

Electropolymerization of *N,N'*-Diphenylguanidine in Non-Aqueous Aprotic Solvents and Alcohols

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Abstract

Electrooxidation of *N,N'*-diphenylguanidine (1,3-diphenylguanidine) was investigated in aprotic (acetonitrile, acetone, dimethyl sulfoxide, dimethyl formamide, propyleneoxide, nitromethane) and alcoholic (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, benzyl alcohol) non-aqueous solvents at platinum electrode with cyclic voltammetry. Its concentration was 5 mM in most cases. In acetonitrile and acetone a sharp voltammetric peak appeared around 1 V vs. reference and currents measured in the subsequent scans showed that the electrode fouled quickly. In dimethyl formamide, the anodic peak heights decreased slowly in the subsequent scans but in dimethyl sulfoxide weak deactivation could be observed both in smaller and in higher concentration. In alcohols, continuous deactivation could be also observed during electrooxidation of *N,N'*-diphenylguanidine.

The permeability studies showed that the structure of the formed polymer films varied significantly according to the solvent used for electrodeposition.

Keywords

N,N'-diphenylguanidine, non-aqueous solvent, electrooxidation, cyclic voltammetry

1 Introduction

The behavior of different organic compounds during their electrochemical reaction provides interesting findings in many respects. Their redox properties determine the usefulness in the different applications mainly electrochemical reversibility, and some materials can foul the electrode surface by electrodeposition.

Guanidines are a large group of nitrogen containing organic compounds which are interesting mainly due to their redox properties and coordination chemistry [1-11]. They can bind readily to metal cations and form complexes having different properties and therefore they proved themselves to be appropriate in many applications. Guanidine benzene derivatives can build up Ag⁺ bridged multicore metal complexes which have semiconducting properties [12] and metal ion bridged polymers also form with silver dicyanamide [13]. Their color changes remarkably by the degree of protonation and due to electrochemical reactions [14-16]. Guanidines having ferrocene moiety are redox active and they have attracted wide interest in anion sensing, mainly acetate [17], and showed anticancer activity [18].

Functionalization with guanidinium moiety can make possible sensing of carboxylates [19, 20], and any other oxoanions [21-23]. Metal-free redox active guanidines were also synthesized and used as reducing agents [24].

Electrodeposition of films with low conductivity is under intensive research due to several practical applications. One of them is size exclusion as the films grown onto the electrode surface make possible the controlled release of molecular or ionic species. For low conductivity layers polyphenols serve as a good example and their transport properties have been widely investigated [25-28].

In general, *N,N'*-diphenylguanidine is used in rubber industry as it can facilitate the vulcanisation process also at lower temperatures and as intermediate in pharmaceutical industry. The compound has toxicity for humans and aquatic organisms. According to our knowledges, the electrochemistry of *N,N'*-diphenylguanidine has not explored yet so the subject of this publication is the study of this compound in non-aqueous solvents and estimation of the transport properties of the formed polymer films.

2 Experimental

The solvents used were analytical grade and *N,N'*-diphenylguanidine was the product of Fluka as well as 1,4-dihydroxybenzene was purchased from Reanal. As presence of a few quantity of water can influence the electrochemistry of several organic compounds in non-aqueous solvents the water content of solvents was minimized by addition of anhydrous Na_2SO_4 to them before preparation of solutions. The experiments were carried out at ambient temperature with a platinum disc working electrode (1 mm in diameter, sealed in polyetheretherketone), platinum wire counter electrode connected to a potentiostat (eDAQ Pty. Ltd., Australia). The reference electrode was a silver wire in all non-aqueous solvents and in aqueous solvents a standard calomel electrode (SCE). The working electrode was thoroughly polished with 1, 0.3 and 0.05 μm alumina on a polishing cloth and then ultrasonicated in deionized water, finally washed with deionized water. All electrodes were dried by rinsing with anhydrous acetone before all measurements to further minimize introduction of water to the electrochemical cell. Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte. After taking a cyclic voltammogram the solutions were always stirred before recording the next one to renew the solution layer presenting close to the electrode surface depleted by diffusion of electroactive material. This step was essential to be sure the observed current decrease is attributed to electrode deactivation.

For micro-Raman spectroscopic investigations of the electrodeposited films a LABRAM HR spectrometer (Horiba Jobin Yvon, Lille, France) was applied by focusing the red laser light onto the electrode surface and the monochromatic light used for illumination had a 632.81 nm wavelength.

3 Results and discussion

3.1 Complementary studies of voltammetric behavior of solvents

In two recent works, phenol was studied by using voltammetric methods in alcohols and aprotic non-aqueous solvents [28, 29]. The main findings concerning the used solvents will be summarized here in some words which is important by studies with *N,N'*-diphenylguanidine. Their cyclic voltammograms can be found in these papers and they were taken in presence of 50 mM TBAP supporting electrolyte. The results obtained with alcohols in one of these earlier works will be summarized in the following

part of the paragraph. They started to oxidize above 1 V but they had no oxidation peak between 0 and 2 V, only the current increased continuously by increasing the potential. This is the working potential window for anodic oxidation of *N,N'*-diphenylguanidine as it will be shown in the later sections. The most remarkable current increase was observed by methanol which has the highest electroactivity of the selected alcohols. Ethanol and 1-propanol had also significant but smaller background currents above 1 V, electrooxidation of higher molecular weight alcohols resulted lower currents. No relevant cathodic peak or wave appeared at higher potentials than 0 V vs. Ag wire.

By the same supporting electrolyte concentration, the voltammograms of the selected aprotic solvents were also taken in an other work [29]. It was demonstrated that none of them had any peak in their voltammogram. Acetonitrile provided a wide potential window for anodic studies, acetone began to oxidize around 2 V, in case of dimethyl formamide and dimethyl sulfoxide significant anodic current increases could be observed above 1.7 V. In studies here, two additional solvents (propylene oxide, nitromethane) were selected and their potential window had to be established. Fig. 1 shows their cyclic voltammograms between 0 and 2 V in presence of 50 mM TBAP supporting electrolyte. Propylene oxide is stable in this potential window according to the observed low currents but nitromethane showed higher electroactivity and significant increase in anodic currents close to 2 V where oxidation of the solvent occurs. It has a small reduction peak around 0.45 V which can be assigned to the electroreduction of products presenting at the electrode surface.

The capacitive behaviour plays usually predominant role in the continuous anodic current increase by scanning to

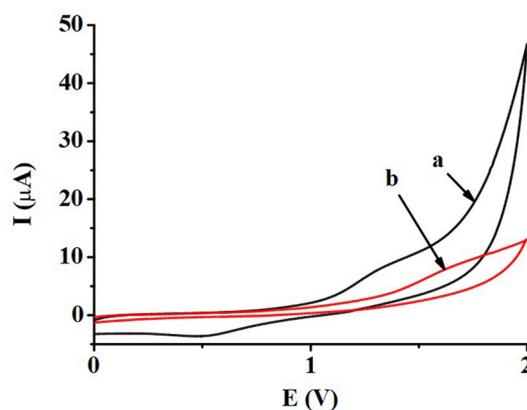


Fig. 1 Cyclic voltammogram of nitromethane (curve a) and propylene oxide (curve b) (scan rate 0.1 V/s, supporting electrolyte 50 mM TBAP)

more positive potentials. On the other hand, the significant ohmic drop influences also the shape of curves. In these situations, the solvents are neutral materials and the concentration of supporting electrolyte is very small compared with the solvent. The most of investigated solvents should exhibit some electroactive behavior between 0 and 2 V, particularly alcohols prone to oxidation. Due to the very low support ratio (ratio of electroactive material concentration and supporting electrolyte concentration) the anodic peaks shift to very positive potentials. This is the reason for the experience that no relevant peaks appeared in voltammograms of solvents used here and also in the two earlier works cited in this paragraph.

3.2 Electrochemical investigation of *N,N'*-diphenylguanidine in the aprotic solvents

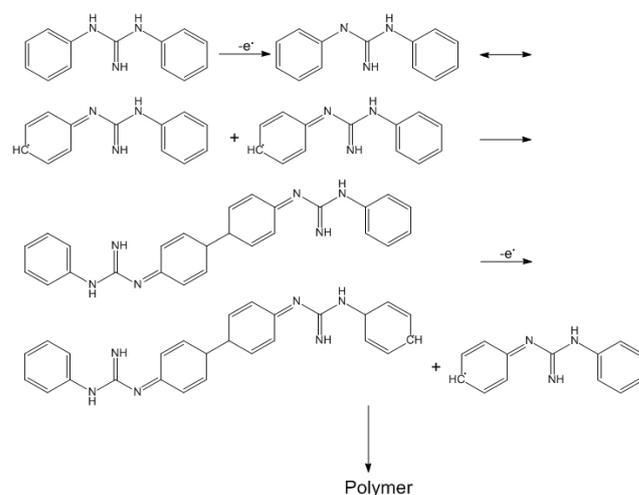
In the first part of investigations the electrochemistry of *N,N'*-diphenylguanidine was explored in the different non-aqueous solvents used. Five subsequent cyclic voltammograms were recorded with 0.1 V/s scan rate between 0 and 2 V in solutions substrate dissolved in 5 mM concentration. Fig. 2 shows the recorded voltammograms for each solvent, respectively. Except for dimethyl formamide and dimethyl sulfoxide a rapid fouling could be observed. The observed oxidation peaks are due to the formation of radicals in the first oxidation step which reacted with other radicals or monomers resulting in a polymer film adherent to the platinum surface. Looking at the first voltammograms recorded in each solvent after the appearance of the oxidation peak the currents increased again due to the electrooxidation of solvents. The peak heights are relatively small due to the continuous fouling.

To make consequences about the composition of polymer micro-Raman studies were performed. Fig. 3 displays the spectrum for *N,N'*-diphenylguanidine and that of polymer electrodeposited from acetonitrile. The spectrum of substrate contains characteristic peaks: at around 3080 cm^{-1} for Ar-H stretching vibrations, 1280 and 1180 cm^{-1} for C-N stretching of aromatic amine moieties. A high intensity peak centered close to 1000 cm^{-1} can be assigned to the ring breathing mode being usually strong in Raman. At around 1600 cm^{-1} a complex peak can be found due to stretching vibrations of benzene ring and C=N bond. The peak at around 3050 cm^{-1} can be assigned to Ar-H stretching and the one at 3390 cm^{-1} to N-H stretching. At wavenumbers lower than 1000 cm^{-1} peaks corresponding to deformation vibrations appear.

The peaks characteristic for the monomer substrate can be found also in the spectrum of the electrodeposited material but they are slightly shifted as a consequence of polymerization. The peak near 1000 cm^{-1} is intensive also here indicating the stacking of unsaturated rings. The peak at 3390 cm^{-1} observed by the substrate is almost absent here showing the disappearance of amine N-H bonds due to the electrooxidation.

When *N,N'*-diphenylguanidine is oxidized electrochemically, the first step is the formation of a radical on the nitrogen atom of one of the -NH- group as illustrated in Scheme 1. This hypothesis can be reinforced by the spectroscopic results as the peaks of polymer appeared near the same wavenumbers. Then, the electronic structure of the neighboring benzene ring reorganizes being capable of the coupling with an other radical. The other -NH- group can also oxidize and a chain polymer might form which deactivates the electrode surface. As -NH- group is strongly electron donating the para position is the most preferred for the unpaired electron after the formation of the radical similarly to electropolymerization of aniline [30, 31].

In dimethyl formamide, the deactivation of electrode was slow indicating the formation of polymer which covers the electrode surface but in parallel to this process the solvent could dissolve significant amount of oligomers and polymers. In dimethyl sulfoxide, the decrease of peak currents was slow in the subsequent scans suggesting that majority of the formed oligomers dissolved readily so platinum surface was accessible for the unreacted monomers. The sharp current increase after 1.7 V is attributable to the electrooxidation of solvent. Accessibility of electrode surface for solvent molecules became inhibited strongly by the formed compact



Scheme 1 Mechanism of electropolymerization of *N,N'*-diphenylguanidine

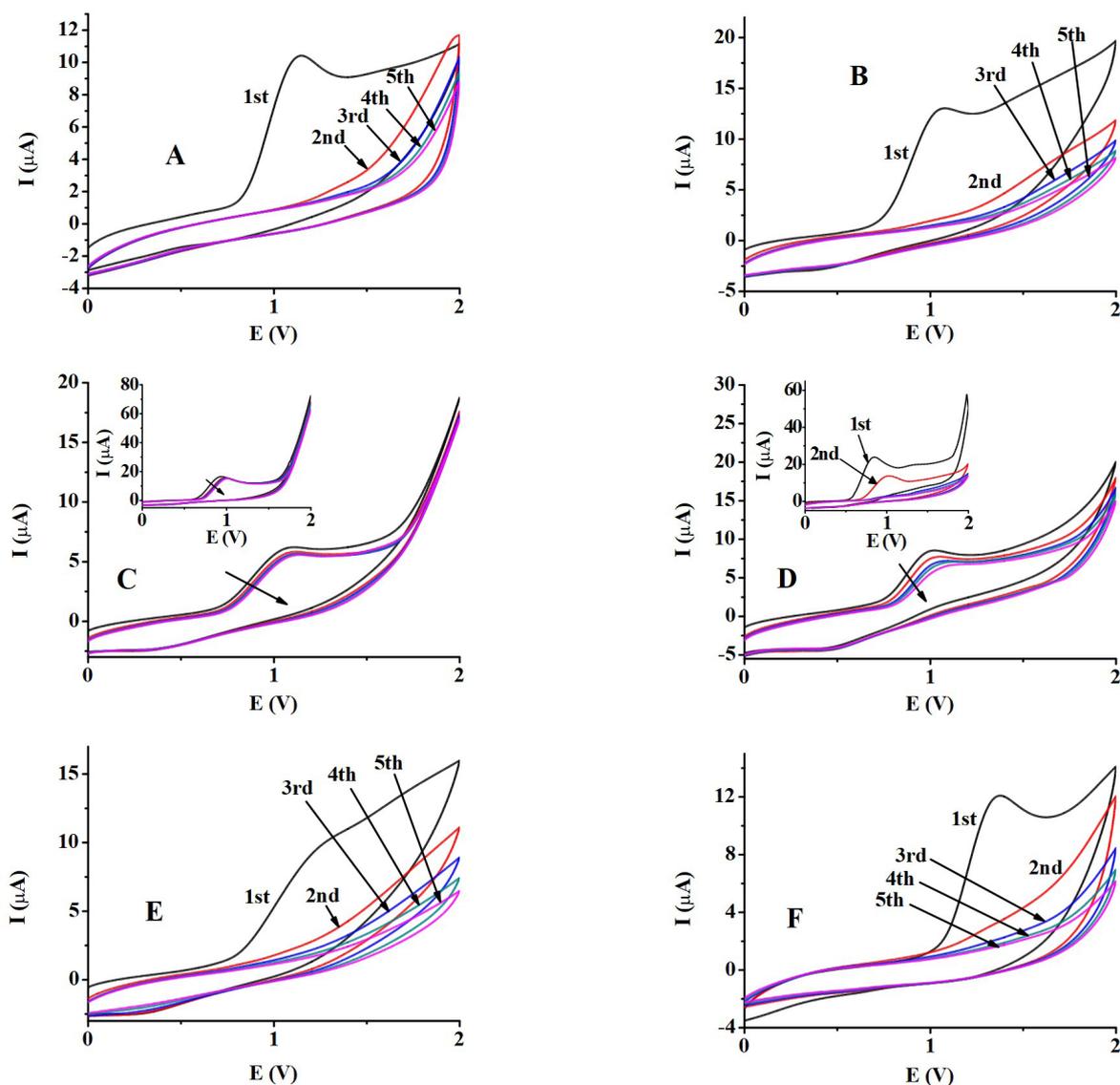


Fig. 2 Subsequent cyclic voltammograms of 5 mM *N,N'*-diphenylguanidine in the aprotic solvents A) acetonitrile, B) acetone, C) dimethyl sulfoxide, D) dimethyl formamide, E) propyleneoxide, F) nitromethane; supporting electrolyte 50 mM TBAP, $v=0.1$ V/s. Inset graphs in part C and D: cyclic voltammograms of the substrate in 25 mM concentration.

film in nitromethane as currents close to 2 V are lower compared with the voltammogram of pure nitromethane (Fig. 1). In propylene oxide there was not any peak only an oxidation wave which is unusual by macroelectrodes and concentrations in the mM range. The probable cause is the overlapping with solvent electrooxidation as the anodic wave of propylene oxide begins around 1.5 V (Fig. 1). It appears immediately after the potential where *N,N'*-diphenylguanidine starts to oxidize (around 1.25 V). These two phenomena results in wave instead of a well-defined peak.

The experiments were repeated with higher concentration of *N,N'*-diphenyl guanidine (25 mM) in dimethyl formamide and dimethyl sulfoxide. The related curves

are displayed in the corresponding inset graphs of Fig. 3. They show clearly that in dimethyl formamide the electrode deactivation was faster than in solution containing the soluted material in lower concentration. The significant shift of anodic peak of second scan relative to the first one clearly indicates the presence of insulating layer. This signal was absent in the voltammograms of 5 mM *N,N'*-diphenylguanidine so solvent electrooxidation can be excluded. It is only present in the first voltammogram while it is absent in the second one because of the potential shift towards higher anodic potentials. Due to the higher concentration the rate of polymerization was higher resulting more insoluble oxidation products which then

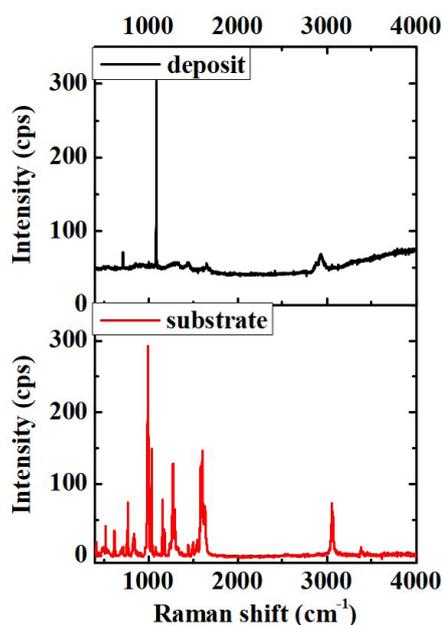


Fig. 3 The micro-Raman spectra of *N,N'*-diphenylguanidine substrate and electrodeposited film

adsorbed on the platinum surface and therefore blocked the diffusion of monomers to it. Dimethyl sulfoxide proved itself to be an appropriate solvent for the formed polymers also in higher concentration which is shown by the slow decline of anodic peak heights of the corresponding subsequent voltammograms. Interestingly, the slope of the current increase between 1.7 and 2 V in dimethyl formamide is higher by elevating *N,N'*-diphenyl guanidine concentration indicating that the current is attributed not only to the solvent but the product oligomers formed in the previous charge transfer process can be oxidized further on the C=NH group also in this solvent.

3.3 Electrochemical studies of *N,N'*-diphenylguanidine in alcohols

In order to get more insights into the electrochemistry of *N,N'*-diphenylguanidine ($c = 5 \text{ mM}$) subsequent cyclic voltammograms were recorded also in alcohols between 0 and 1.5 V in the presence of 50 mM TBAP supporting electrolyte ($v = 0.1 \text{ V/s}$). The voltammograms are depicted in Fig. 4 taken in the different alcohols. The first oxidation peak appeared in the range between 0.8 and 1 V vs. Ag wire in case of the different alcohols except for methanol where the peak appeared at 0.65 V. The signal can be attributed to the anodic oxidation of the monomer and subsequent polymerisation similarly to the aprotic solvents discussed in Subsection 3.2. The anodic peak of the first voltammogram shifts to more positive potentials

by increasing the molecular weight of the solvent. It is in accordance with the dielectric constants of these solvents as the higher the alkyl or aryl group the lower is the permittivity [32]. This property highly influences the degree of association of ions originating from the supporting electrolyte and therefore the solution conductivity. The peak current of the first scan in case of benzyl alcohol is a little smaller than in case of the other alcohols indicating that its viscosity is the highest of the selected alcohols [33].

In the repetitive cycles the height of current peaks decreased continuously due to the continuous deactivation of electrode and the oxidation potentials shifted continuously to more positive values in the aliphatic alcohols due to the formation of resistive layers. In case of benzyl alcohol this process was the most obvious of all alcohols as the third voltammogram already does not contain a relevant peak attributable to the substrate. The currents at higher potentials increased continuously suggesting that the solvent molecules could reach the electrode surface. In summary, the formed polymers in case of majority of solvents have a highly porous structure.

3.4 Permeability studies of the formed films from *N,N'*-diphenylguanidine

One of the most important properties of polymer films deposited onto electrodes is their permeability towards the different molecules. It can give information about the film compactness. Redox molecules enter the film by diffusion through its pores and the apparent diffusion coefficient characteristic for the porous systems is smaller than the diffusion coefficient in the free solution phase. In voltammetric and amperometric techniques the presence of porous film on the electrode surface is indicated by smaller signals in the same solution of redox material than with bare electrode. When the bare electrode is used the magnitude of current signal is proportional to the diffusion coefficient characteristic for the free solution phase. Cyclic voltammetry provides also a fast method for estimation of film permeability. Similarly to the previous experiments, five subsequent scans were run in the 5 mM solutions of *N,N'*-diphenylguanidine prepared with the outlined solvents in the same potential windows, respectively. The working electrode was then soaked in the pure solvents and thoroughly washed with them to remove the unreacted monomers and traces of supporting electrolyte. Finally the solvent was allowed to evaporate completely. The selected redox active compound was 1,4-dihydroxybenzene and cyclic voltammograms were taken in its aqueous

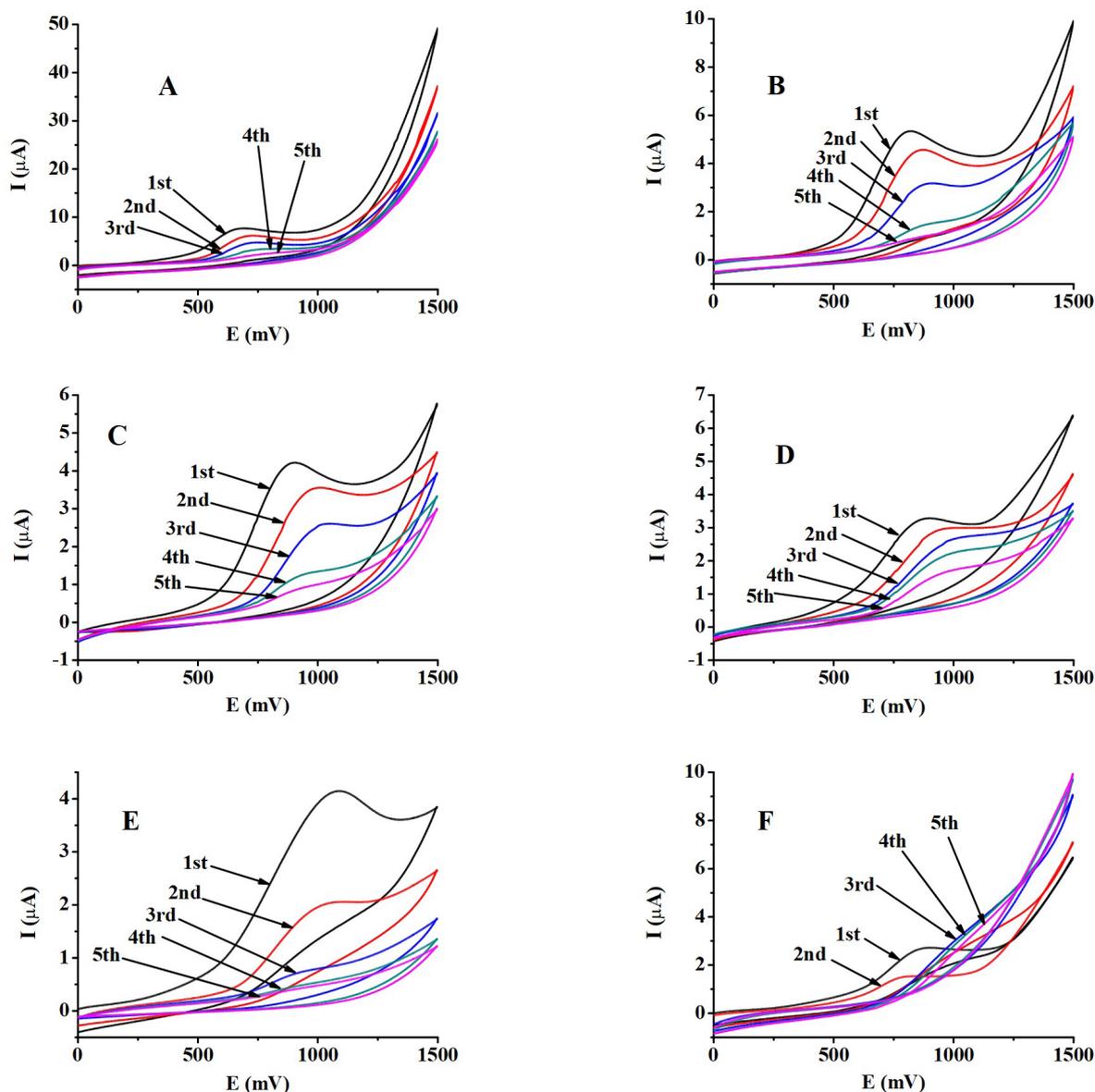


Fig. 4 Repetitive cyclic voltammograms of 5 mM *N,N'*-diphenylguanidine in the different alcohols A) methanol, B) ethanol, C) 1-propanol, D) 1-butanol, E) 1-pentanol, F) benzyl alcohol; supporting electrolyte 50 mM TBAP, $\nu=0.1$ V/s

solution between 0 and 1 V vs. SCE ($c=0.01$ M, $\nu=0.1$ V/s). The pH of this aqueous solution was adjusted to 7 with 0.1 M phosphate buffer. The heights of anodic peaks were divided by peak current measured with the bare electrode and the obtained results are summarized in Table 1.

The data show clearly that the most compact layers could be electrodeposited from acetonitrile and acetone and the significant shift of potentials of the redox probe oxidation waves to the more positive values evidences also that. In case of other solvents oxidation peak appeared instead of waves. Similarly compact and therefore weakly permeable layers formed in propylene oxide and nitromethane. The

weakest diffusion hindrance could be observed in case of dimethyl sulfoxide indicating that the majority of formed products were removed from the platinum surface by dissolution during electrooxidation in dimethyl sulfoxide. The films electrodeposited from dimethyl formamide and methanol were highly permeable indicating the high porosity of the formed layer. The findings are in accordance with the voltammetric results discussed in Subsection 3.2 and were supported by investigations under optical microscope.

The permeability results show that most of the obtained films can release molecules with large flux. The compactness of polyphenol layers investigated in earlier works [28, 29]

Table 1 Results of permeability tests of the electrodeposited polymer films from *N,N'*-diphenylguanidine monomer in the different solvents using the 0.01 M aqueous solution of 1,4-dihydroxybenzene (pH=7, $v=0.1$ V/s). Solvents where only a wave showed up are marked by an asterisk.

	E_{pa} (V)	Current peak recovery (%)
BARE ELECTRODE	0.61	100
Acetonitrile*	0.8	42.5
Acetone*	0.8	35
Dimethyl formamide	0.62	85
Dimethyl sulfoxide	0.62	88.5
Propylene oxide	0.88	55
Nitromethane	0.85	43.75
Methanol	0.64	86.25
Ethanol	0.74	70
1-Propanol	0.73	71.25
1-Butanol	0.72	62.5
1-Pentanol	0.72	68.75
Benzyl alcohol	0.7	72.5

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were more significant than that of electropolymerized *N,N'*-diphenylguanidine in the same solvents. The only exception is dimethyl sulfoxide due to the low degree of deactivation and regarding the alcohols the permeability of film formed in methanol was remarkably high.

4 Conclusion

In general, electrode deactivation was observed in case of all solvents except for dimethyl sulfoxide by investigating the electrochemistry of *N,N'*-diphenylguanidine. The structure of the formed films depends strongly on the solvents as it was verified by the permeability studies. The results might be useful for future studies for example creation of modified electrodes and surfaces also for adsorptive capabilities of the polymer formed during electropolymerization of the studied compound or by investigating its properties for other selected applications.

Acknowledgement

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