Coexistence of Substituted Phenols Reduces the Fouling Ability of Phenol in Non-aqueous Solvents

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Abstract
The electrooxidation of phenol showed different rate of deactivation by varying the concentration of substituted phenols (4-chlorophenol, 4-methoxyphenol, 4-tert-butylphenol). This was due to the more favourable solubility properties of the product copolymers compared with poly(phenyleneoxide) the product which forms when only unsubstituted phenol is present. The nature of substituent, switching potential and oxidation potentials of the studied phenols were significant in prevention of electrode fouling. The best reproducibility could be achieved upon addition of 4-chlorophenol. This offered a possibility for estimation of phenol concentration in non-aqueous systems.

Keywords
phenol, copolymerization, voltammetry, non-aqueous

1 Introduction
There have been several publications concerning with the electrooxidation of phenols in non-aqueous systems. The majority of substituted phenols form dimers as products of their electrooxidation typically the ones having one or more tert-butyl groups [1–4] and chlorophenols [5]. Previously, we found that some para-substituted phenol give reproducible current signal in acetonitrile on platinum electrode in 50 mM concentration [6]. Notably, this concentration is higher than those generally used by other researchers (mainly in the range of 0–5 mM) showing that the products readily dissolve in acetonitrile and it is also true for many other non-aqueous solvents.

In the related works aiming at investigation of phenols they were studied mostly presenting only themselves in the solution prepared with non-aqueous solvents. A few papers have reported the electrochemical formation of copolymers of phenols [7–10]. In addition, phenol would reportedly foul an electrode in non-aqueous media. The effect of addition of substituted phenols is the topic of this work. The majority of phenols deactivate an electrode in aqueous systems and only additives like surfactant molecules can contribute to the higher reproducibility. Therefore it was promising to investigate the copolymerization of phenol for analytical utilization in non-aqueous systems.

2 Experimental
Analytical grade chemicals were used in all experiments and sodium perchlorate (NaClO₄) was used as supporting electrolyte throughout this work. Platinum disc (~1 mm in diameter) was the working electrode sealed in polyetheretherketone, silver wire as reference and platinum wire as counter electrode. The electrochemical experiments were carried out with a potentiostat (Dropsens, Spain).

The surface of working electrode was polished before the experiments with alumina (1 mm average particle size) on a polishing cloth. After thorough washing with deionized water it was ultrasonicated and finally washed again with deionized water. This procedure ensured the removal of physically adsorbed particles.

3 Results and discussion
Our previous studies about the electrochemistry of substituted phenols in non-aqueous acetonitrile on platinum electrode allows us to suppose they might modify the electrochemical behavior of phenol. Namely, the primary product is a phenoxy radical in the electrooxidation of phenols but they are different concerning the subsequent processes. Apart from the nature of the phenol in question, it is highly influenced by the solvent and substrate concentration.
In the first step of study phenol was investigated coexisting with the substituted phenols dissolved in 5 mM in acetonitrile. Only one peak showed up, a composite of phenol and 4-chlorophenol as well as 4-tert-butylphenol electrooxidation (Fig. 1). By comparing the two phenol derivatives a remarkable difference can be seen as in case of 4-tert-butylphenol the currents decline more steeply after the anodic peak suggesting that the formed polymer has stronger adhesion to the electrode surface. In a previous work [11] the anodic peak current of the second scan for phenol dropped to approximately one tenth value of the first one in acetonitrile. However, phenol concentration was significantly higher (50 mM) and this is high enough for the significant contribution to the rapid deactivation.

Three experiments were carried out with a solution serie with a uniform phenol concentration (5 mM) by varying the concentration of the substituted phenols between 0 and 12.5 mM. Five cyclic voltammetric scans were taken in each solution with platinum electrode having renewed surface made with polishing and the anodic peak currents served as data for evaluation. Peak current values for a solution were normalized to the value of the first scan.

Fig. 2 shows the normalized peak currents for phenol in the presence of 4-chlorophenol for voltammetric scans where the switching potential was 2 V. Herein, it can be seen from the normalized data that addition of 4-chlorophenol slows down the fouling when presenting in excess. As phenol and 4-chlorophenol oxidize simultaneously, a highly porous copolymer forms. This involves the phenyleneoxide units attributable to phenol and only they couple with each other when only this compound is dissolved in the solution. The resulted poly(phenyleneoxide) can build up a coherent insulating layer on the electrode surface in absence of any other substrate. Obviously, the involvement of units in the organic layer originating from electrooxidation of 4-chlorophenol reduces the chain length of polymeric product and the adhesion to the electrode surface.

The above experiments with 4-chlorophenol were repeated by extending the switching potential to 2.5 V. This was set also by investigation of the other phenol derivatives (4-tert-butylphenol and 4-methoxyphenol). Fig. 3 reveals the normalized peak currents for the three phenol derivatives. The reason for modification of switching potential is an earlier observation during phenol electrooxidation. At higher potentials than 2 V the previously (scanning in the range between 0 to 2 V) formed deposit can be partially removed from the electrode surface. Especially in case of 4-chlorophenol we can compare the results for the two different switching potentials (2 and 2.5 V). It can be seen that the peak current values for each solution were more reproducible for 2.5 V due to the efficient removal of copolymer. Similar results could be obtained also for the other two phenols. Fig. 3 (a) contains the data for measurements and when only phenol was present led to a very bad reproducibility. This was due to the incomplete removal of poly(phenyleneoxide) and no tendency could be observed in subsequent peak currents as the variable quantities of residual deposits influenced the results with a degree of random behavior. Uniformity of data were significantly improved by adding 4-chlorophenol to the solutions.

The results for 4-tert-butylphenol and 4-methoxyphenol are visibly different from that of 4-chlorophenol. The data for 4-tert-butylphenol suggest that a scarcely soluble copolymer forms being difficult to remove electrochemically (reinforcing the observation displayed in Fig. 1). Its oxidation and that of phenol were the same indicated by the
appearance of only one peak In accordance with the earlier results. The unsatisfactory reproducibility for 4-methoxyphenol arises mainly from the markedly different oxidation potential from that of phenol. Fig. 4 reveals the very visible peak separation (first CVs) where peak at around 1.25 V is related to 4-methoxyphenol and peak at around 1.8 V is attributable to phenol according to earlier studies [6].

The reason for the observations (displayed in Fig. 3 (c) in presence of 4-methoxyphenol is the diminished concentration in front of the surface of electrode when phenol begins to oxidize. Previously the solution volume in the neighborhood of platinum disc was depleted while phenol becomes predominant here as substrate. The reduced diffusion flux of 4-methoxyphenol from the bulk is insufficient for the high occurrence of its units in the copolymer, therefore predominantly phenyleneoxide units will build up the formed insulating layer.

The above experiments highlighted that the most reproducible results of phenol electrooxidation can be obtained with 4-chlorophenol. Therefore this finding was utilized for the establishment of phenol concentration on the current signal in acetonitrile. Cyclic voltammograms were taken in solutions where the concentration of 4-chlorophenol was uniform (5 mM). For three measurements the averages are displayed in Fig. 5 and the average value for the solution containing only 5 mM 4-chlorophenol was subtracted from all other values. The current differences (ΔI) between measured for phenol in presence of 5 mM 4-chlorophenol and measured in 5 mM 4-chlorophenol solution were plotted on the ordinate of calibration graph. These current

Fig. 3 Normalized peak currents for 5 mM phenol in acetonitrile for different concentrations of 4-chlorophenol (a), 4-tert-butylphenol (b) and 4-methoxyphenol (c) (supporting electrolyte 50 mM NaClO₄, scan rate 0.1 V/s, switching potential 2.5 V)

Fig. 4 The first voltammograms taken for 5 mM phenol in solutions containing 4-methoxyphenol in different concentrations (supporting electrolyte 50 mM NaClO₄, scan rate 0.1 V/s, switching potential 2.5 V)

Fig. 5 Dependence of peak current changes of phenol in the presence of 5 mM 4-chlorophenol in acetonitrile (black dots) and in the absence of 4-chlorophenol (red dots) (supporting electrolyte 50 mM NaClO₄, scan rate 0.1 V/s, switching potential 2.5 V)
differences depend linearly on the phenol concentration with low scattering of parallel measurements. This figure contains also the same data for the same concentrations of phenol in absence of 4-chlorophenol where the current of solvent was subtracted from the data. A saturation-like dependence could be observed in accordance with the high susceptibility of phenol to fouling. On the other hand, the very high scatterings of data in absence of additives make them unreliable for analysis of phenol.

The cyclic voltammetric experiments were repeated in other non-aqueous solvents with phenol and 4-chlorophenol (acetone, nitrobenzene, 2-butanone, 1-propanol) and similarly reliable results could be obtained to that obtained in acetonitrile.

The promising results obtained upon addition of 4-chlorophenol suggest that this procedure would be appropriate for the estimation of the phenol concentration in non-aqueous samples. It is worth to note that more reliable and faster methods exist for quantification of phenolic compounds in organic solvent based matrices. These involve for example spectrophotometry [12], non-aqueous capillary electrophoresis [13], potentiometry [14] and conductometry [15]. Nevertheless the results detailed herein gave useful information for the coexistence of different phenols in the non-aqueous electrolysis solutions.

There is a contradictory between results shown in Fig. 3 (a) and calibration experiments with phenol (Fig. 5). In the previous case the electrode was polished before measurement in each solution (signals changed significantly). In the calibration experiments with 4-chlorophenol polishing was not necessary only washing when calibration solutions were changed. These facts indicate that the best performance of the method for analysis can be attained without polishing (of course the whole procedure should be started with cleaned electrode).

Amperometry was also tested in determination of phenol in presence of 5 mM 4-chlorophenol in the same conditions as by the cyclic voltammetric experiments. The electrode was polarized to 2.5 V for 5 minutes and currents at the end of measurements were taken into consideration. As seen in Fig. 6 the three parallel measurements of amperometric signals have high scattering and significantly deviate from linearity. Here we encounter a contradictory by making comparison with the cyclic voltammetric results despite the restoring of bulk concentration with stirring after each measurement. Consequently, this technique seems unreliable because of the high scattering. The possible explanation for the observations is that the electrode potential was high enough to be diffusion controlled for both phenol and 4-chlorophenol. As diffusion coefficient for phenol is higher than that of 4-chlorophenol the ratio of phenyleneoxide units will be higher in the copolymer which is less soluble.

4 Conclusion
In this work the results showed that phenol forms copolymers and that obtained with 4-chlorophenol using cyclic voltammetry might gain further analytical utilization in the future. In summary, the findings highlight the importance of the oxidation potential of the added phenol derivative. This phenomenon can be helpful in further studies of copolymer electrodeposition to control the porosity.

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