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Studies of Phenol Electrooxidation Performed on Platinum Electrode in Dimethyl Sulphoxide Medium. Determination of Unreacted Phenol by the Effect of 4-Vinylbenzenesulphonate on the Electrooxidation Process

László Kiss,*[a, b] Sándor Kunsági-Máté,[a, b] and Péter Szabó[c]

Abstract: The electrooxidation of phenol was studied in the presence of sodium 4-vinylbenzenesulfonate in various quantities. When the sulphonate was dissolved in equal or higher quantities than phenol the peak currents increased gradually and suppression of electropolymerization was observed. When the sulphonate quantity was smaller than that of phenol brown films fouled the electrode. The observed phenomenon was utilized in an analytical procedure namely determination of unreacted phenol in electrolysis solution with linear dynamic range between 0 and 50 mM and 2.96 mM detection limit. The shape of curve became saturated-like above 50 mM.

Keywords: Dimethyl sulphoxide · Electrocopolymerization · Phenol · Sodium 4-vinylbenzenesulphonate

1 Introduction

Phenol and many aromatic hydroxyl compounds are widely investigated in a high variety of media and their behavior is significantly affected by the solvent used. Although water is mainly in focus as solvent due to its practical interest (development of permselective layer, corrosion protection, wastewater treatment) but numerous electrochemical investigations are found in literature carried out in organic solvents. When phenol is electrochemically oxidized presenting itself in solution, an insulating poly(phenyleneoxide) film develops and some works utilized its properties [1–7]. However, polymers prepared from phenols are known as very weak electronic conductors, silylated poly(phenyleneoxides) have outgoing conductivity [8].

Within an investigation of phenol electrochemical behavior in different organic solvents, it was found that it is anodically oxidized at around 2 V in dimethyl sulphoxide. The steep current increase attributable to this process overlapped with electrooxidation of phenol whose peaks could be hardly seen on the voltammograms but poly(phenyleneoxide) formation was visibly observed [9]. Its adherence to the surface of platinum electrode was very weak.

The need for development of new electroanalytical methods has a wide interest especially in special environments. However, the electrode fouling is usually an undesired effect as it destroys signal magnitude and reproducibility. A finding showed recently that by examining phenol in non-aqueous solvents the electropolymerization can be utilized in analytical procedures by using an additive 4-chlorophenol which is also susceptible to electrochemical polymerization but not as highly as phenol [10]. As a matter of fact a copolymer formed including phenyleneoxide units originating from phenol and this polymeric product can dissolve in some organic solvents. In an other work by investigating phenol anodic oxidation in aqueous solutions in presence of 4-vinilbenzenesulphonate the electrode deactivation was suppressed so the fouling rate decreased significantly compared with case when only phenol was present [11]. The aim of this earlier work was the studying of effect of unsaturated additives on electropolymerization of phenol but the observed phenomenon was inappropriate for development of analytical methods. So, earlier investigations highlighted that the prevention of deposit formation due to a coexisting additive in solution can contribute to analytical procedures. The blocking effect can be also favorably utilized as will be discussed herein. In this work, the effect of additive sodium 4-vinylbenzenesulfonate on the electro-

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[a] L. Kiss, S. Kunsági-Máté
University of Pécs, Department of Organic and Pharmacological Chemistry, Honvéd street 1, H-7624 Pécs, Hungary
E-mail: kissl@gamma.ttk.pte.hu

[b] L. Kiss, S. Kunsági-Máté
János Szentágothai Research Center, Ifjúság útja 20, Pécs H-7624, Hungary

[c] P. Szabó
Environmental Analytical and Geoanalytical Research Group, János Szentágothai Research Center, Ifjúság street 20, H 7624 Pécs, Hungary

oxidation of phenol in environment of dimethyl sulfoxide is studied. Then, this solvent-dependent behavior was utilized for determination of unreacted phenol in an electrolysis solution.

2 Experimental

The chemicals used were analytical and spectrophotometric grade (Reanal, Sigma Aldrich) except for sodium 4-vinylbenzenesulphonate which was synthesis grade (Alfa Aesar). A platinum disc sealed in polyetheretherketone was the working electrode with 1 mm diameter. A platinum rod was the counter and a silver wire the reference electrode. The instrument used for carrying out the electrochemical experiments was a potentiostat (Dropsens, Spain) with a software Drop View 8400. Prior to use the surface of working electrode was polished with alumina and thoroughly washed with deionized water. As a final cleaning step it was rinsed with dry acetone to avoid the introduction of water into the investigated systems. The supporting electrolyte was tetrabutylammonium perchlorate (TBAP) in majority of studies. For elemental analysis of deposited samples was accomplished with an EA 1110 CHNS Fisons instrument. Capturing of surface images was carried out with a Jeol JSM-IT500HR (Jeol, Tokyo, Japan) scanning electron microscope (SEM) using the secondary electron mode and a 30 kV acceleration voltage. Before the microscopic studies the layers deposited onto the surface of platinum electrode were cleaned by thorough washing with doubly deionized water to remove the solvent and unreacted species and then finally dried. During the drying the electrode was closed from the atmosphere to avoid disturbances caused by the presenting particles in the air.

3 Results and Discussion

3.1 Electrooxidation of Sodium 4-vinylbenzenesulphonate

The first step in the investigations was studying the influence of supporting electrolyte on the electrochemical behaviour of sodium 4-vinylbenzenesulphonate additive. So, the sulphonate was investigated itself in dimethyl sulphoxide in 0.1 M concentration and in the presence of 0.1 M TBAP (Figure 1). The ten subsequent voltammograms in the two cases have visible differences. One of them is the usual current increases at higher potentials due to the decomposition of solvent when TBAP was also present in solution. The latter reduced the ohmic drop thus solvent molecules could oxidize below 2.5 V. It was not observed when only sodium 4-vinylbenzenesulphonate was present probably due to the low degree of dissociation of the electrolyte. Some molecules of this compound underwent anodic oxidation and promoted the polymerization, then in the backward scannings of voltammograms an additional anodic peak showed up at the same potential as in the forward scannings at around 2 V which suggests an unusual behaviour. As a matter of fact a layer forms in the forward scans and this will be then removed partially from the electrode surface making free it again. A question may arise from that why these anodic peaks can not be seen when TBAP is also present. To explain this we can conclude that TBAP contributed to the reaching of enough high potentials necessary for the partial cleaning of electrode surface by setting the maximum switching potential 2.5 V. The higher peak currents attributable to the unsaturated compound also verify this.

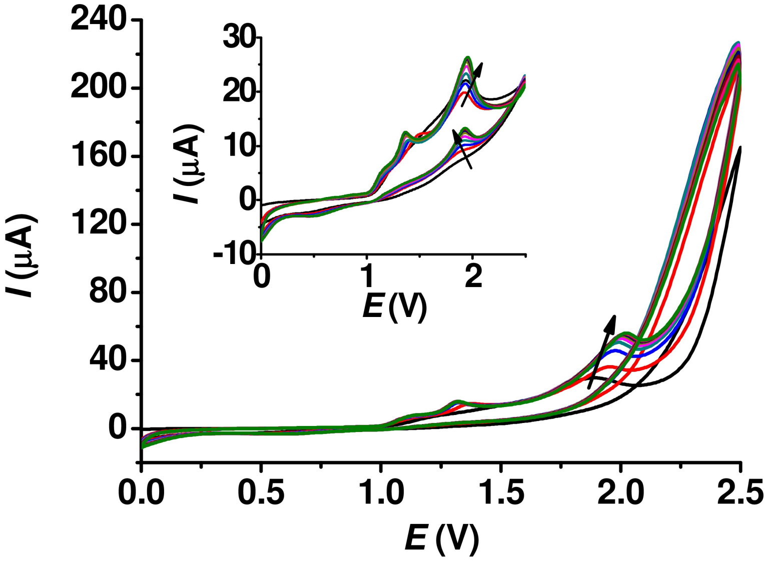

Fig. 1. Cyclic voltammograms of 0.1 M sodium 4-vinylbenzenesulphonate in presence of 0.1 M TBAP and in its absence (inset graph), $v = 0.1$ V/s.

3.2 Effect of Phenol: Sodium 4-vinylbenzenesulphonate Concentration Ratio on the Electrodeposition Process

The above experiments highlighted that use of TBAP is necessary to see also the signal related to phenol electrooxidation below 2.5 V. Then, these examinations were followed by establishment of the effect of sodium 4-vinylbenzenesulphonate quantity on electrochemistry of phenol keeping constant the concentration of the latter in each solutions. The phenol concentration was 50 mmol/L in the solutions prepared with dimethyl sulfoxide. The concentration of supporting electrolyte was 0.1 mol/L. Five subsequent cyclic voltammograms were recorded in each solutions keeping them quiescent to see the effect of sodium 4-vinylbenzenesulphonate on the electropolymerization process. When only phenol was present the curves were very similar to that obtained in an earlier work where phenol was studied in dimethyl sulphoxide. It is obvious from the graphs that by increasing the concentration of sodium 4-vinylbenzenesulphonate the voltammetric peaks are more and more clearly seen but no significant tendency in increase of intensities were observed (Figure 2). Increasing the additive concentration above 100 % of phenol did not cause any further change so its application at concentrations at least at that of phenol seemed to be optimal in the further experiments. These observations highlighted that appearance of peaks in presence of 4-vinylbenzenesulphonate can be attributed to temporal exclusion effect of the forming copolymer composed of phenyleneoxide and vinylbenzenesulphonate units. As a matter of fact the phenoxyl radicals originating from phenol electrooxidation accelerate the copolymer formation which then covers the platinum surface. It is remarkable that in solutions where the molar ratio of phenol and additive was 1:1 similar peaks appeared in the backward scans as in case when the additive was studied alone but in this situation the film composed partly of phenyleneoxide units. The organic film formed in this way dissolved continuously into the bulk during the recording the scan and the electrode surface became again accessible to electroactive molecules indicated by the smaller anodic peaks appeared by scanning backward.

Elemental analyses were accomplished to decide if 4-vinylbenzenesulphonate moieties are involved in the formed polymer. Before the elemental analyses the deposited films were thoroughly washed with doubly deionized water and then with dry acetone to remove the unreacted reactants and fast removal of residuals of sodium 4-vinylbenzenesulphonate was possible. These portions of polymers were collected in two closed vessels and left to dry. The polymer prepared in solution of phenol and the polymer of phenol in presence of 40 % (molar) additive were compared. Application of higher molar ratios of additive resulted in scarce polymeric product remaining on the electrode surface. The results showed that the elemental composi-

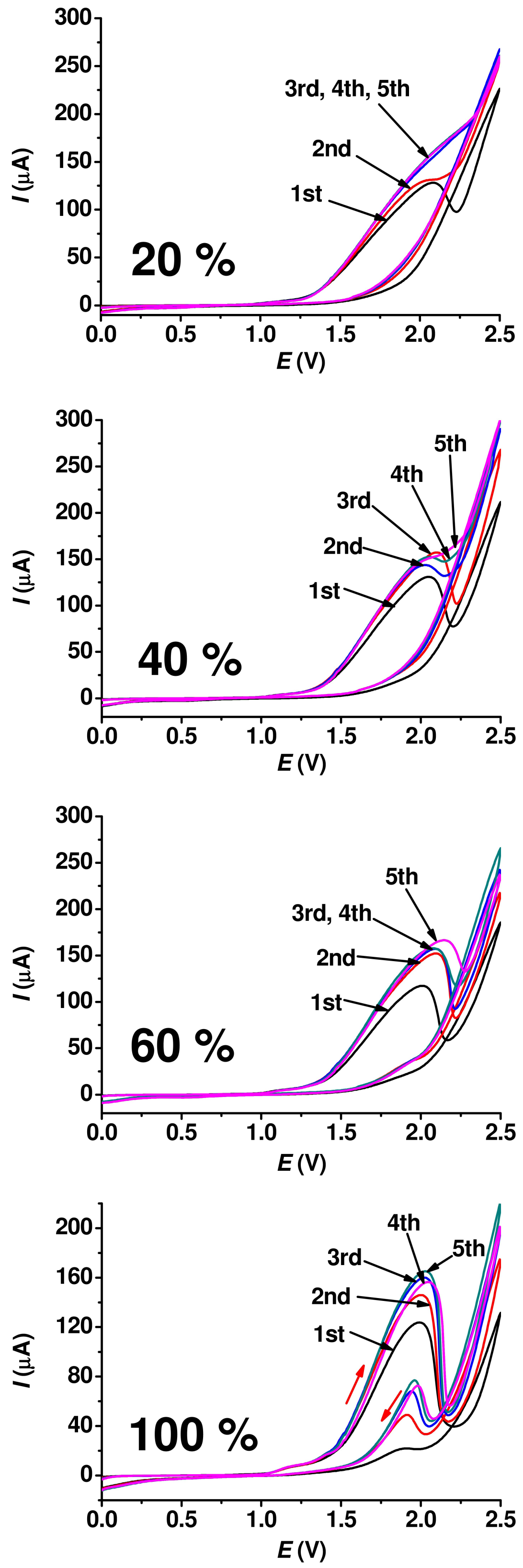

Fig. 2. Subsequent voltammograms recorded in solutions of 50 mM phenol prepared with dimethyl sulphoxide containing sodium 4-vinilbenzenesulphonate in different quantities (v = 100 mV/s, supporting electrolyte 0.1 M TBAP). Red arrows in the last figure indicates the direction of scan.

tions correspond to that of poly(phenyleneoxide) as seen in Table 1 (C:H:O≈6:4:1). Only 3.6 n/n % sulphur was present in the polymer deposited in presence of sodium 4-vinilbenzenesulphonate. This result was due to some undissolved polymers with high poly(phenyleneoxide) content. These results are in accordance with the voltammetric results which themselves showed that a copolymerization reaction takes place between the additive and electrogenerated phenoxyl radicals, the copolymers dissolve into the bulk and predominantly poly(phenyleneoxide) remains on the electrode surface.

The above results suggest a suppression caused by sodium 4-vinylbenzenesulphonate in the electropolymerization of phenol. It was reinforced by experiences obtained with naked eye. Increasing the amount of additive the brown deposit continuously disappeared by increasing the amount of additive and at 1:0.8 phenol-additive concentration ratio only the clean platinum surface could be seen and under optical microscope layer formation were not also noticed. Images taken with a scanning electron microscope reinforced more deeply this observation (Figure 3). On the rough surface of polyphenol bundles and stackings are clearly seen (part a). When the electrodeposition was carried out in presence of 4-vinylbenzenesulphonate (part b) only some islands formed consisting of polyphenol showing its drastically decreased quantity remaining at the surface. Their arrangement in rows is due to the collection and evaporation of deionized water after washing the deposits. This shows the weak adherence of these particles to the platinum surface.

Electrolysis of a solution containing 50 mM phenol and an other solution containing 50 mM phenol and 40 mM sodium 4-vinilbenzenesulphonate was carried out at 2 V constant potential. The time of electrolysis was 15000 s in both solutions. Figure 4 shows the two solutions after electrolysis. The difference in colour is remarkable as when only phenol was present higher molecular weight polymers formed indicated by the deep brown colour of the solution. When also sodium 4-vinylbenzenesulphonate was added a solution with very light yellow colour could be obtained suggesting the more frequent termination of chains of poly(phenyleneoxide) due to the additive and very frequent insertion of 4-vinylbenzenesulphonate units into the polymer chains. The differences in colour are due to the enhanced conjugation of the formed soluble polymers therefore in solution containing only phenol the absorbance shifted to the visible range which was observed in earlier spectrophotometric and fluorimetric measurements [9]. On the other hand, in presence of additive parallel to copolymer formation a small quantity of poly(phenyleneoxide) also forms (see microscopic studies) and copolymers containing predominantly vinylbenzenesulphonate units have weak absorbance.

Table 1. Results of elemental analysis of deposited films shown by molar ratios.

Deposit	C	H	O	S
Only from phenol	0.565	0.332	0.103	0
From phenol and additive	0.501	0.367	0.096	0.036

3.3 Influence of Supporting Electrolyte on Phenol Electrooxidation in Presence of Sodium 4-vinylbenzenesulphonate

Supporting electrolytes containing the same cation tetrabutylammonium were collected to study phenol electrooxidation in dimethyl sulphoxide so the anions changed. Approximately the same characteristics could be observed when BF_4^- and PF_6^- were the anions as in case of ClO_4^- and the latter is one of the most frequently used in studies carried out in non-aqueous environments (Figure 5). Unuseful results came from examinations of tetrabutylammonium chloride as this salt itself was electroactive in the used potential range as oxidation peak appeared attributable to Cl^- ion oxidation while in presence of phenol more flat curves were recorded due to the very high background currents. Therefore in the further investigations tetrabutylammonium perchlorate was used.

3.4 Estimation of Phenomenon in Analytical Purposes

The behavior of phenol in presence of additive sodium 4-vinylbenzenesulphonate delineated in the previous sections suggests that it can be useful for analytical applications. As dimethyl sulphoxide proved an excellent solvent for preparation of relatively thick and mechanically removable layers poly(phenyleneoxide) synthesis by electrolysis is easily elevated. In these cases the procedure is started from higher substrate concentration and the quantity of unreacted material can be measured. In these cases, as the sample is more or less colloidal due to the dissolved polymers the choice of electroanalysis is advantageous. Therefore a calibration procedure was carried out taking five subsequent cyclic voltammograms between 0 and 2.5 V with 0.1 V/s scan rate between concentations 0 and 100 mM for phenol using dimethyl sulphoxide as solvent. The concentration of sodium 4-vinylbenzenesulphonate and TBAP was uniform (100 mM). The previous experiments showed that among the subsequent voltammograms the fifth one had the maximum value (as a matter of fact it was the saturation value) their peak currents seemed to be optimal for analytical purposes. Taking more scans than five resulted smaller peak heights in the further scans. The electrode was polished between each experiment and three measurements were averaged for each concentration and the averaged fifth peak current values were used for evaluation. The fifth curves are displayed in Figure 6 and their shape was very similar influenced

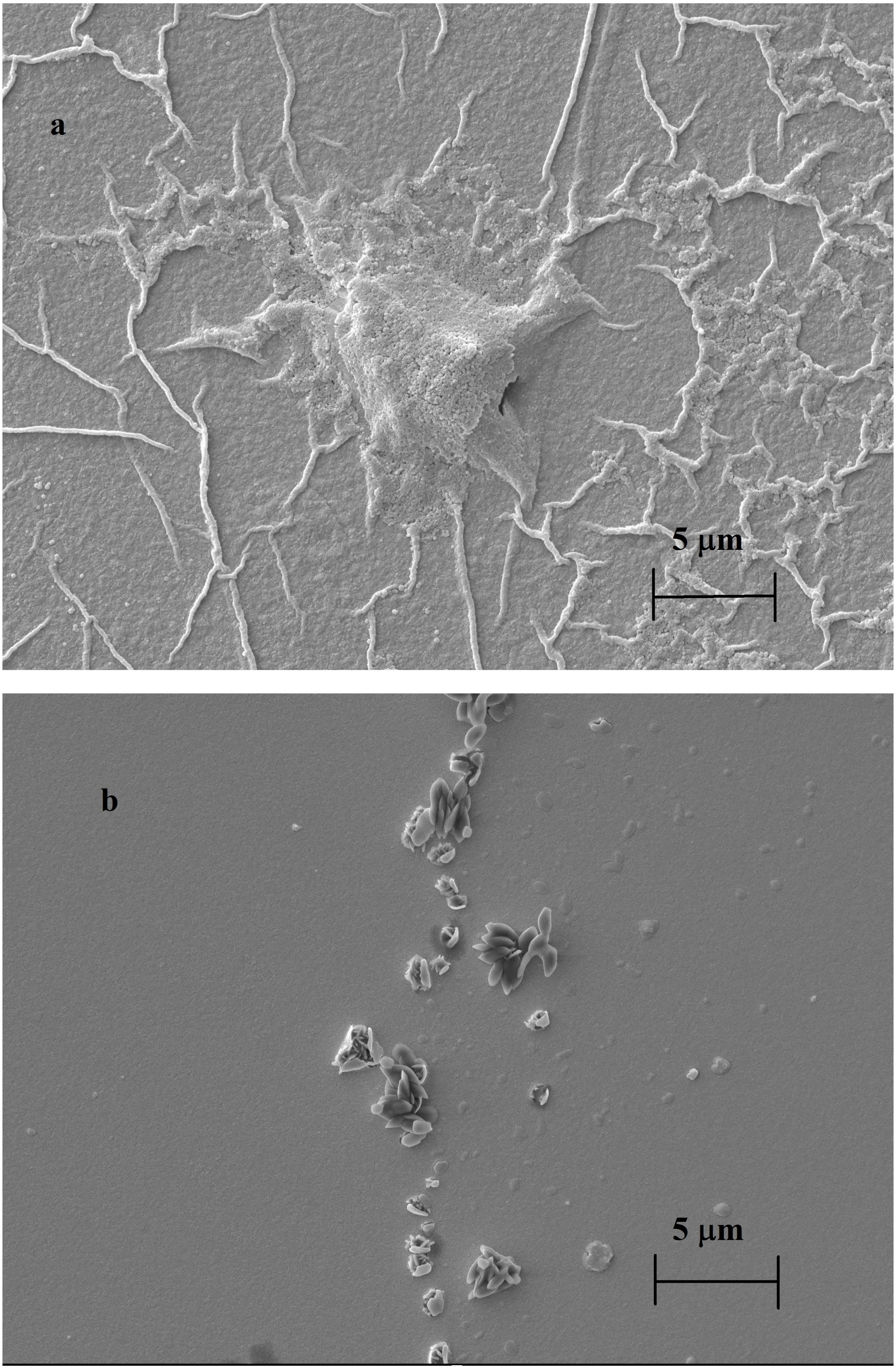

Fig. 3. Scanning electron microscopic images of polyphenol (a) and the electrode surface after electrolysis in solution containing equimolar phenol and sodium 4-vinylbenzenesulphonate (b).

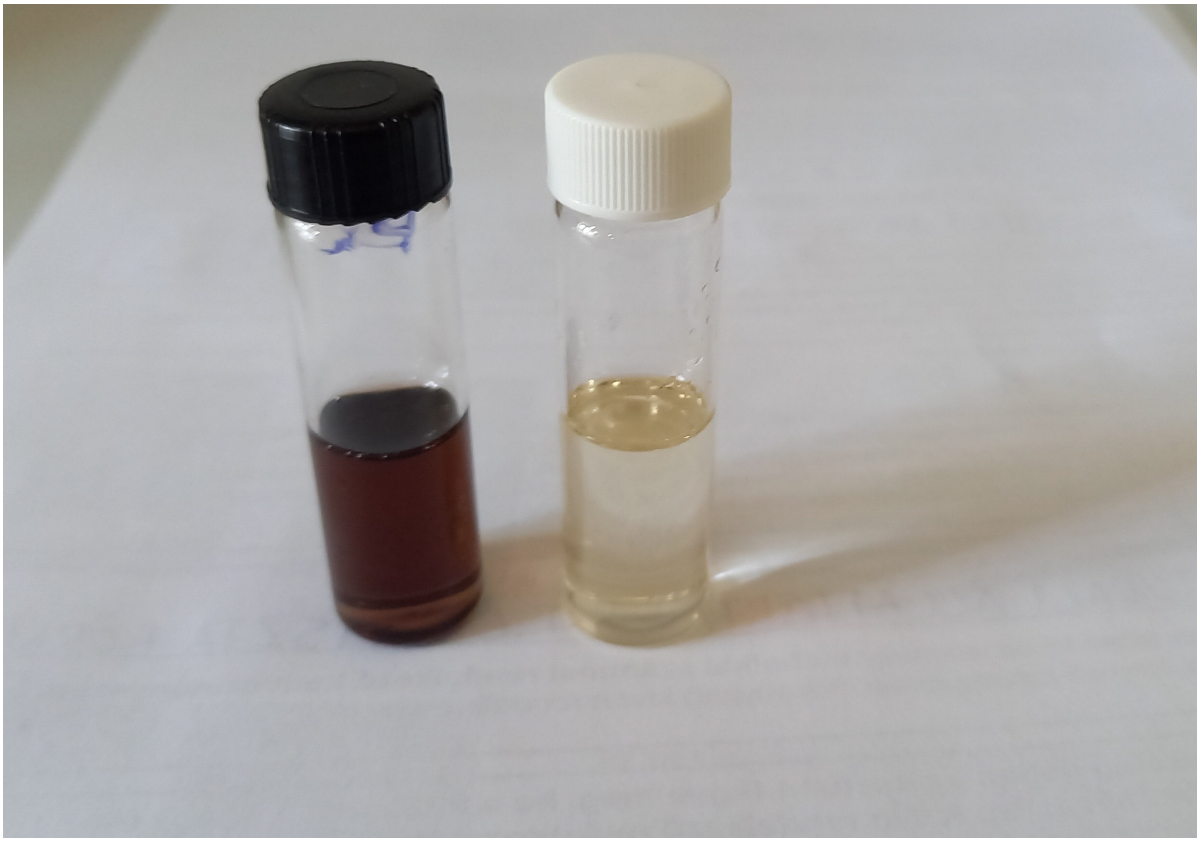

Fig. 4. The picture of the solution of 50 mM phenol prepared with dimethyl sulphoxide (left) and that of solution containing 50 mM phenol and 40 mM sodium 4-vinylbenzenesulphonate (right).

predominantly by electrooxidation of phenol. Only in case of smallest studied concentration the peak heights attributable to phenol and 4-vinylbenzenesulphonate ion were comparable showing that their oxidation potentials are not exactly the same.

The calibration curve in Figure 7 clearly shows that at phenol concentrations lower than 100 mM the reproducibility is acceptable and it has a linear stage at the smaller concentrations which then turns to saturation at the higher concentrations. As electrolysis can still be accomplished in 100 mM solutions a solution of 100 mM phenol was prepared with dimethyl sulphoxide containing 100 mM TBAP. The working electrode was a 3 mm diameter platinum disc to enhance the production of poly(phenyleneoxide) keeping the potential at 2.5 V in quiescent solution. After each 500 s electrolysis time the polymeric products were mechanically removed and then electrolysis was continued. After twenty electrolysis 2 cm^3 of electrolysis solution was transferred with micropipette to an other vial and 2 cm^3 of dimethyl sulphoxide solution containing 0.2 M sodium 4-vinylbenzenesulphonate and 0.1 M TBAP was mixed with it. So, the same conditions were ensured as in the calibration. Taking into account the peak current of the fifth curve of the subsequent cyclic voltammetric ones and using the linear range of calibration curve 72.3 mM residual phenol could be obtained after multiplication by 2 because of the twice dilution of substrate during sample preparation. Taking a look at the calibration curve the twice dilution was an appropriate choice as the possible concentrations lie in this way on the linear stage so a linear fit is enough for analytical evaluation if electrolysis is started from 100 mM phenol concentration whose equation is $Ip(\mu A) = (22.78 \pm 0.086) + (1.196 \pm 0.003)c(mM)$. The detection limit was 2.96 mM by using the scattering of currents of the fifth voltammograms of three separate scannings in solution of 100 mM 4-vinylbenzenesulphonate in presence of 100 mM TBAP.

4 Conclusion

The investigation of phenol in dimethyl sulphoxide in presence of sodium 4-vinylbenzenesulphonate led to interesting results so anodic peak currents of phenol could be clearly seen. The studies verified further that usefulness of unsaturated compounds in investigations of compounds susceptible to oxidative polymerization is high and has further possibilities for other applications in analysis and electrosynthesis.

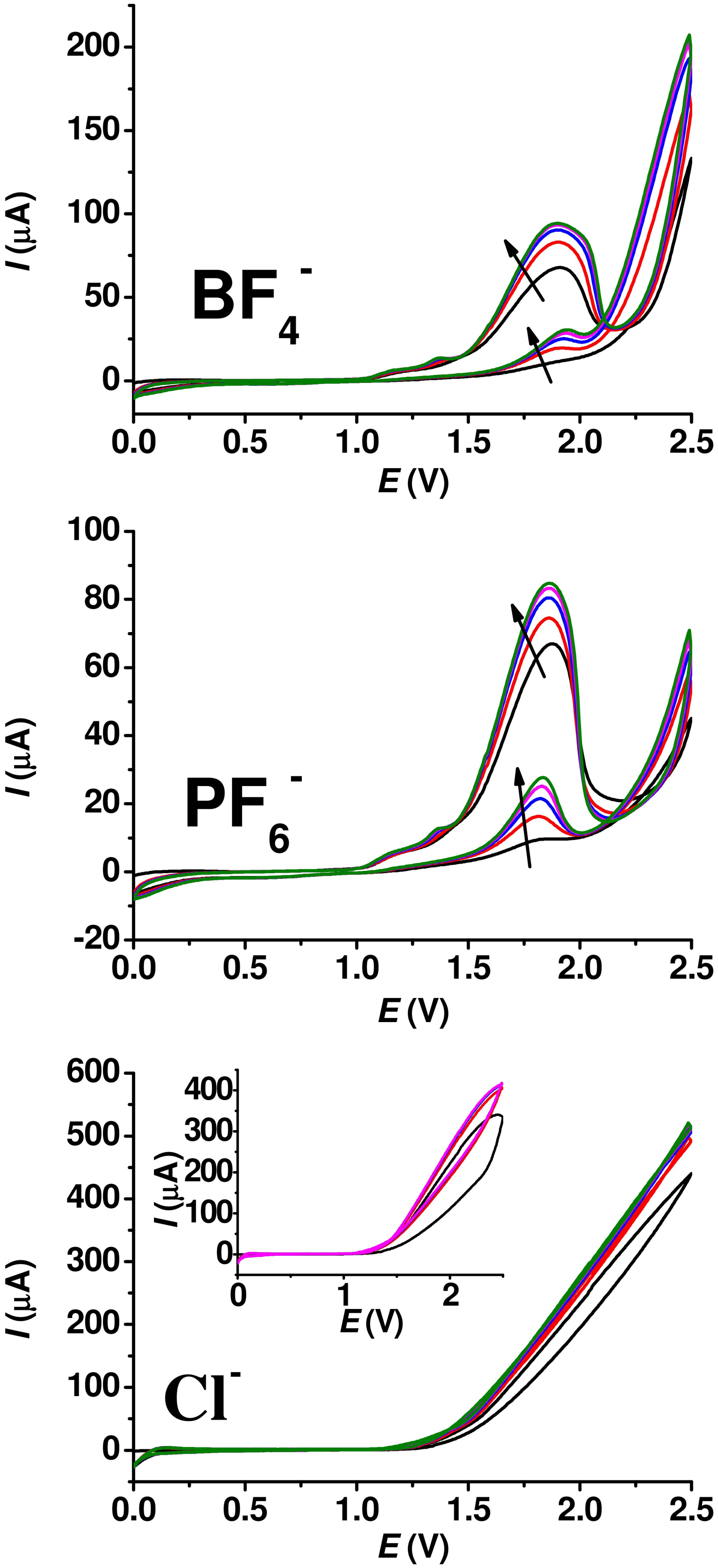

Fig. 5. Influence of supporting electrolytes on the voltammetric behaviour of phenol in presence of 0.1 M sodium 4-vinyl-benzenesulphonate and 0.1 M supporting electrolytes (phenol concentration 50 mM, inset graph in the last figure is related to the case when only TBACl was present).

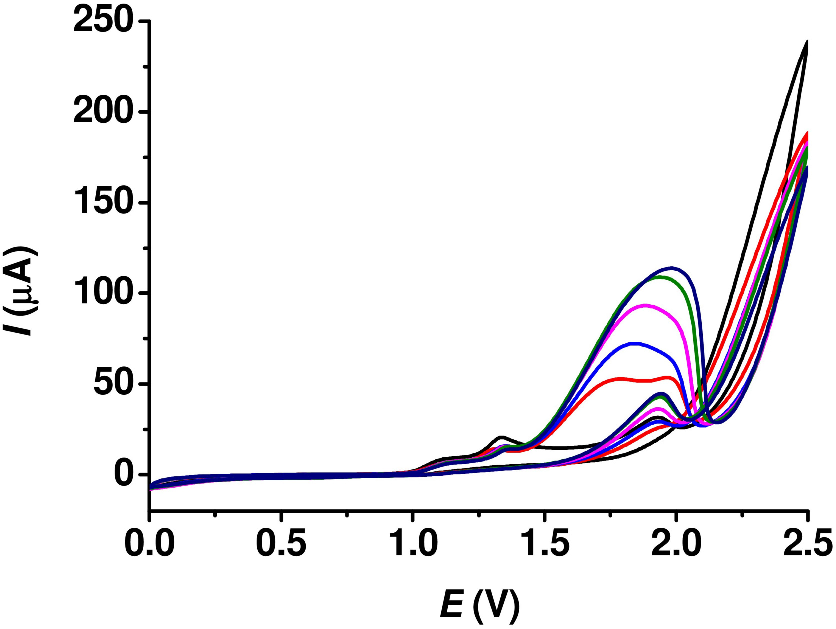

Fig. 6. The fifth cyclic voltammetric curves of phenol in different concentrations (0, 20, 40, 60, 80, 100 mM with anodic peak heights increasing from black to navy) in presence of 100 mM TBAP and 100 mM 4-vinylbenzenesulphonate ($v=0.1$ V/s)

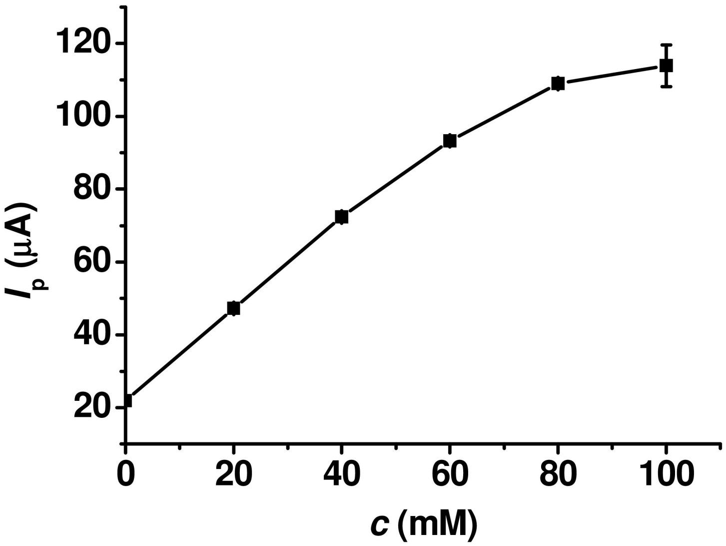

Fig. 7. Calibration curve for phenol in dimethyl sulphoxide in presence of 100 mM sodium 4-vinylbenzenesulphonate and 100 mM TBAP ($v=0.1$ V/s).

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Data Availability Statement

Research data are not shared.

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