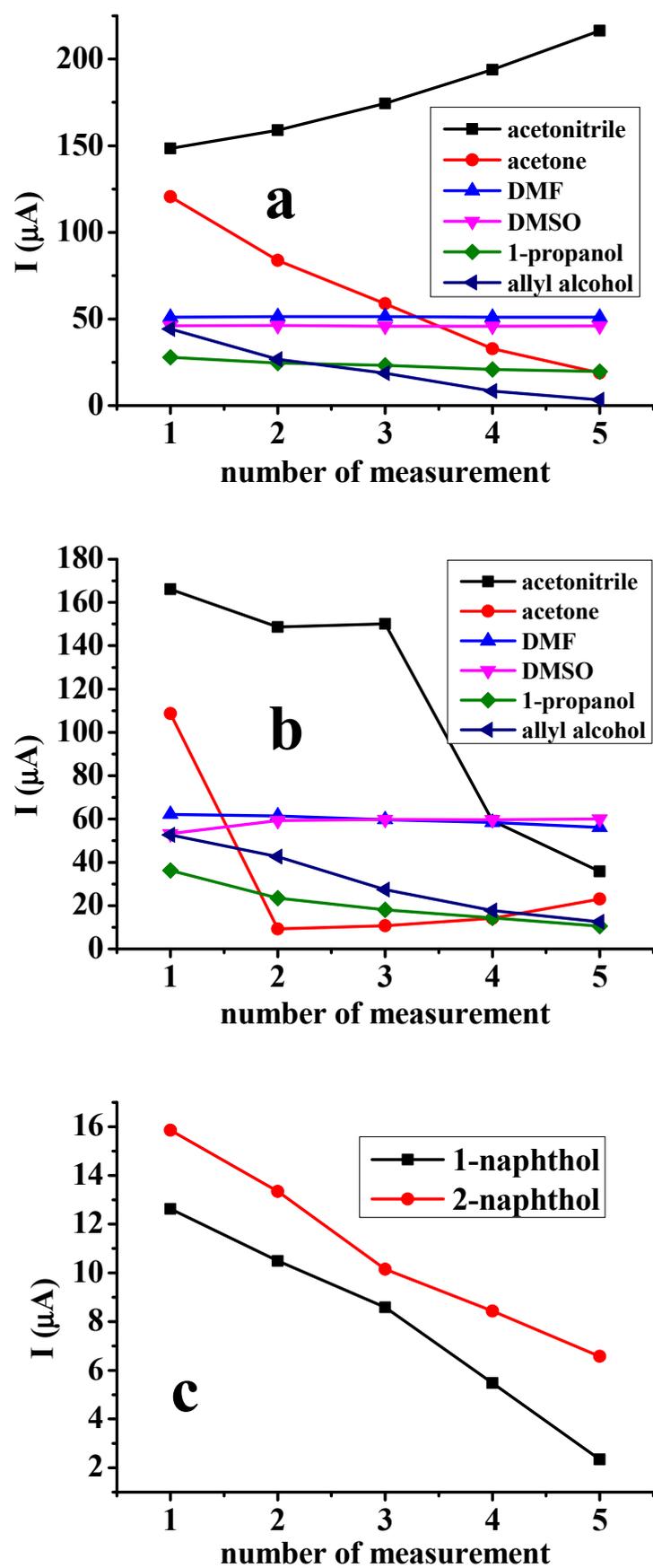


Figure 1. Cont.

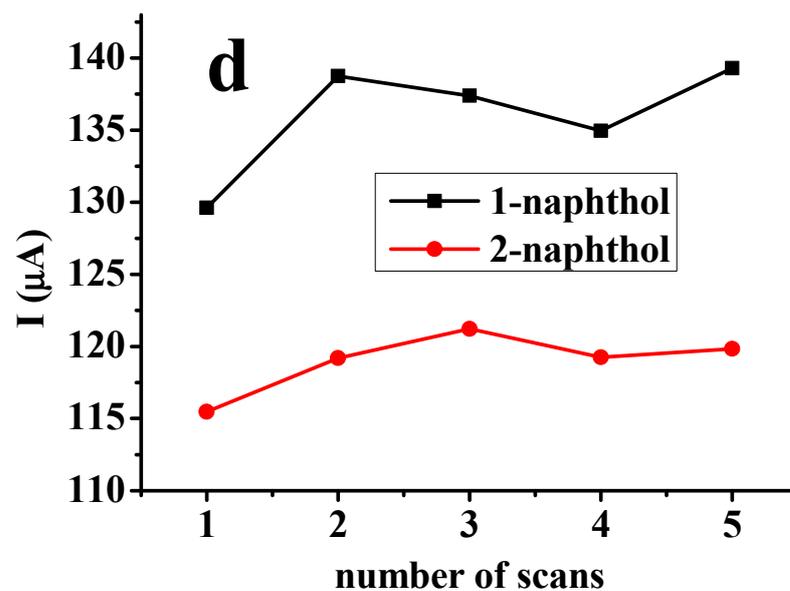


Figure 1. Anodic peak currents of 1-naphthol (a) and 2-naphthol (b) in different non-aqueous solvents ($c = 20$ mM, supporting electrolyte 50 mM TBAP), (c) is related to peak currents recorded in 1-pentanol, and (d) in CH_2Cl_2 .

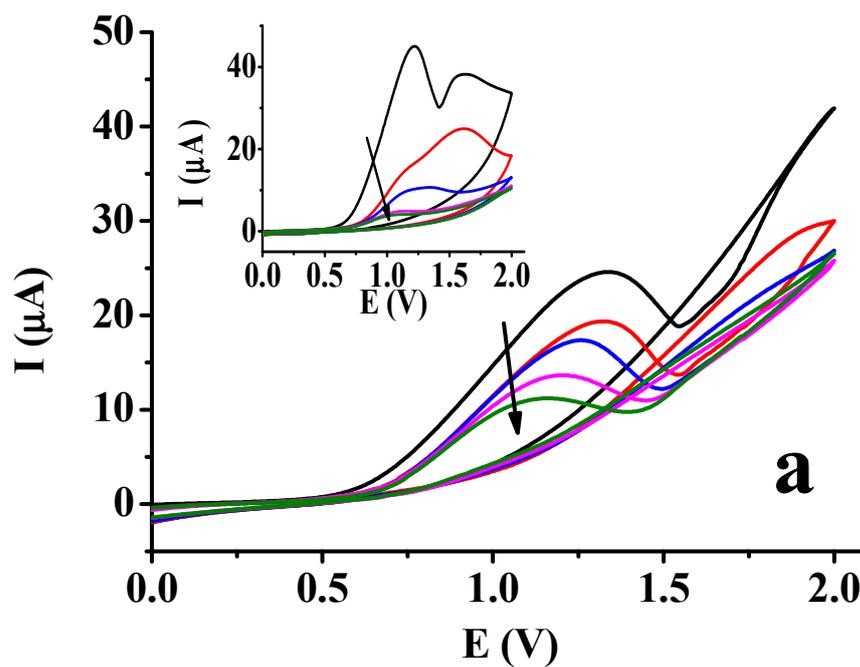


Figure 2. Cont.

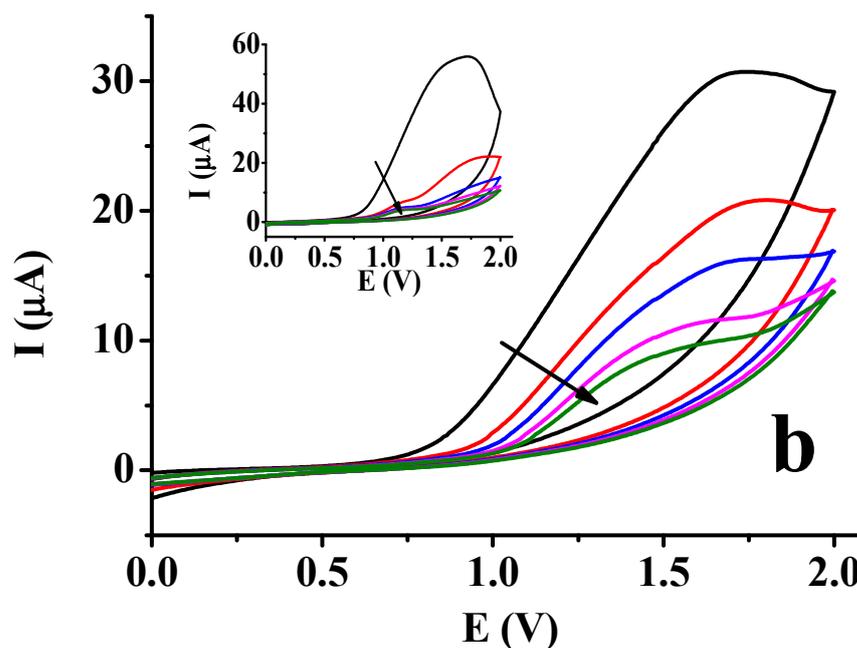


Figure 2. Cyclic voltammograms for 1-naphthol (a) and 2-naphthol (b) in 1-propanol ($c = 20$ mM, $c(\text{TBAP}) = 50$ mM, in inset graphs: curves taken in allyl alcohol).

However, some earlier investigations showed that dichloromethane can serve as a good solvent for the preparation of stable films from derivatives, but contrarily the maximum currents for the naphthol isomers did not show a decreasing tendency (Figure 1d). The currents show some scattering and low increasing tendency, but it cannot be stated that the polymers have a conducting nature. This can be excluded especially due to the fact that the electrode surface remained practically as shiny as before electrodeposition. Similar polymers developed in CH_2Cl_2 , but their favorable solvation in this solvent prevented the propagation of film growth.

Electropolymerization of phenol led to markedly different results when mesityl oxide and methyl isobutyl ketone were used as solvents, as published in an earlier work [30]. The differences between the two solvent molecules originate from the carbon–carbon double bond found in mesityl oxide which is responsible for the identical properties and composition of deposits. Similarly to allyl alcohol, in mesityl oxide the insertion of solvent molecules takes place between the naphthoxyl units. The earlier works with phenyl ethers highlighted that peak currents tended to a steady-state value above the value of the first scan and structural properties in accordance with it were seen through optical images [31]. Figure 3 shows the remarkable differences between the two isomers and the two solvents where the subsequent cyclic voltammograms can be seen taken between 0 and 2 V and between 0 and 2.5 V, adjusting the potential window to the appearance of anodic peaks where they showed up. Earlier, we found generally that the electrode deactivation is faster in methyl isobutyl ketone than in mesityl oxide. Here in the case of the naphthol isomers different results were obtained. The voltammograms show that the speed of deactivation was smaller for 1-naphthol in both solvents, suggesting a less compact layer developed during the electrochemical polymerization than for 2-naphthol. In contrast, the scanning optical images reveal only small islands of polymers formed in methyl isobutyl ketone resulting from electrooxidation of 1-naphthol (Figure 4). Continuous deactivation took place by taking the 10 repetitive cyclic voltammograms. In the case of 2-naphthol, nothing was seen on the platinum surface. This contradiction is due to the dissolution of anodically formed polymers during the subsequent soaking in the pure solvent. This latter step is essential for the complete removal of unreacted substrates and residual supporting electrolytes from the surface, as after solvent evaporation they could be able to build up islands and then be seen as islands in the micrographs. From the polymer of 1-naphthol,

some islands remained but the polymer of 2-naphthol accumulated at some places in the form of large islands which was also checked by microscopy. This suggests that the electropolymer of 2-naphthol binds less strongly to the platinum surface in non-aqueous solvents which is in contrast to aqueous solutions. However, the fouling in solution of 1-naphthol prepared with mesityl oxide is continuous and not very fast, suggesting that the forming polymer has a low conductivity in contrast with acetonitrile due to the insertion of solvent molecules during the radical polymerization. In solutions of 2-naphthol, the peak currents fell to a small value in the second scan compared with the first one.

The microscopic results confirm that visible film deposition occurred in mesityl oxide which was obvious for 1-naphthol. At first glance, it seems coherent. A lot of densely packed small islands were characteristic of 2-naphthol. Together with the voltammetric results, it can be concluded that the deposit of 1-naphthol releases the monomers better than that of the other isomers.

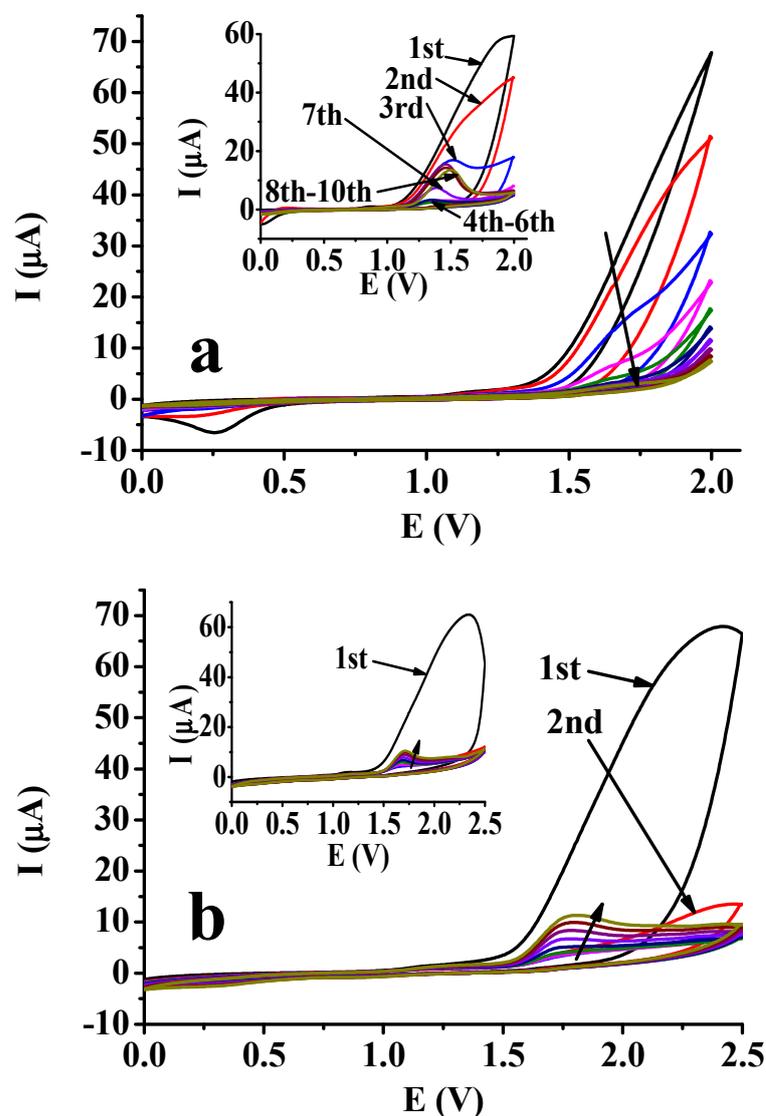


Figure 3. Ten successive cyclic voltammograms for 1-naphthol (a) and 2-naphthol (b) in mesityl oxide (inset graph: in methyl isobutyl ketone) ($c = 20$ mM, supporting electrolyte 50 mM TBAP).

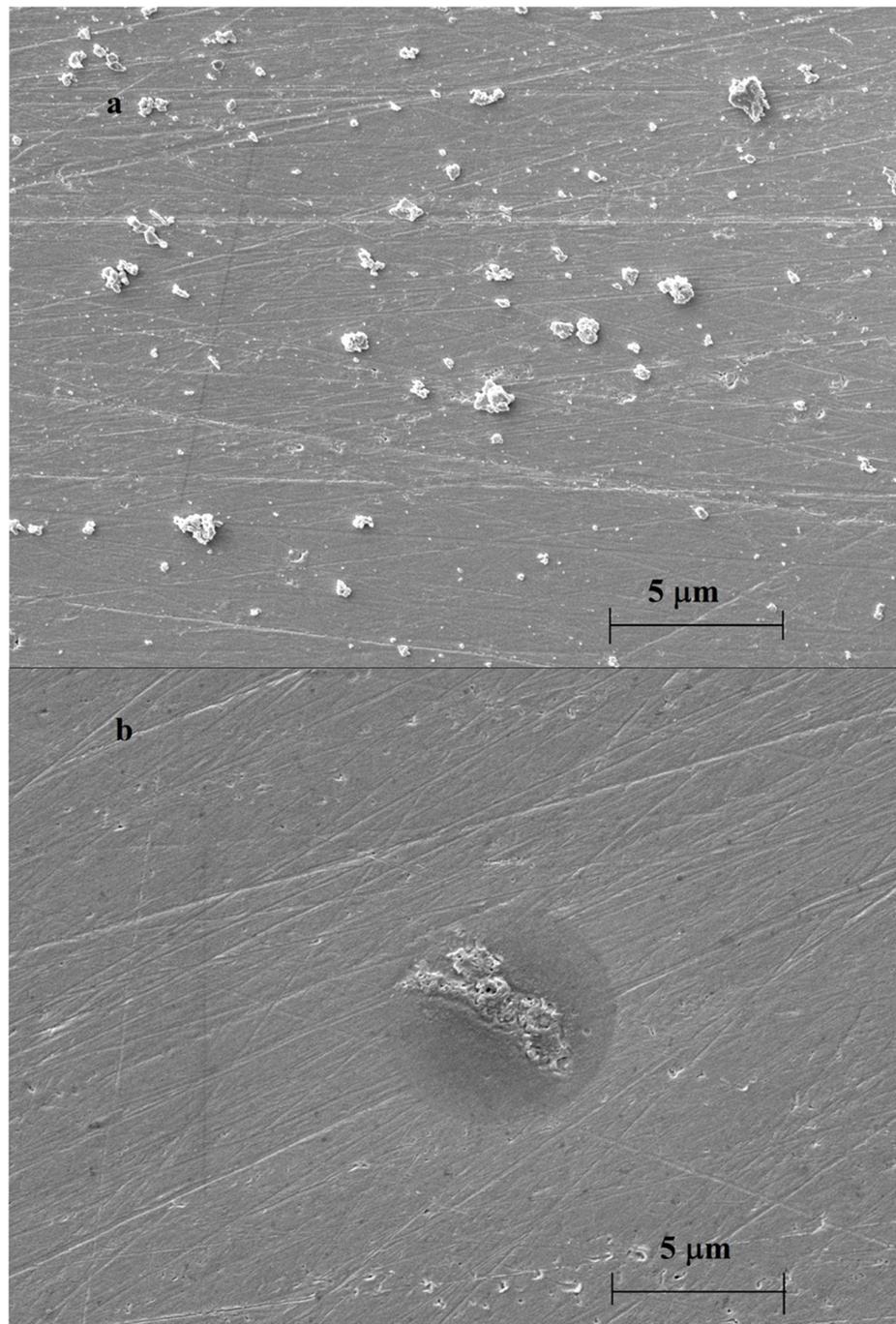


Figure 4. Cont.

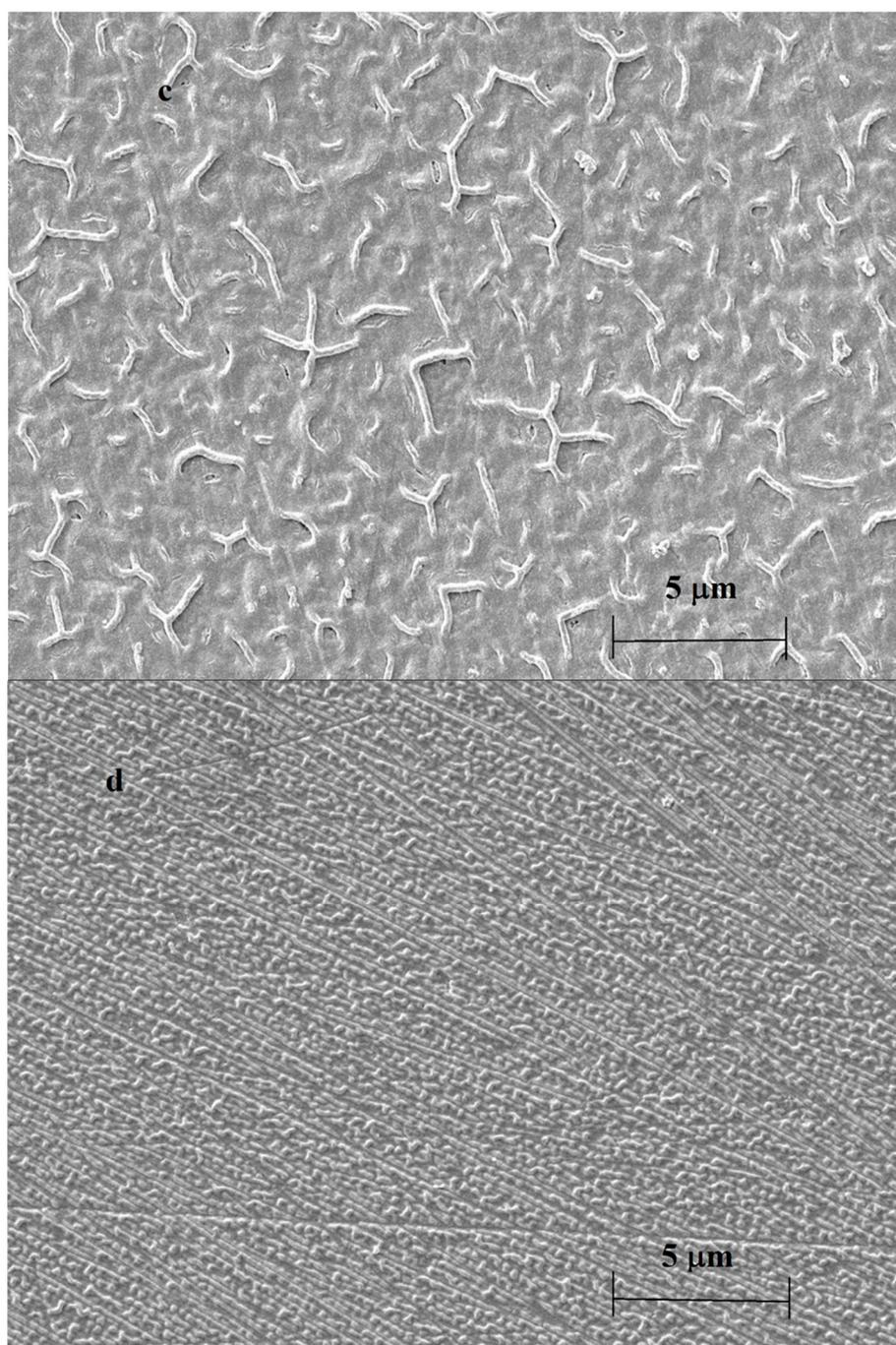


Figure 4. Scanning electron micrographs of layers after 10 successive voltammograms for 1-naphthol electropolymer deposited from MIBK (a), 2-naphthol from MIBK (b), 1-naphthol from MZO (c), and 2-naphthol from MZO (d) ($c = 20$ mM, supporting electrolyte 50 mM TBAP).

2.2. Effect of Dimethyl Formamide Solvent on Electrode Renewal

It was shown in the previous section that dimethyl formamide was one of the solvents where the current signals were highly reproducible. As naphthols have low solubility in water, it is interesting to investigate from the viewpoint of polymer electrosynthesis and electroanalysis how a miscible organic solvent affects their behavior where their solubilities are excellent. Therefore, its addition to water as a co-solvent was carried out to assess the effect of its ratio on peak current reproducibility. The two parts of Figure 5 show that increasing the ratio of DMF in the mixed solvent dramatically improves the signal reproducibility, and at ratios higher than 70 $v/v\%$ for 1-naphthol and above

50 *v/v*% for 2-naphthol it is excellent. The removal of polymeric products of 2-naphthol by solvation is easier due to the presence of the non-aqueous co-solvent in accordance with the previous findings. On the other hand, the application of solvent mixtures is not useful in electroanalytical procedures for the determination of naphthols, as for good reproducibility the predominance of a non-aqueous solvent is needed.

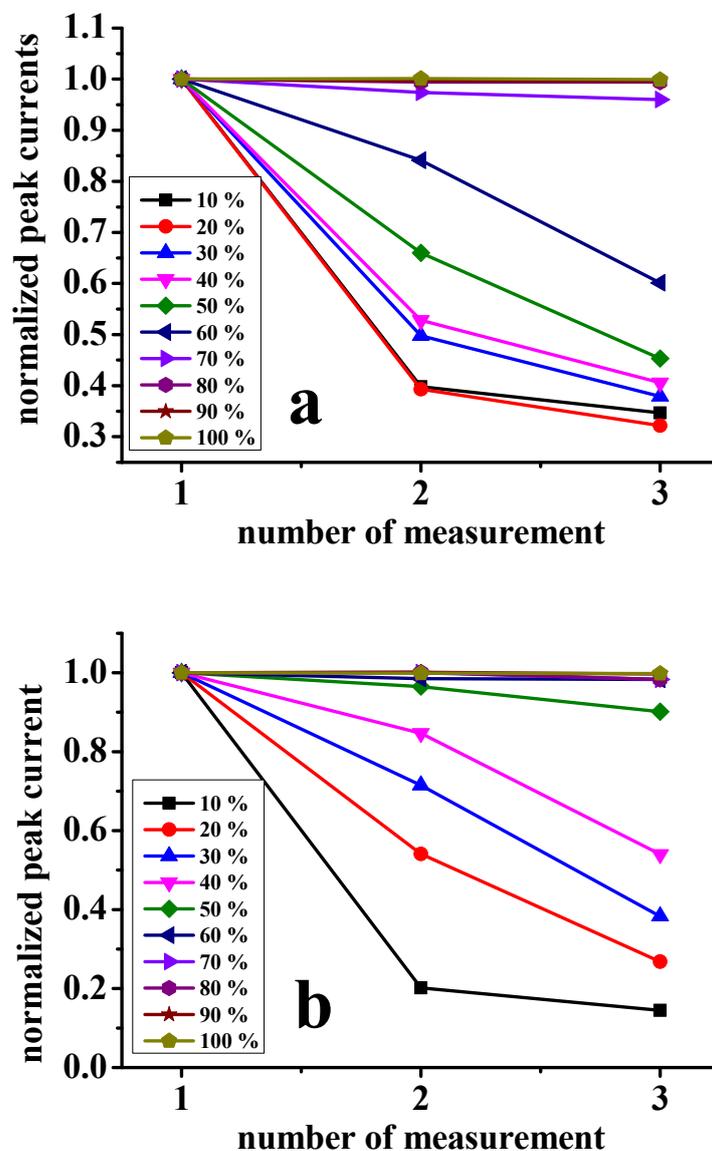


Figure 5. Normalized peak currents for different *v/v*% dimethyl formamide in solutions mixed with water containing 1 mM 1-naphthol (a) and 1 mM 2-naphthol (b) ($v = 0.1$ V/s, supporting electrolyte 10 mM TBAP).

In studies carried out in pH 7 aqueous solutions, the concentration of naphthols was 1 mM, respectively. This concentration is close to their solubilities in water. Without any cleaning step in the second voltammogram, an anodic peak did not show up at all by either substrate, indicating the high degree of electrode fouling as observed generally as an irreversible and rapid fouling process [18]. Previously, it was found that in solvents with high DMF content, the formed oligomers were dissolved, so its ability to remove polymers developed in aqueous solutions was also assessed. The insertion of one-minute soaking periods into two scans significantly renewed the surface of platinum after the anodic polymerization steps (Figure 6). There was a discrepancy with the observations

in DMF–water mixtures, as longer immersion times were not enough for the complete renewal in pure DMF, but its solvation properties proved excellent for polynaphthols. The reason might be that in an aqueous environment, due to the scarce solubility of polymers with higher molecular weight remaining at the electrode, more radicals can join to the forming polymer. So, more time was needed for solvation by DMF molecules. Two minutes and longer immersion periods were already enough to restore the initial surface state, and ultrasonication made the necessary time shorter.

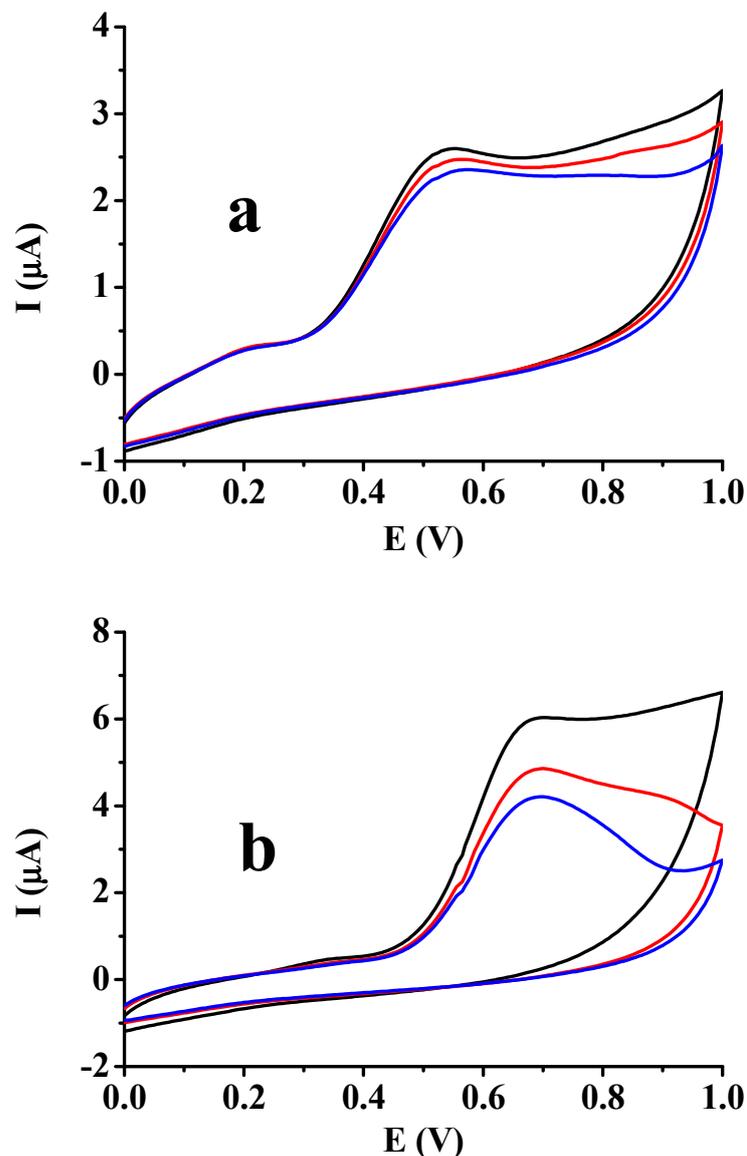


Figure 6. Repeated voltammograms in aqueous solutions containing 1 mM 1-naphthol (a) and 2-naphthol (b) adjusted the pH to 7 with 0.05 M phosphate buffer (black curve: initial scan, red curve: scan after the first immersion and 1 min immersion in DMF, blue curve: scan after the second one and an additional 1 min immersion in DMF).

2.3. Suppression Ability of Naphthols in Electropolymerization of Selected Organic Monomers

Dimethyl sulfoxide was the other solvent where the naphthol isomers did not show any significant electrode fouling. There are some phenols that undergo electrochemical polymerization in each solvent in the absence of additives. This solvent has on the other hand outstanding properties as shown earlier with polyaniline composite film [32]. A thick and porous film formed in it, composed of poly(phenyleneoxide) which is not characteristic of many other non-aqueous solvents. Typically, such a compound is phloroglucinol so this

polyhydroxy phenol was studied together with naphthols in dimethyl sulfoxide. The reason for this choice was that theoretically poly(phloroglucinol) can bind other organic molecules also through hydrogen bonds due to the two hydroxyl groups found per monomer unit. The third hydroxyl group disappears during the anodic polymerization and then it will be involved in the ether linkages. The scanning electron micrographs of poly(phloroglucinol) can be seen in Figure 7 deposited from the 50 mM phloroglucinol solution. The micrograph clearly demonstrates (part a) that a coherent deposit forms from phloroglucinol, and parts b and c show that polymers with different structures grow when the naphthol isomers are also present in solution, respectively. On the other hand, scratches on the electrode surface are hardly seen in the micrographs, with visualizing the thickness of deposits also being characteristic of co-deposition with naphthols. The differences upon the addition of naphthols to the electrolysis solution were clearly seen also with the naked eye through the change in intensity of brownish color as a consequence of film thicknesses. Colors originating from light interference were further indicators of the thicknesses. From solutions where copolymerization occurred with naphthols, rougher deposits formed, clearly demonstrated by the micrographs and holes also developed which are deeper due to the copolymer of 2-naphthol. The copolymerization improves the solvation properties of products so a higher percentage will be removed by dissolution. As a consequence, thinner layers remain on the electrode than the thickness of poly(phloroglucinol). By elucidating the observations, it can be concluded that the radicals formed from naphthols quench the electropolymerization of phloroglucinol, leading to the growth of shorter polymer chains and naphthoxyl moieties, and significantly improving their solubilities. The remaining part with a rougher surface and structure with higher porosity consists mainly of units originating from phloroglucinol.

The above observations allow the consequences that copolymerization has on the electrode to be more accessible to other molecules. Similar observations demonstrated in an earlier work [33] that 4-chlorophenol is an appropriate suppressor of phenol electropolymerization. This latter result in the findings herein indicates that if one of the studied monomers is not susceptible to fouling alone in the respective solvent, it will dramatically prevent the film growth from the other monomer.

The electrodeposited layers of naphthols were examined from the viewpoint of analytical usefulness by using 4-methoxyphenol as a redox active material. This phenol derivative has a significantly lower susceptibility to fouling compared with the majority of the other derivatives when it is electrochemically oxidized. A 5 mM solution was prepared from it with acetonitrile and another 5 mM aqueous pH = 7 solution buffered with 0.05 M phosphate buffer. In these conditions, 4-methoxyphenol provides reproducible voltammetric signals, so heights of linear sweep voltammetric peaks were compared with those obtained with the bare platinum electrode by normalization, leading to the values of the recoveries.

The anodic peak current recoveries in Table 1 show remarkably that in a non-aqueous acetonitrile solvent, the peak currents are higher generally than in an aqueous solution. This indicates that the films have a predominantly apolar nature. In solvents where MIBK and MZO built layers of 1-naphthol, the recoveries are close to the values obtained with a bare electrode, and moreover, some accumulation occurred. The dependence on a number of deposition scans is more significant for 2-naphthol in the aqueous phase, and smaller values were characteristic in acetonitrile. These observations show the higher accumulation ability of 1-naphthol-based films, and micrographs show that the cause is the higher density of polymer particles and higher porosity. The recovery values approximating 100% in aqueous solution in the case of films deposited from MIBK are in accordance with the microscopic findings as there is a large area on the platinum surface freely available for the 4-methoxyphenol molecules. It implies, together with the SEM results, that the ketone groups presenting in the oxocompound solvents have a significant role in coiling the deposit, concentrating it in islands, forming organic matter that remains on platinum after all washing pretreatments.

The really surprising results came from the film growth suppression studies in dimethyl sulfoxide solvent used for deposition. The homopolymer of phloroglucinol has significant resistance towards the electrooxidation of 4-methoxyphenol independently of the number of voltammetric scans. On the contrary, when the deposition was repeated together with naphthols, accumulation could be observed when a few scans were applied. By thickening the films, a higher diffusion resistance developed. These findings verify that the rougher surface and development of chambers underneath the deposits improve the accumulation ability of films.

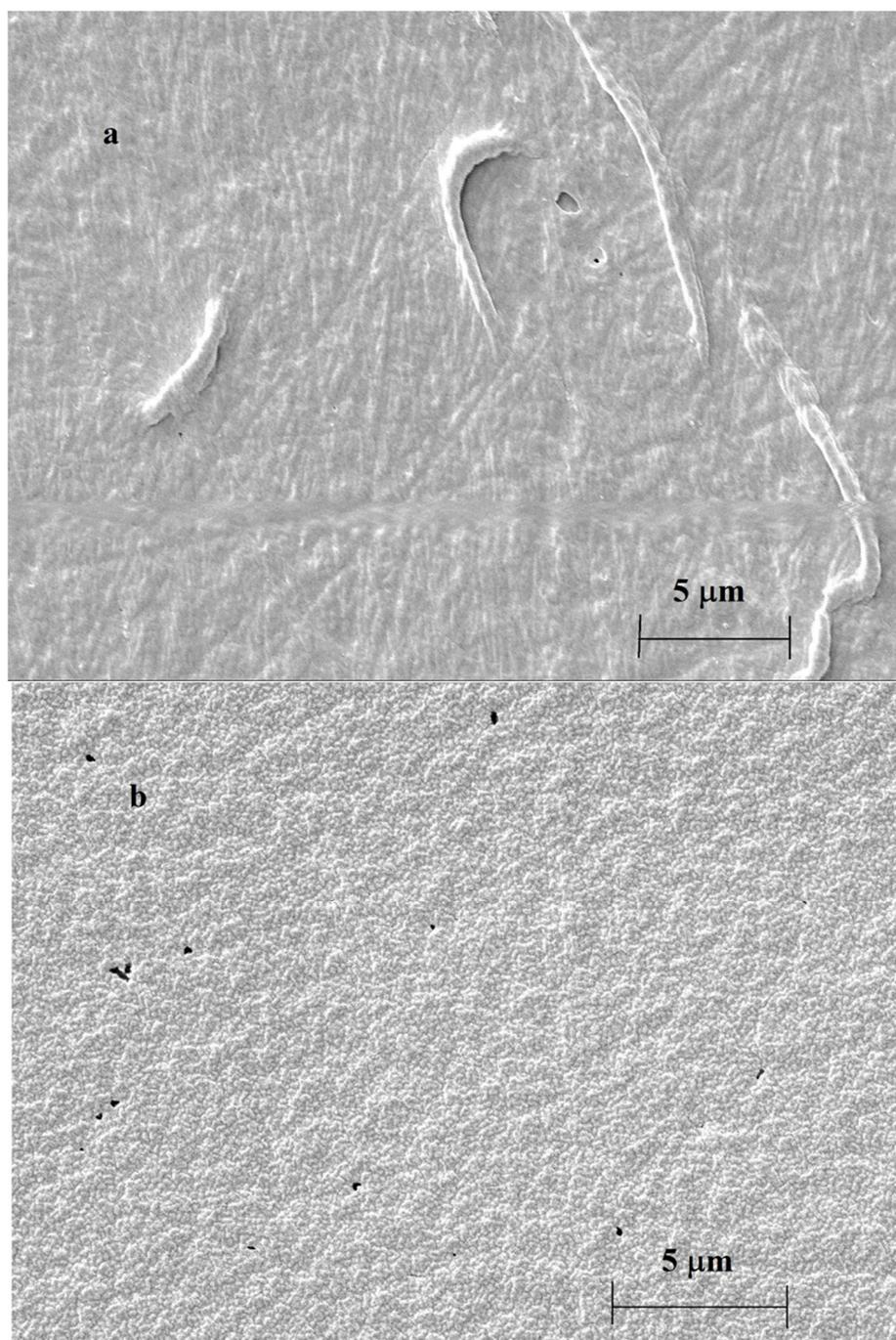


Figure 7. Cont.

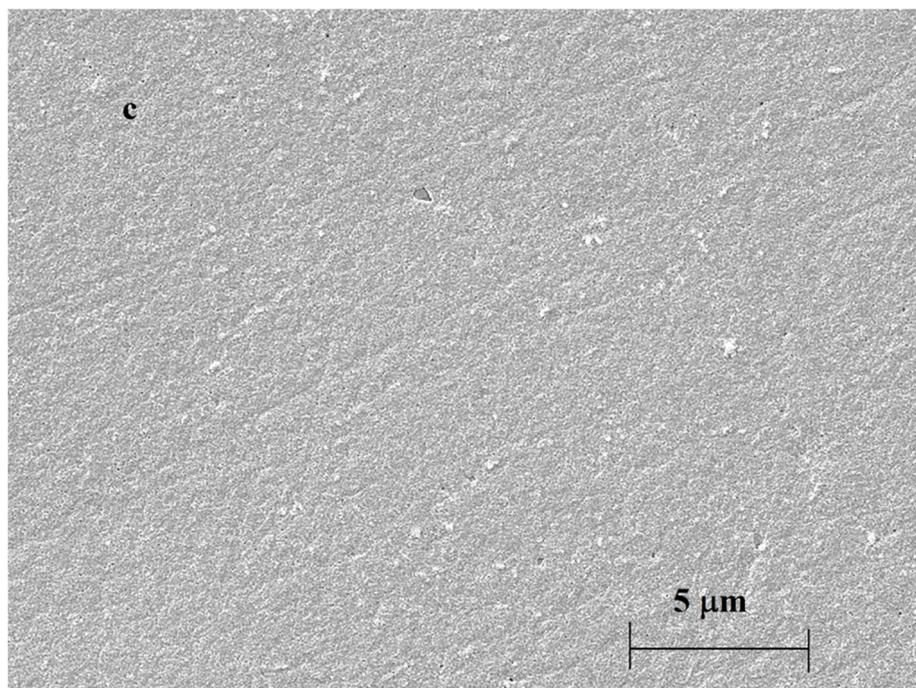


Figure 7. Scanning electronic microscopic images of electrodeposited film from 50 mM solution of phloroglucinol prepared with dimethyl sulfoxide (a), in the presence of 50 mM 1-naphthol (b), and in the presence of 50 mM 2-naphthol (c).

Table 1. Normalized 4-methoxyphenol peak current recoveries for the different deposits in aqueous and organic solvents (1-NP: 1-naphthol, 2-NP: 2-naphthol).

Deposit	1st CV		2nd CV		3rd CV		10th CV	
	Org.	Aq.	Org.	Aq.	Org.	Aq.	Org.	Aq.
1-NP MIBK	107.6	89.2	107.7	81.1	105.8	54.5	104	36.3
2-NP MIBK	96	52.4	94.1	49.4	94	47	94.4	46.4
1-NP MZO	109	86.3	111.1	78.9	108.7	45.4	100.5	41.4
2-NP MZO	92.6	60	91.6	49.6	91.5	46.6	99	42.2
FLO	81.9	89.9	91.7	89.4	58.6	77.4	48	58.2
FLO+1-NP	107	96.9	100	95.2	97	63.6	60.3	55.5
FLO+2-NP	101.6	94.9	106.6	81.4	104	63.9	87	52.8

3. Materials and Methods

The purity of all chemicals used corresponded to spectroscopic and HPLC grade, and they were used as received. The platinum disc working electrodes have 1 and 3 mm diameters, and the platinum wire counter and silver wire reference electrode (in aqueous systems saturated calomel) were embedded in the solutions building up a three-electrode cell and connected to a potentiostat (Dropsens, Spain, Oviedo). Before all investigations, the surface of the platinum disc sealed in polyetheretherketone was cleaned by polishing with alumina on a polishing cloth (eDAQ). This cleaning procedure was followed by thorough washing with tap water and then with deionized water. Due to studies in non-aqueous systems, the disturbance of water traces should be minimized, so before use, the final cleaning step was rinsing with dry acetone. An apolar supporting electrolyte, tetrabutylammonium perchlorate (TBAP), was used, and in aqueous solutions, 0.05 mol/L pH = 7 phosphate buffer was used.

The microscopic images of certain deposits were acquired with a scanning electron microscope (Jeol JSM-IT500HR (Jeol, Tokyo, Japan)) at the highest magnification. Before depositing such layers, the platinum electrodes were cleaned thoroughly in an ultrasonic

bath, washed thoroughly with deionized water, and finally with dry acetone to remove everything from the metal surface as completely as possible, making them ready for use. In the evacuated chamber of the microscope, the electrodes were fixed upright in a specific holder at their top with the deposited layer.

4. Conclusions

The investigations showed that the anodic behavior of naphthols is very different depending on the solvent. The copolymerization studies in the two good solvents for the oxidation products (dimethyl sulfoxide and dimethyl formamide) demonstrated strong suppression ability towards electropolymerization of other monomers. Controlled layer growth under suppression can serve as a promising route for electrode modification to enhance sensitivity towards certain analytes.

Author Contributions: Conceptualization, L.K.; writing—original draft preparation, L.K.; writing—review and editing, S.K.-M.; visualization, P.S.; supervision, L.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Hungarian National Research Development and Innovation Office (NKFI), grant number NKFI-137793, and by the New National Excellence Program of the Ministry for Innovation and Technology Project no. TKP2021-EGA-17.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Abd El-Rahman, H.A. Stability and behaviour of poly-1-naphthol films towards charge transfer reactions. *Thin Solid Films* **1997**, *310*, 208–216. [[CrossRef](#)]
2. Abdelaal, M.Y. Electrochemical polymerization of naphthols in aqueous medium. *Int. J. Polym. Mater.* **2005**, *54*, 151–159. [[CrossRef](#)]
3. Meneguzzi, A.; Ferreira, C.A.; Pham, M.C.; Delamar, M.; Lacaze, P.C. Electrochemical synthesis and characterization of poly(5-amino-1-naphthol) on mild steel electrodes for corrosion protection. *Electrochim. Acta* **1999**, *44*, 2149–2156.
4. Cinta, E.P.; Torresi, S.I.C. Resonant Raman spectroscopy as a tool for determining the formation of a ladder structure in electropolymerized poly(5-amino-1-naphthol). *J. Electroanal. Chem.* **2002**, *518*, 33–40. [[CrossRef](#)]
5. Ohsaka, T.; Ohba, M.; Sato, M.; Oyama, N.; Tanaka, S.; Nakamura, S. Formation of a novel electroactive film by electropolymerization of 5-amino-1-naphthol. *J. Electroanal. Chem.* **1991**, *300*, 51–66. [[CrossRef](#)]
6. Mostefai, M.; Pham, M.; Marsault, J.; Aubard, J.; Lacaze, P. Study of the redox process of poly(5-amino-1-naphthol) thin film by in situ Raman spectroscopy. *J. Electrochem. Soc.* **1996**, *143*, 2116–2119. [[CrossRef](#)]
7. Pham, M.; Mostefai, M.; Simon, M.; Lacaze, P. Electrochemical synthesis and study of poly(5-amino-1-naphthol) film in aqueous and organic media. *Synth. Met.* **1994**, *63*, 7–15. [[CrossRef](#)]
8. Chitravathi, S.; Swamy, B.E.K.; Mamatha, G.P.; Sherigara, B.S. Electrochemical behavior of poly(naphthol green B)-film modified carbon paste electrode and its application for the determination of dopamine and uric acid. *J. Electroanal. Chem.* **2012**, *667*, 66–75. [[CrossRef](#)]
9. Kuskur, C.M.; Swamy, B.E.K.; Jayadevappa, H. Poly(naphthol green B) modified carbon paste electrode for the analysis of paracetamol and norepinephrine. *Ionics* **2019**, *25*, 1845–1855. [[CrossRef](#)]
10. Kuskur, C.M.; Swamy, B.E.K.; Jayadevappa, H. Poly(naphthol green B) modified carbon paste electrode for catechol and hydroquinone. *J. Electroanal. Chem.* **2017**, *804*, 99–106. [[CrossRef](#)]
11. Cai, C.X.; Xue, K.H. Electrochemical characterization of electropolymerized film of naphthol green B and its electrocatalytic activity toward NADH oxidation. *Microchem. J.* **1998**, *58*, 197–208. [[CrossRef](#)]
12. Chandra, U.; Swamy, B.E.K.; Gilbert, O.; Sherigara, B.S. Poly(naphthol green B) film based sensor for resolution of dopamine in the presence of uric acid: A voltammetric study. *Anal. Methods* **2011**, *3*, 2068–2072. [[CrossRef](#)]
13. Lu, B.; Liu, C.; Li, Y.; Xu, J.; Liu, G. Conducting polynaphthalenes from 1,1'-binaphthyl and 1,1'-bi-2-naphthol via electropolymerization. *Synth. Met.* **2011**, *161*, 188–195. [[CrossRef](#)]
14. Lu, B.; Yan, J.; Xu, J.; Zhou, S.; Hu, X. Novel electroactive proton-doped conducting poly(aromatic ethers) with good fluorescence properties via electropolymerization. *Macromolecules* **2010**, *43*, 4599–4608. [[CrossRef](#)]
15. Baibarac, M.; Daescu, M.; Socol, M.; Bartha, C.; Negrila, C.; Fejer, S.N. Influence of reduced graphene oxide on the electropolymerization of 5-amino-1-naphthol and the interaction of 1,4-phenylene diisothiocyanate with the poly(5-amino-1-naphthol)/reduced graphene oxide composite. *Polymers* **2020**, *12*, 1299. [[CrossRef](#)]

16. Meana-Esteban, B.; Kvarnström, C.; Geschke, B.; Heinze, J.; Ivaska, A. Electrochemical polymerization of 2-methoxynaphthalene. *Synth. Met.* **2003**, *139*, 133–143. [[CrossRef](#)]
17. Richard, K.M.; Gewirth, A.A.J. Observation of electrode poisoning during the electro-oxidation of aromatic alcohols on (111)Au. *Electrochem. Soc.* **1996**, *143*, 2088–2092. [[CrossRef](#)]
18. Ciriello, R.; Cataldi, T.R.I.; Centonze, D.; Guerrieri, A. Permselective behaviour of an electrosynthesized, nonconducting thin film of poly(2-naphthol) and its application to enzyme immobilization. *Electroanalysis* **2000**, *12*, 825–830. [[CrossRef](#)]
19. Ciriello, R.; Guerrieri, A.; Pavese, F.; Salvi, M.A. Electrosynthesized, non-conducting films of poly(2-naphthol): Electrochemical and XPS investigations. *Anal. Bioanal. Chem.* **2008**, *392*, 913–926. [[CrossRef](#)] [[PubMed](#)]
20. Guerrieri, A.; Lattanzio, V.; Palmisano, F.; Zambonin, P.G. Electrosynthesized poly(pyrrole)/poly(2-naphthol) bilayer membrane as an effective anti-interference layer for simultaneous determination of acetylcholine and choline by a dual electrode amperometric biosensor. *Biosens. Bioelectron.* **2006**, *21*, 1710–1718. [[CrossRef](#)]
21. Pham, M.C.; Moslih, J.; Chauveau, F.; Lacaze, P.C. In situ multiple internal reflection Fourier transform infrared spectroscopic (MIRFTIRS) study of the electrochemical immobilization of heteropolyanions in poly(1-naphthol) coated electrodes. *J. Appl. Electrochem.* **1991**, *21*, 902–909. [[CrossRef](#)]
22. Rehan, H.H. Electrosynthesis and characterization of new conducting copolymer films from 1-naphthol and methyl naphthyl ether. *Polym. Int.* **2000**, *49*, 645–653. [[CrossRef](#)]
23. Kiss, L.; Kunsági-Máté, S. Assessment of non-aqueous solvents in the electrooxidation of resorcinol, phloroglucinol, pyrogallol, and role of co-solvent in determination of pyrogallol with microelectrode voltammetry. *Stud. Univ. Babeş-Bolyai Chem.* **2021**, *66*, 159–170.
24. Gulnaz, R.N.; Vitaliy, V.Y.; Natalia, V.N.; Dmitry, E.K.; Albina, Y.Z.; Alexandr, I.K. Redox-switchable binding of ferrocyanide with tetra(viologen)calix [4] resorcine. *J. Incl. Phenom. Macrocycl. Chem.* **2012**, *72*, 299–308.
25. Liska, A.; Rosenkranz, M.; Klíma, J.; Dunsch, L.; Lhoták, P.; Ludvík, J. Formation and proof of stable bi-, tri-, and tetradical polyanions during the electrochemical reduction of cone-polynitrocalix[4]arenes. An ESR-UV-vis spectroelectrochemical study. *Electrochim. Acta* **2014**, *140*, 572–578. [[CrossRef](#)]
26. Liska, A.; Vojtisek, P.; Fry, A.J.; Ludvík, J. Electrochemical and quantum chemical investigation of tetranitrocalix[4]arenes: Molecules with multiple redox centers. *J. Org. Chem.* **2013**, *78*, 10651–10656. [[CrossRef](#)]
27. Liska, A.; Flídrová, K.; Lhoták, P.; Ludvík, J. Influence of structure on electrochemical reduction of isomeric mono- and di-, nitro- or nitrosocalix[4]arenes. *Monatsh. Chem.* **2015**, *146*, 857–862. [[CrossRef](#)]
28. Vitaly, V.Y.; Gulnaz, R.N.; Natalya, V.N.; Albina, Y.Z.; Dmitry, E.K.; Yulia, S.S.; Margit, G.; Wolf, D.H.; Andrey, A.K.; Alexandr, I.K. Electrodriven molecular system based on tetraviologen calix[4]resorcine and dianion 1,5-bis(*n*-sulfonatophenyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane. *Electrochim. Acta* **2013**, *111*, 466–473.
29. Kiss, L.; Kovács, F.; Kunsági-Máté, S. Role of allyl alcohol and sodium 4-vinylbenzenesulphonate in the electrooxidation of phenol. *Chem. Phys. Lett.* **2021**, *764*, 138270. [[CrossRef](#)]
30. Kiss, L.; Kovács, F.; Li, H.; Kiss, A.; Kunsági-Máté, S. Electrochemical polymerization of phenol on platinum and glassy carbon electrodes in mesityl oxide. *Chem. Phys. Lett.* **2020**, *754*, 137642. [[CrossRef](#)]
31. Kiss, L.; Kovács, F.; Kunsági-Máté, S. Investigation of anodic behaviour of phenylethers in non-aqueous solvents on platinum and glassy carbon electrodes. *J. Iran. Chem. Soc.* **2021**, *18*, 1677–1687. [[CrossRef](#)]
32. Yin, S.X.; Lu, W.T.; Guo, C.Y. Enhancing thermoelectric performance of polyaniline/single-walled carbon nanotube composites via dimethyl sulfoxide-mediated electropolymerization. *ACS Appl. Mater. Interfaces* **2021**, *13*, 3930–3936. [[CrossRef](#)] [[PubMed](#)]
33. Kiss, L. Coexistence of substituted phenols reduces the fouling ability of phenol in non-aqueous solvents. *Period. Polytech-Chem.* **2022**, *66*, 409–413. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.