



## Electropolymerization of chlorinated phenols on a Pt electrode in alkaline solution. Part II: An electrochemical quartz crystal microbalance study

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### Abstract

Electropolymerization of phenol and mono-, di-, tri-, pentachlorophenols was studied using EQCM on a Pt electrode at 0.78 V (SHE) in 1 M NaOH solution containing 0.1 M of the corresponding phenol. The highest electropolymerization rate was found for ortho-substituted chlorophenols indicating a weak fouling of the electrode. Low electropolymerization rates for para-substituted chlorophenols suggest a low permeability of the polymer film, resulting in rapid electrode fouling. The EQCM data suggest that electropolymerization of chlorophenols occurs without Cl-elimination for the monomers with unsubstituted ortho and para positions. Dechlorination is most pronounced for electropolymerization of para-substituted isomers. The mechanism of electropolymerization of chlorophenols is discussed.

### 1. Introduction

Practical application of electrochemical destruction of hazardous phenolic species is complicated in most cases due to electrode fouling. Ether- and quinone-type oligomeric and/or polymeric non-soluble compounds [1–14], formed as a result of the coupling of phenoxy radicals generated in the initial oxidation step, block the electrode surface. This leads to electrode deactivation and prevents effective phenol electrooxidation.

Ortho- and para-linked 1,2,4-, 1,2,6- and 1,2,4,6-polyphenol derivatives are usually formed in the course of electropolymerization of phenols as a result of preferable stabilization of phenoxy radicals *via* the ortho and para positions with respect to the original hydroxyl group. The stability of the radical species formed also depends on mesomeric and inductive effects caused by the nature of the substituents and their position in the benzene ring.

The presence of bulky substituents might cause a steric hindrance resulting in deviations from general electropolymerization routes. In the case of chlorinated phenols with Cl-substituted ortho and para positions electropolymerization proceeds through radical–substrate coupling followed by elimination of the chloride ion. About 19% loss of chloride occurs during oxidative polymerization of 2,6-dichlorophenol, while in the case of pentachlorophenol electropolymerization proceeds exclusively through the Cl-elimination route [8].

The electrochemical stability of chlorophenols increases with their degree of chlorination. This, as well as

the electrode fouling by the polymeric species formed limits the application of the electrochemical degradation method for the destruction of phenols. However, immobilization of phenols on high surface area electrodes due to electropolymerization might be used alternatively for remediation of aqueous solutions instead of electrochemical degradation [8]. To understand the polymerization features better, a comparative study of electropolymerization of chlorinated phenols was carried out in the present work with systematic variation of the degree of chlorination of the monomers and their isomerism.

Generally, the distribution of electropolymerization products depends on the stability of the radical formed, the structure and reactivity of the monomer molecule, reaction medium (solvent, solution pH), the electrode material, its potential, and on the phenol concentration [1–14]. In a previous paper [15] we studied Pt electrode fouling in alkaline solutions of phenol and mono-, di-, tri- and pentachlorophenols by means of cyclic voltammetry (CV). To lessen the number of variables, in the present paper the electropolymerization of phenol and chlorinated phenols was studied on a Pt electrode at constant anode potential in alkaline solutions of the corresponding phenols. Moreover, to discriminate between the electropolymerization and the deep oxidation (ring-opening) or the formation of soluble oxidation products the electrochemical quartz crystal microbalance (EQCM) was employed as a mass-sensitive probe to selectively monitor the electropolymerization kinetics. Possible electropolymerization mechanisms of chlorinated phenols

are discussed on the basis of EQCM data. The polymeric and oligomeric species formed were further characterized by FTIR and the GC-MS analyses as will be presented elsewhere (Z. Ežerskis and Z. Jusys, in preparation a,b).

## 2. Experimental details

AT-cut quartz crystals (International Crystal Manufacturing Company, Inc., USA) of 10 MHz fundamental frequency home-sputtered by Pt from both sides (piezo-electric-active area  $0.22 \text{ cm}^2$ , geometric area  $0.25 \text{ cm}^2$ , real surface area  $2.15 \text{ cm}^2$ ) were used for the EQCM measurements. Quartz crystals were mounted between two silicone rubber o-rings attached to the bottom of the cell (working volume  $2 \text{ cm}^3$ ) so that only one crystal face was exposed to the solution and served as a working electrode. The EQCM measurements were carried out using a home-built 10 MHz frequency oscillator, a precision frequency counter Č-64, and two digital voltmeters B7-46/1 (Russia) connected to a PC through an IEEE-488 interface. Potential control was ensured using a potentiostat PI-50-1 and a function generator PR-8 (Russia). A Pt wire counter electrode and a Ag/AgCl/KCl<sub>sat</sub> reference electrode were used (all potentials given below are vs standard hydrogen electrode, SHE). The EQCM set-up used is described in detail elsewhere [16].

Prior to the EQCM measurements, the working electrode was immersed in a mixture of concentrated  $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$  (1:1) for 10–20 s, and then, carefully rinsed with distilled water and cycled in 1 M NaOH solution from  $-0.8$  to  $0.8 \text{ V}$  (SHE).

With the electrode now in a solution of the corresponding phenol at  $-0.8 \text{ V}$ , the working electrode potential was stepped from  $-0.8$  to  $0.78 \text{ V}$ , simultaneously recording the current and the electrode mass transients for 5–25 min at  $0.78 \text{ V}$ . Analogous EQCM experiments were carried out in the supporting electrolyte and the corresponding mass-charge values were subtracted from those measured in phenolic solutions. The current and frequency values were measured and stored on the PC every 1.3 s.

The polyphenolic films were assumed to be rigidly attached to the electrode surface [5, 17]. The change in the resonant frequency of the quartz crystal was converted to the electrode mass using Sauerbrey's equation [18]. The sensitivity of the EQCM system employed with respect to the piezoelectric area was  $1.023 \text{ ng Hz}^{-1}$ .

Solutions (0.1 M) of phenol and chlorophenols (from Aldrich, Riedel-de Haen, Fluka, Germany) in 1 M NaOH were used. Chemicals of 'pure' and 'analytical' grade were used. Ar gas was bubbled through the solutions to remove oxygen in the supply reservoir. All the solutions were prepared using triply distilled water. Experiments were performed at  $20 \pm 1 \text{ }^\circ\text{C}$ .

## 3. Results

### 3.1. Electropolymerization of phenol and monochlorophenols on Pt studied by EQCM

The EQCM data show that the electrooxidation of phenol and monochlorophenols on a Pt electrode at  $0.78 \text{ V}$  (SHE) leads to a decrease in resonant frequency of the quartz crystal, corresponding to an increase in electrode mass due to electropolymerization (Figure 1a). The electropolymerization occurs at nearly constant rate after a 3–10 min induction period (Figure 1b), depending on the monomer. The electropolymerization rate is highest for 2-chlorophenol, resulting in thick film formation and detaching of the Pt sublayer from the

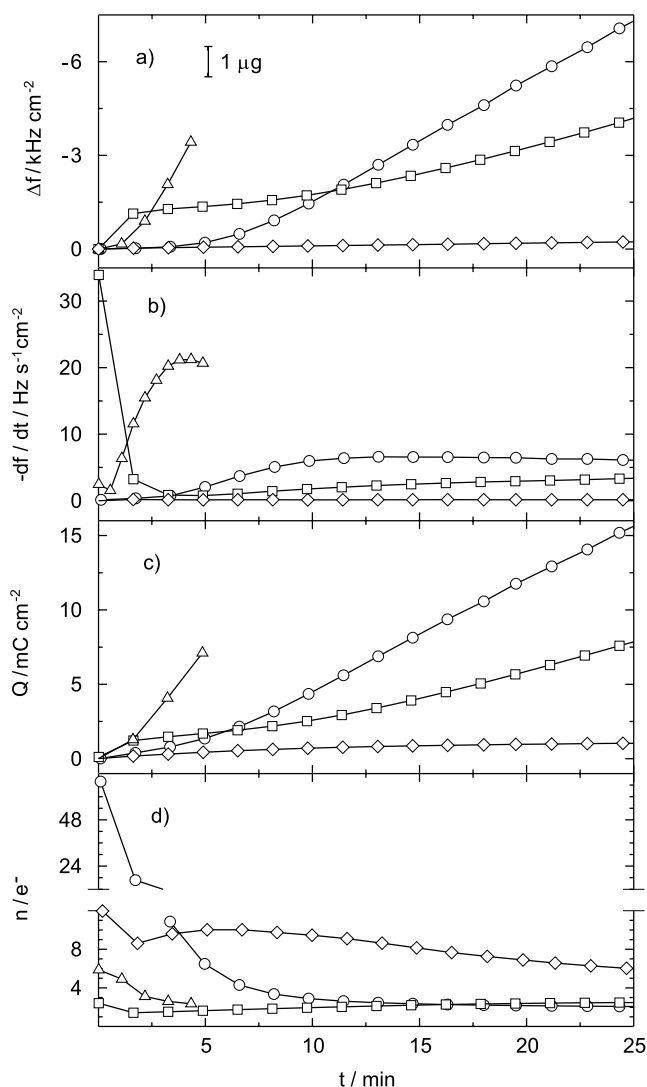


Fig. 1. Kinetic EQCM dependences of electrooxidation–electropolymerization: (a) change of quartz crystal frequency; (b) polymerization rate; (c) anodic oxidation charge; (d) electron number consumed for the electropolymerization of one molecule of the monomer. Key: phenol (○); 2-chlorophenol (Δ); 3-chlorophenol (□); 4-chlorophenol (◇). Working electrode: Pt, sputtered on 10 MHz quartz crystal; working solutions: 1 M NaOH, containing 0.1 M of phenol and monochlorophenols; oxidation potential:  $0.78 \text{ V}$  (SHE);  $T = 20 \text{ }^\circ\text{C}$ .

quartz surface after 5 min of reaction. A steady-state electropolymerization rate was achieved after the induction period (Figure 1b), and decreased in the order: 2-chlorophenol > phenol > 3-chlorophenol > 4-chlorophenol. This sequence correlates well with the electrode fouling rate observed in corresponding CV experiments [15]. This suggests that the most compact polymer film is formed in the case of 4-chlorophenol, hindering monomer access to the electrode and preventing further electropolymerization. The permeability of the film is the highest (the highest electropolymerization rate and the lowest fouling rate [15]) in the case of 2-chlorophenol, probably due to the irregular structure of the polymer formed, allowing monomer diffusion within the film and continuing electropolymerization [19]. The differences in polymer structure and permeability may be due to the differences in the structure and the isomerism of the monomers, their reactivity and initial orientation of the adsorbed molecules, as discussed previously [15].

An increase in oxidation charge with time (Figure 1c), proportional to the total increase in electrode mass (Figure 1a), suggests that the electrochemical polymerization rate is monitored by the EQCM. Phenolic groups are almost absent in the polymer film since they are either involved in monomer linking through the C—O—C ether links, or oxidized to quinone-type species as confirmed by FTIR (Z. Ežerskis and Z. Jusys, in preparation a). Thus, the access of counter ions ( $\text{Na}^+$ ) (hydrated by water molecules) and their contribution to the mass of the film should be negligible (some water entrapment into the film, however, is possible). This allows calculation, from the EQCM data, of the number of electrons ( $n$ ) per electropolymerization of one monomer molecule.

The corresponding numbers of electrons per monomer molecule electropolymerization are plotted in Figure 1d as a function of time. High  $n$  values in the initial stages of electropolymerization of phenol and 2-chlorophenol might be due to their oxidation (to quinone species or with ring-opening) as confirmed by FTIR (Z. Ežerskis and Z. Jusys, in preparation a) and/or due to the formation of soluble oligomeric species [5]. The number of electrons in most cases was  $2e^-$ /monomer molecule. However, for 4-chlorophenol the  $n$  value remains stable and significantly higher – about  $6e^-$ /monomer molecule.

### 3.2. Electropolymerization of dichlorophenols on Pt studied by EQCM

The EQCM data for electropolymerization of dichlorophenols on a Pt electrode at 0.78 V (SHE) in alkaline solution are shown in Figure 2. A decrease in the resonant frequency of the quartz crystal (an increase in electrode mass) confirms that the electropolymerization of dichlorophenols occurs during their potentiostatic oxidation on Pt (Figure 2a). The electropolymerization rate depends strongly on the isomerism of the monomer

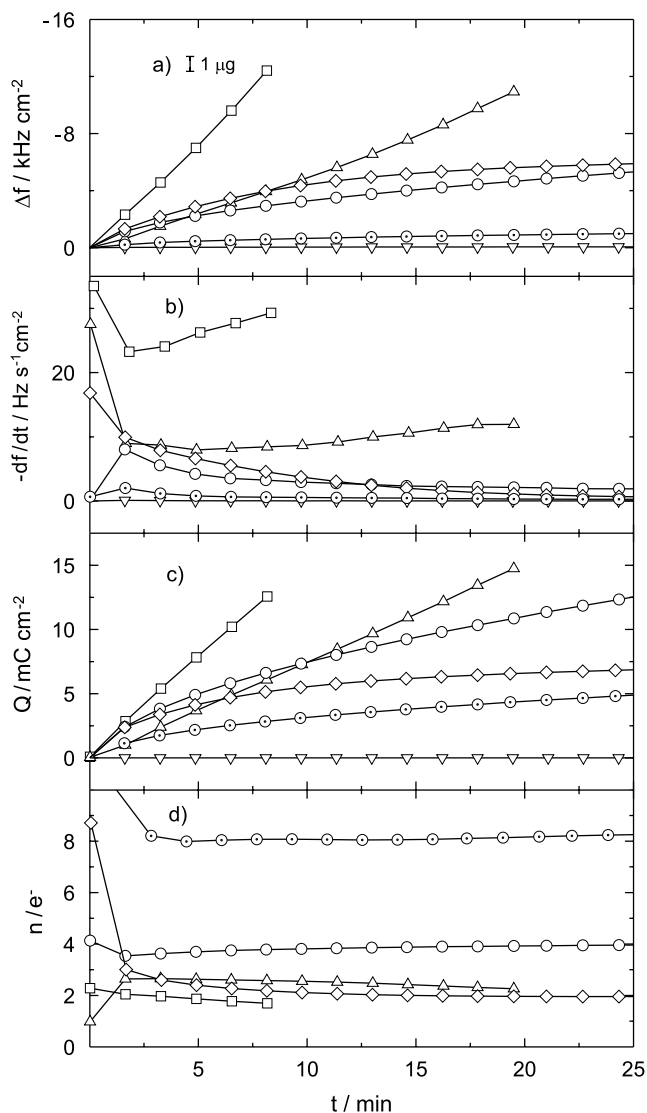


Fig. 2. Kinetic EQCM dependences of electrooxidation–electropolymerization: (a) change of quartz crystal frequency; (b) polymerization rate; (c) anodic oxidation charge; (d) electron number consumed for the electropolymerization of one molecule of the monomer. Key: 2,6-dichlorophenol (○); 2,5-dichlorophenol (□); 2,3-dichlorophenol (△); 2,4-dichlorophenol (⊙); 3,4-dichlorophenol (▽); 3,5-dichlorophenol (◇). Working electrode: Pt, sputtered on 10 MHz quartz crystal; working solutions: 1 M NaOH, containing 0.1 M of dichlorophenols; oxidation potential: 0.78 V (SHE);  $T = 20^\circ\text{C}$ .

(Figure 2a,b). The highest electropolymerization rate is achieved for 2,5-dichlorophenol; the electrode mass increases almost linearly with time (Figure 2a), suggesting good permeability of the film, due to its branched structure, indicated by the asymmetric features of the monomer. This is in agreement with the CV data indicating a low fouling of the electrode in alkaline 2,5-dichlorophenol solution [15]. A linear increase in the charge (Figure 2c) occurs simultaneously with increase in mass (Figure 2a) during the electropolymerization of 2,5-dichlorophenol. The number of electrons per electropolymerization of 2,5-dichlorophenol molecule, found from the corresponding gravimetry and coulometry data, is close to  $2e^-$ /monomer (Figure 2d).

The electropolymerization rate for 2,3-dichlorophenol is approximately half of that for 2,5-dichlorophenol (Figure 2a–c). A linear increase in the electrode mass and electropolymerization charge with time suggests a sufficient permeability of the polymer film. This is supported by a weak Pt electrode fouling in 2,3-dichlorophenol solution found in CV experiments [15]. Therefore, the electropolymerization rate for 2,3-dichlorophenol, approximately half of that for 2,5-dichlorophenol, is most likely due to a lower reactivity of the corresponding monomers rather than the difference in permeability of the polymer films. The number of electrons per 2,3-dichlorophenol molecule electropolymerization is ca.  $2e^-$  per monomer (Figure 2c).

An increase in electrode mass during the electropolymerization of 2,6-dichlorophenol and that of 3,5-dichlorophenol shows similar features (Figure 2a). Initially (within first 2 min), the increase in mass is comparable to that of 2,3-dichlorophenol, however, the electropolymerization rate continuously decreases with time (Figure 2a,b). This suggests that the permeability of the polymer film diminishes with increase in the thickness of the film [19]. Partial deactivation of the electrode occurs also during the CV experiments in alkaline solutions of corresponding dichlorophenols [15]. However, despite similar features in the electrode mass changes (Figure 2a), the increase in the charge for 2,6-dichlorophenol electropolymerization is about double compared to that for 3,5-dichlorophenol (Figure 2c). This leads to approximately double number of electrons per 2,6-dichlorophenol molecule electropolymerization (ca.  $4e^-$ /monomer) compared to 3,5-dichlorophenol (about  $2e^-$ /monomer) (Figure 2d).

Electropolymerization rates are the lowest for 2,4-dichlorophenol and 3,4-dichlorophenol (Figure 2a,b).

This is in agreement with the CV data – a complete fouling of the electrode occurs after the first positive-going potential scan in alkaline 2,4-dichlorophenol and 3,4-dichlorophenol solutions [15]. Both EQCM and CV data suggest formation of a thin, compact and non-permeable film on the electrode surface in the case of electropolymerization of these monomers. However, the electropolymerization charge for 2,4-dichlorophenol is comparable to that of 3,5-dichlorophenol (Figure 2c). This results in the number of electrons per 2,4-dichlorophenol molecule electropolymerization ca.  $8e^-$ /monomer (Figure 2d, Table 1). The number of electrons per 3,4-dichlorophenol monomer was not calculated due to a rather low electropolymerization rate.

### 3.3. Electropolymerization of trichlorophenols and pentachlorophenol on Pt studied by EQCM

The EQCM data for electropolymerization of 2,3,6-, 2,4,5-, 2,4,6-trichlorophenols and pentachlorophenol are shown in Figure 3. As follows from Figure 3a,b the increase in electrode mass during electropolymerization of 2,3,6-trichlorophenol is the highest among these trichlorophenols and is comparable with that for 2,6-dichlorophenol (Figure 2a,b). The electropolymerization charge for 2,3,6-trichlorophenol (Figure 3c) is about 1/3rd of the 2,6-dichlorophenol electropolymerization charge (Figure 2c). However, due to an additional Cl-substituent in 2,3,6-trichlorophenol molecule (a higher mass of the monomer) compared to 2,6-dichlorophenol, the number of electrons per monomer electropolymerization is about the same in both cases (Figures 3d and 2d). This suggests that electropolymerization mechanism is similar in both cases and the Cl-substituent in meta position of 2,3,6-trichlorophenol is not eliminated.

Table 1. Experimental EQCM data for potentiostatic electrooxidation–electropolymerization of phenol and its chlorinated derivatives on Pt electrode at 0.78 V (SHE). Electrooxidation duration 25 min,  $T = 20^\circ\text{C}$ . Solution containing 1 M NaOH and 0.1 M of corresponding phenol

Monomer	Mass change <sup>a</sup> , $\Delta m$ ( $\mu\text{g cm}^{-2}$ )	Electrooxidation charge <sup>a</sup> , $Q$ ( $\text{mC cm}^{-2}$ )	Electrochemical equivalent, $E = \Delta m/qF$ ( $\text{g mol}^{-1}$ )	Number of electrons, $n = M/E$
Phenoxide	7.42	15.53	44.3	2.1
2-MCP <sup>b</sup>	4.38	7.40	55.4	2.3
3-MCP	4.28	7.86	51.0	2.5
4-MCP	0.233	1.02	22.4	5.7
2,4-DCP	1.00	4.88	19.5	8.3
2,5-DCP <sup>b</sup>	7.38	8.0	81.0	2.0
2,6-DCP	5.42	12.51	40.5	4.0
3,5-DCP	6.04	6.84	81.0	2.0
2,3-DCP <sup>c</sup>	11.52	15.07	67.5	2.4
3,4-DCP	0.067	0.014	–	–
2,4,6-TCP	0.619	19.95	2.8	70
2,3,6-TCP	5.28	8.19	61.4	3.2
2,4,5-TCP	0.10	0.977	9.4	21
PCP	0.024	7.49	–	–

Phenoxide:  $M = 93 \text{ g mol}^{-1}$ ; MCP – monochlorophenoxides ( $M = 127.5 \text{ g mol}^{-1}$ ); DCP – dichlorophenoxides ( $M = 162 \text{ g mol}^{-1}$ ); TCP – trichlorophenoxides ( $M = 196.5 \text{ g mol}^{-1}$ ); PCP – pentachlorophenoxide ( $M = 265.5 \text{ g mol}^{-1}$ ).

<sup>a</sup> The values given are with respect to  $1 \text{ cm}^2$  of the real surface of the electrode.

<sup>b</sup> Electrooxidation duration: 5 min.

<sup>c</sup> Electrooxidation duration: 20 min.

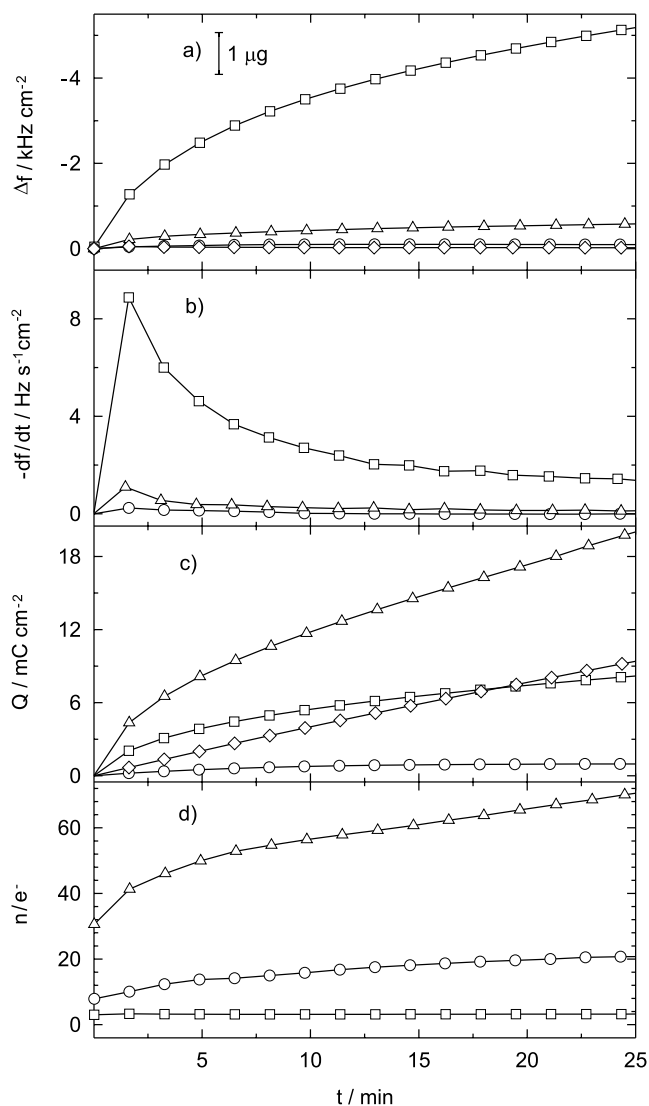


Fig. 3. Kinetic EQCM dependences of electrooxidation–electropolymerization: (a) change of quartz crystal frequency; (b) polymerization rate; (c) anodic oxidation charge; (d) electron number consumed for the electropolymerization of one molecule of the monomer. Key: 2,4,5-trichlorophenol (○); 2,3,6-trichlorophenol (□); 2,4,6-trichlorophenol (△); pentachlorophenol (◇). Working electrode: Pt, sputtered on 10 MHz quartz crystal; working solutions: 1 M NaOH, containing 0.1 M of the trichlorophenols and pentachlorophenol; oxidation potential: 0.78 V (SHE);  $T = 20$  °C.

The highest electropolymerization rate for 2,3,6-trichlorophenol among trichlorophenols (Figure 3a,b) is in agreement with the lowest electrode fouling rate for 2,3,6-trichlorophenol found in the CV experiments [15]. In contrast, the electrode fouling occurs after the first positive-going scan in 2,4,5-trichlorophenol solution according to the CV data [15] and the mass increase for 2,4,5-trichlorophenol electropolymerization is the lowest among the trichlorophenols studied. However, a small electropolymerization charge is still measured for 2,4,5-trichlorophenol. This may be due to a partial diffusion of low molecular weight substances from the electrode and/or a deeper oxidation to quinone and more saturated species. These effects may result in the

increase in number of electrons per 2,4,5-trichlorophenol electropolymerization up to 20 (Figure 3d).

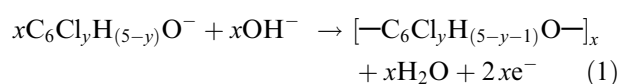
Apparently, an additional charge, gained due to a deeper oxidation of 2,4,6-trichlorophenol and pentachlorophenol, or the diffusion of smaller oligomers (caused by their weaker adhesion to the electrode) into the solution result in an even higher number of electrons per monomer for 2,4,6-trichlorophenol (Figure 3d) and pentachlorophenol (not shown). A comparatively high oxidation charge for 2,4,6-trichlorophenol and pentachlorophenol electrooxidation also suggests that electrode fouling is not complete in accordance with the CV data for these chlorophenols [15].

#### 4. Discussion

The EQCM data for electropolymerization of phenol and the chlorophenols studied are summarized in Table 1.

The electrochemical equivalent ( $E$ ) values, calculated according to the equation  $E = M/n$  (where  $M$  is a molar mass of the monomer and  $n$  the number of electrons per monomer molecule electropolymerization) from the gravimetry and coulometry data for the corresponding monomers, are listed in Table 1. It was assumed that (i) the polymer films are rigidly attached to the electrode; (ii) the non-faradaic contributions to the mass of the electrode are negligible.

The experimental values for the number of electrons ( $n$ ) per electropolymerization of monomer molecule (Table 1) in most cases differ from the theoretical value, which is equal to  $2e^-$ /monomer, if the electropolymerization process occurs exclusively *via* the quinol–ether mechanism [20–23] according to the equation:



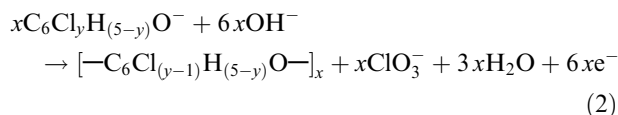
where  $4 \geq y \geq 0$  for electropolymerization through active ortho and para positions (at least one unsubstituted ortho or para position is present).

Deviations from the mass-to-charge balance according to Equation 1 may be explained by the following reasons:

1. A mass deficit – low molecular weight oligomers (dimers, trimers, etc.), formed during electrochemical oxidation, may diffuse away from the electrode [5]. Apparently, this effect is more pronounced for the electrooxidation of 2,4,6-trichlorophenol and pentachlorophenol.
2. An extra charge – the polymeric substances formed are further oxidized to quinone structures and more saturated species (with the cleavage of the benzene ring). The additional charge is required for these reactions while the mass of the electrode is not changing (or the changes are small). This effect is most pronounced for electrooxidation of phenol,

trichlorophenol and pentachlorophenol as confirmed by FTIR (Z. Ežerskis and Z. Jusys, in preparation a).

3. Both mass deficit and extra charge may occur during the electropolymerization through the nucleophilic-radical substitution ( $S_{RN}1$ ) mechanism [24, 25]. Chloride anions eliminated from the active ortho and para positions should be further oxidized at 0.78 V (SHE) in alkaline medium. Assuming oxidation of eliminated chloride to chlorate, the total equation for electropolymerization of chlorophenols *via* the  $S_{RN}1$  mechanism can be written as follows:



where  $5 \geq y \geq 1$  (at least one Cl-substituent is present in active ortho or para positions). Chloride elimination diminishes the mass of the species involved in the polymer structure compared to the original monomer. On the other hand, chloride oxidation to chlorate anion considerably increases the total oxidation charge (3-fold compared to the quinol-ether mechanism (1)). Both of these factors may contribute significantly to the mass-to-charge balance in the EQCM measurements.

Assuming the first two effects are negligible, the theoretical values of the electrochemical equivalent ( $E$ ) and the number of electrons ( $n$ ) can be calculated, if the electropolymerization occurs exclusively either according to Equations 1 or 2. It should be noted, that the number of electrons per monomer molecule oxidation/polymerization in Equations 1 and 2 is valid for linear (non-branched) polymers. However, in the case of significant crosslinking the number of electrons would be somewhat higher.

The  $n$  values for corresponding monomers calculated according to Equations 1 and 2 are listed in Table 2. It is evident, that the electrochemical equivalent for electropolymerization through the different routes (either (1) or (2)) differs up to four times and can be used as a measure to distinguish between the reaction mechanisms (note, that the electropolymerization of tetrachlorophenols was not studied experimentally in the present work).

It is important to mention that the molar mass of the species derived during the electropolymerization

through the  $S_{RN}1$  mechanism is smaller compared to the initial chlorophenol monomer due to Cl-elimination. As a consequence, only an apparent number of electrons per monomer (Table 1) can be found, not taking into account this difference for the electropolymerization through the  $S_{RN}1$  mechanism (compare the definitions of  $n$  in Tables 1 and 2). Therefore, the apparent number of electrons cannot be used for evaluation of the electropolymerization routes. However, the electropolymerization mechanism can be estimated from a comparison between the experimental value of the electrochemical equivalent (Table 1) with theoretical  $E$  values, calculated according to either quinol-ether or  $S_{RN}1$  mechanism for corresponding monomers (Table 2).

Comparison of the experimental values of the electrochemical equivalent (Table 1) and the corresponding theoretical values (Table 2) for electropolymerization of phenol, 2-monochlorophenol and 3-monochlorophenol on a Pt electrode shows that the experimental  $E$  values are close to those calculated according to Equation 1. Deviations of the electrochemical equivalent from theoretical values may be caused by the factors discussed in assumptions 1 and 2. However, for the electropolymerization of 4-chlorophenol the experimental  $E$  value (Table 1) is closer to the theoretical, calculated for the electropolymerization through the  $S_{RN}1$  mechanism (Table 2).

Comparison of the experimental (Table 1) and theoretical (Table 2)  $E$  values for the electropolymerization of dichlorophenols shows that for 2,4-dichlorophenol polymerization mainly proceeds through the  $S_{RN}1$  mechanism. In the case of 2,6-dichlorophenol the process occurs *via* the mixed quinol-ether and  $S_{RN}1$  mechanism. Electropolymerization of 2,5-, 2,3- and 3,5-dichlorophenol occurs *via* the quinol-ether mechanism rather than the  $S_{RN}1$  mechanism.

Analogous comparison of the experimental (Table 1) and theoretical (Table 2)  $E$  values for the electropolymerization of trichlorophenols shows that 2,3,6-trichlorophenol is electropolymerized through the mixed quinol-ether and  $S_{RN}1$  mechanism.

In the case of 2,4,6-trichlorophenol and pentachlorophenol electrooxidation, such a comparison is complicated, possibly, due to diffusion of soluble oligomeric products from the electrode and further oxidation of polymers to quinone structures, as discussed earlier.

Table 2. Theoretical values of the electrochemical equivalent ( $E$ ) and the number of electrons ( $n$ ) per molecule of phenol electrooxidation-electropolymerization *via* quinol-ether or  $S_{RN}1$  mechanisms

Monomer	$M$	Quinol-ether mechanism (Equation 1)		$S_{RN}1$ mechanism (Equation 2)	
		Equivalent $E = (M - 1)/2$	Number of electrons $n = (M - 1)/E$	Equivalent $E = (M - 35.5)/6$	Number of electrons $n = (M - 35.5)/E$
$\text{C}_6\text{H}_5\text{O}^-$	93	46.0	2	–	–
$\text{C}_6\text{H}_4\text{ClO}^-$	127.5	63.3	2	15.3	6
$\text{C}_6\text{H}_3\text{Cl}_2\text{O}^-$	162	80.5	2	21.1	6
$\text{C}_6\text{H}_2\text{Cl}_3\text{O}^-$	196.5	97.8	2	26.8	6
$\text{C}_6\text{HCl}_4\text{O}^-$	231	115	2	32.6	6
$\text{C}_6\text{Cl}_5\text{O}^-$	265.5	–	–	38.3	6

However, the electropolymerization of 2,4,6-trichlorophenol and pentachlorophenol should occur exclusively through the  $S_{RN}1$  mechanism, since all active ortho and para positions in these monomers are occupied by Cl-substituents.

The proposed modified  $S_{RN}1$  electropolymerization mechanism with elimination/oxidation of chloride is in a fair agreement with the experimental EQCM data and explains the large scatter in the number of electrons per monomer electropolymerization (Table 1). A similar scatter in the apparent number of electrons for electropolymerization of chlorophenols on a gold electrode was found recently using EQCM [26, 27]. However, it should be noted, that the EQCM, measuring only mass and charge changes, cannot provide a direct proof about the products formed in electropolymerization of chlorophenols. The suggested electropolymerization mechanisms are strongly supported by the FTIR and GC-MS characterization of the polymeric and oligomeric species formed as will be discussed elsewhere (Z. Ežerskis and Z. Jusys, in preparation a,b).

## 5. Conclusions

The electropolymerization of phenol and mono-, di-, tri-, pentachlorophenols occurs during potentiostatic oxidation on a Pt electrode in 1 M NaOH solution containing 0.1 M of the corresponding phenol, as evidenced from the electrode mass increase monitored by the EQCM.

The electropolymerization rate is the highest for ortho-substituted phenols (2-chlorophenol, 2,5- and 2,3-dichlorophenol). The electropolymerization is slow for para-substituted phenols (4-chlorophenol, 3,4-dichlorophenol and 2,4,5-trichlorophenol), indicating electrode fouling by the formed film.

The difference in the electropolymerization rate of phenols can be interpreted in terms of a different permeability of the polymer films formed from various starting monomers. The structure and permeability of the film is most likely determined by the degree of chlorination and the isomerism of the corresponding monomer.

The electropolymerization mechanism has been postulated from a comparison of the electrochemical equivalent found from the EQCM data, with the theoretical values calculated for both the quinol-ether (without Cl-elimination) and the nucleophilic-radical substitution (with Cl-elimination) routes. The EQCM

data suggest that the electropolymerization of chlorophenols occurs without Cl-elimination for the monomers with unsubstituted ortho and para positions. Dechlorination is most pronounced for the electropolymerization of para-substituted isomers.

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