

APPLICATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) TO STUDY OF PHENOLIC FILMS

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This paper describes the phenol electrochemical oxidation that occurs with formation of phenolic films on the platinum electrode by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. Both cyclic voltammetry and impedance studies were performed at room temperature, using a GAMRY PC3 potentiostat. The impedance data were recorded in a frequency range from 0.01 Hz to 100 kHz, with a.c. amplitude of 5 mV. The capacitance and resistance curves were recorded at various frequencies, corresponding to the three regions from Nyquist plot, at high frequency (90kHz), where a kinetic stage controls the reaction, at small frequency (100Hz), where a diffusion control is present and at 2 kHz frequency for a mixed control.

INTRODUCTION

Industrial effluents containing toxic and/or biorefractory products are presently a serious environmental problem due to the increasing severity of the legislation on acceptable limits and to the lack of general treatment methods. Among aqueous industrial effluents, those containing organic pollutants cause problems due to the high activation energy barrier for chemical oxidation reactions and to the complexity of the degradation mechanisms.

Phenol is one of these compounds and it is a general protoplasmic poison that is corrosive to any living tissue it contacts. Inhalation can cause irritation to the respiratory system and associated mucosa.¹⁻³ Some studies have suggested that exposure to phenol causes mutations (genetic changes) in humans. While there is no evidence of carcinogenicity of this chemical in humans, it has caused cancer in mice and is considered a suspected carcinogen.⁴

The electrochemical methods can be used for partial or total degradation of toxic organic substances. Destruction of organic compounds by these ways offers the prospect of relatively simple equipment, environmental friendliness, and the

possibility of high-energy efficiency by comparison with other methods.⁵⁻⁷

The chemical literature contains numerous reports of the loss of electrode activity, which accompanies the build-up of polymeric film on the surface of solid electrodes during phenol oxidation.⁸⁻¹⁰ In a previous work¹¹ we proposed the following mechanism for electrochemical oxidation of phenol in sulfuric acid solutions.

The first step in the phenol (I) oxidation is a one-electron oxidation producing the phenoxy radical cation (II) which is a strongly acidic species and can deprotonate rapidly to the neutral radical (III), which, owing to its lower oxidation potential may be further oxidized to the corresponding phenoxonium ions (IV). This second electrode transfer may take place at the electrode and/or in solution.

This cation, acting as a strong electrophile, can react with water to produce hydroquinone (V).

The adjacent adsorbed phenoxy radicals (II) and the neutral radicals (III) can couple to form dimers (VI), trimers and eventually polymers that remain adsorbed on the electrode blocking the surface, *i.e.* electrochemical destruction of phenolic species is complicated due to electrode fouling producing

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oligomeric or polymeric nonsoluble compounds formed as a result of the coupling of phenoxy radicals generated in the initial oxidation step.

However, from a practical point of view, immobilization of phenol on the electrode surface due to electropolymerization might be used as an

alternative to the electrooxidation for pollution remediation of aqueous solutions.

This paper describes the phenol oxidation that occurs with formation of phenolic films on the platinum electrode by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

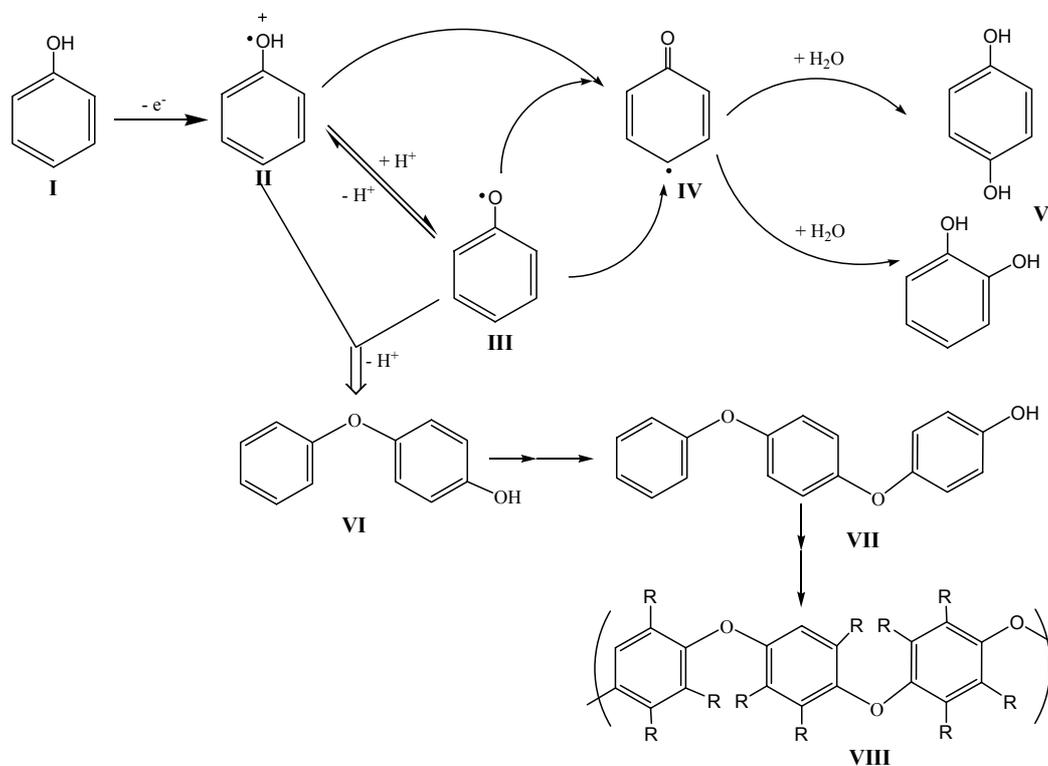


Fig. 1 – Proposed mechanism for electrochemical oxidation of phenol in sulfuric acid. R is hydrogen or other rings of polymeric structure.

The Mott-Schottky technique was used in order to measure capacitance and resistance (*vs.* d.c. potential) of electrode surface covered with a polymeric film. Evolution of capacitance and resistance *vs.* potential and *a.c.* frequency can offer us information about both adsorption and desorption ranges of electroactive species. At a different fixed frequency, small *a.c.* signal potential excitation is applied to the electrochemical cell and the impedance at the working electrode interface is measured at different values of polarization potential.

EXPERIMENTAL

The cyclic voltammetry and electrochemical impedance spectroscopy experiments were carried out in 12mM phenol in 0.5M sulfuric acid as supporting electrolyte, at room temperature, using a three-electrode system. The working electrode was Pt. Also, a platinum wire was used as counter electrode and the potentials were measured against a saturated

calomel electrode placed in a separated compartment and connected with the cell by means of agar-agar bridge.

Cyclic voltammetry measurements were performed using a GAMRY PC3 potentiostat.

The investigation has been done in anodic direction from 0.2 to 1.4 V and before each scan the electrode was prepared to ensure a reproducible surface by polishing, rinsing with distilled water and ultrasonic cleaning for 4 min. in high purity water.

The impedance data were recorded using a GAMRY Instruments EIS 300, over a frequency range from 0.01 Hz to 100 kHz, with an *a.c.* amplitude of 5 mV.

The Mott-Schottky curves were obtained at various values of frequency (1 Hz, 100Hz, 1kHz, 90kHz) in the potential region corresponding to oxidation of phenol 0.2V – 1.3V.

RESULTS AND DISCUSSION

Voltammetric studies

Voltammograms obtained in acid aqueous media show an unique anodic wave at potentials

close to +1.0V and a little cathodic peak which shifted towards more cathodic potentials (figure 2). That implies the irreversibility of the system due to the fast subsequent chemical reaction. The nature of that wave and the various suggestions given by

different authors about the dimerization of the radical formed indicated above, have led us to test either the existence of that kind of process and the mechanism which takes place.

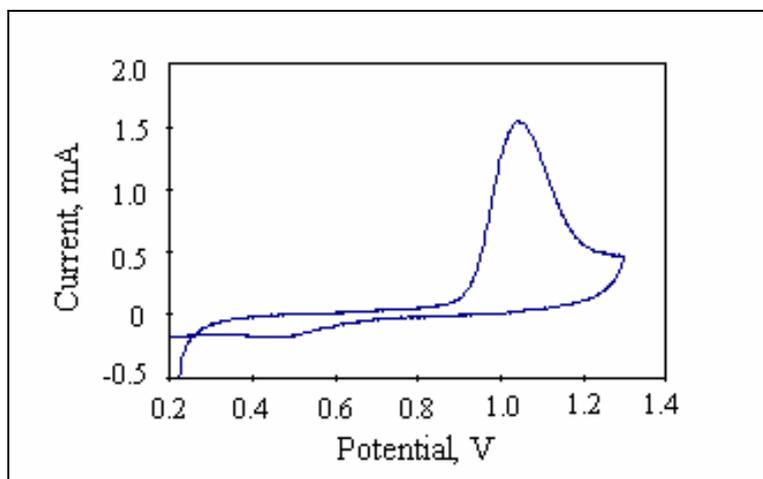


Fig. 2 – Cyclic voltammogram for 8 mM phenol in sulfuric acid 0.5M on Pt electrode.

The properties of the oxidation peak are in complete agreement with an irreversible diffusion (D) controlled reaction. So its peak current (i_p) is proportional to the square root of the sweep rate (v) see also fig. 3 as is given by:

$$i_p = mD^{1/2}v^{1/2}c \quad (1)$$

Also a linearity of peak currents with concentration was found for lower values of concentration up to 10 mM.

On the basis of these results, it can be concluded that, with decreasing concentration and sweep rate, the peak current behaviour of phenol oxidation approaches that of an irreversible diffusion controlled reaction.

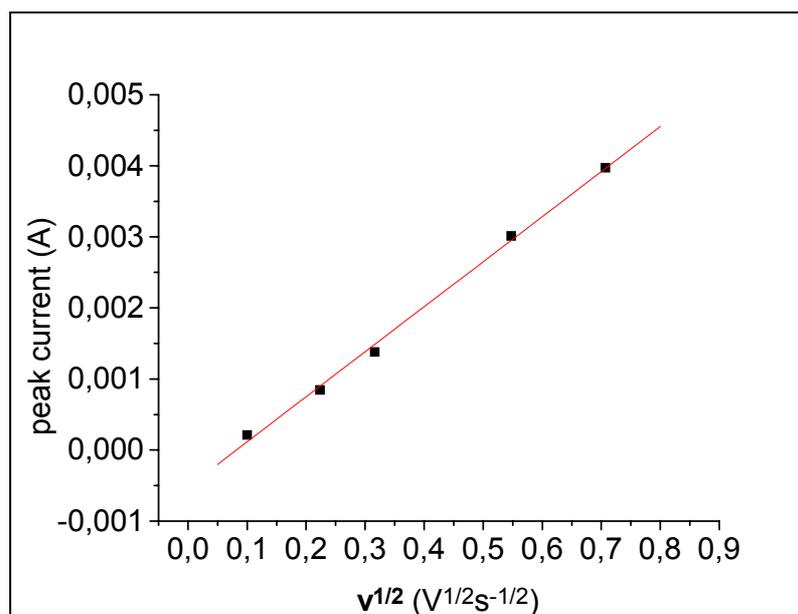
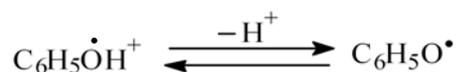
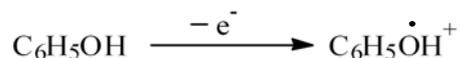


Fig. 3 – Variation of peak currents with square root of scan rates, for the oxidation of 8 mM phenol on platinum electrode.

So first of all voltammetric data show that the first current peak corresponds to a one electron reversible transfer followed by a fast dimerization of the radicals formed by EC mechanism, *i.e.*:



More data concerning the kinetic control were obtained by impedance spectroscopy.

Electrochemical impedance spectroscopy

The Nyquist impedance plot (figure 4) for phenol in acid solution at oxidation half wave potential, displayed Warburg impedance, indicating a diffusion effect.

In fact the impedance diagram gives a capacitive loop and a Warburg impedance, which implies that coverage on the electrode surface with adsorbed species is low and oxidation process is still proceeding on uncovered sites.

The impedance spectra with Warburg impedance and capacitive loop may be analyzed using the electrical circuits shown by figure 5 respectively.

The following figure presents an equivalent circuit specific to mixed control.

Where: R_s represents the solution resistance, R_t is charge transfer resistance, W is Warburg impedance, C_{dl} represents double layer capacitance and C_{pc} is a pseudocapacitance, R_a is pseudoresistance.

The values of elements of circuit are calculated as follows.

At very high frequencies, the Warburg impedance becomes unimportant in relation to R_t and the circuit converges to that of figure 6.

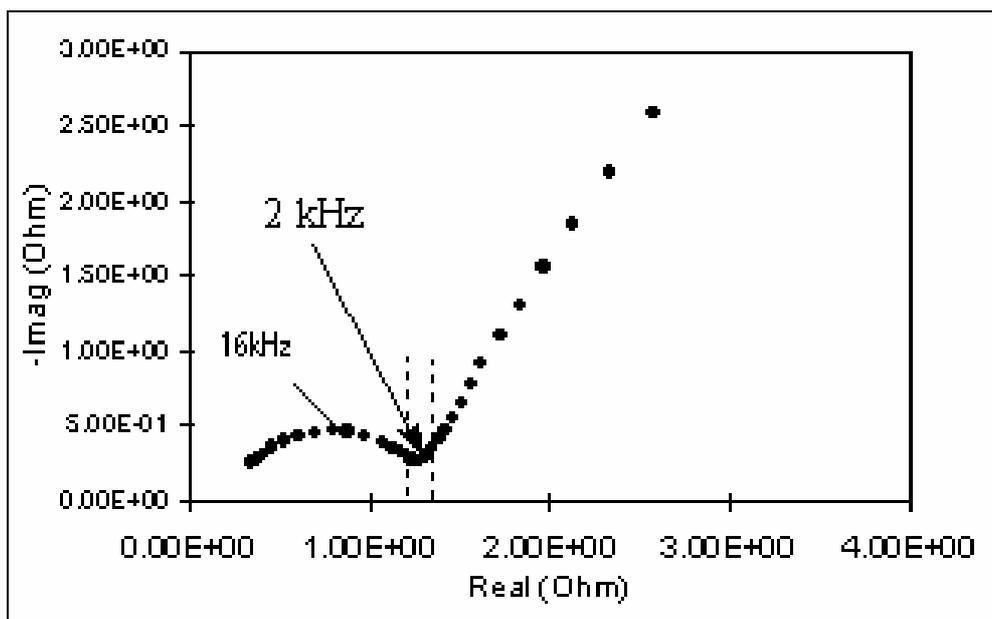


Fig. 4 – Nyquist plot for phenol in sulfuric acid on platinum electrode, at 1 V vs. ECS, frequency range 100 kHz to 0.3 kHz.

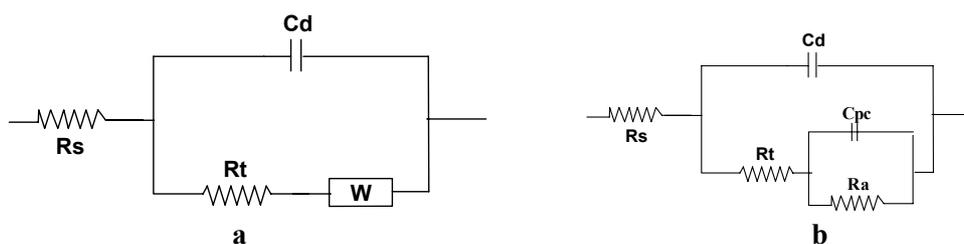


Fig. 5 – Equivalent circuit for a mixed kinetic and diffusion control.

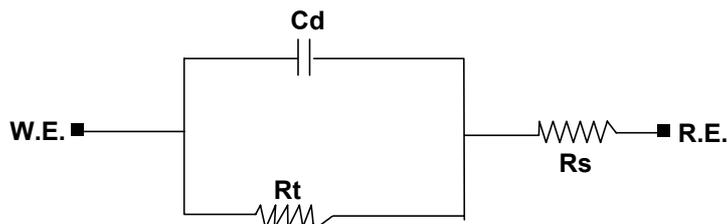


Fig. 6 – Equivalent circuit for a system in which the Warburg impedance is unimportant.

The impedance is: ¹²

$$Z = R_s - j \left(\frac{R_t}{R_t C_d \omega - j} \right) \quad (2)$$

which is expressed as the series combination of two elements Z_{Re} and Z_{Im} , real and imaginary components:

$$Z_{Re} = R_s + \frac{R_t}{1 + R_t^2 C_d^2 \omega^2} \quad (3)$$

and

$$Z_{Im} = \frac{R_t^2 C_d \omega}{1 + R_t^2 C_d^2 \omega^2} \quad (4)$$

Elimination of ω from this pair of equations yields

$$\left(Z_{Re} - R_s - \frac{R_t}{2} \right)^2 + Z_{Im}^2 = \left(\frac{R_t}{2} \right)^2 \quad (5)$$

Hence Z_{Im} vs. Z_{Re} should give a circular plot centered at

$Z_{Re} = R_s + R_t/2$ and $Z_{Im} = 0$
and having a radius of $R_t/2$.

R_t is defined as: ¹³

$$R_t = \frac{RT}{nF i_0} \quad (6)$$

At the maximum value of Z_{Im}

$$\omega = \frac{1}{R_t C_d} \quad (7)$$

From these relations we have determined charge transfer kinetic parameters which are presented in table 1.

The values of these parameters, especially i_0 , corresponds to a one electron reversible (fast) transfer reaction, followed by a fast dimerization of the radicals formed by an EC mechanism.

Table 1

Parameters, which were determinate at high frequencies

R_s	0.25Ω
R_t	0.75Ω
C_d	13.3μF
i_0	0.037A.cm ⁻²

Also, the low value of the charge transfer resistance, 0.75 Ω, shows a fast electron transfer reaction corresponding to phenol oxidation. This represents the first step of the reaction which is followed by polyphenol formation on the electrode surface.

At low frequencies the reactants have to diffuse farther, thereby increasing the Warburg impedance. The real and imaginary components will become

$$Z_{Re} = R_s + R_t + \sigma \omega^{-1/2} \quad (8)$$

$$Z_{Im} = \sigma \omega^{-1/2} + 2\sigma^2 C_d \quad (9)$$

Elimination of ω between these two equations gives

$$Z_{Re} = Z_{Re} - R_s - R_t + 2\sigma^2 C_d \quad (10)$$

The extrapolated line intersects the real axis at $R_s + R_t - 2\sigma^2 C_d$.

σ is the Warburg coefficient defined as: ¹⁴

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \frac{1}{C_0 \sqrt{D}} \quad (11)$$

in which:

ω - radial frequency; D - diffusion coefficient; A - surface area of the electrode; n - number of transferred electrons; C_0 - bulk concentration of the diffusing species;

The Warburg coefficient (σ) calculated from the slope of resistance vs. $\omega^{-1/2}$ plot (figure 8), at room temperature, is $120 \Omega s^{-1/2}$.

Parameters which were determined at low frequencies are presented in the following table 2.

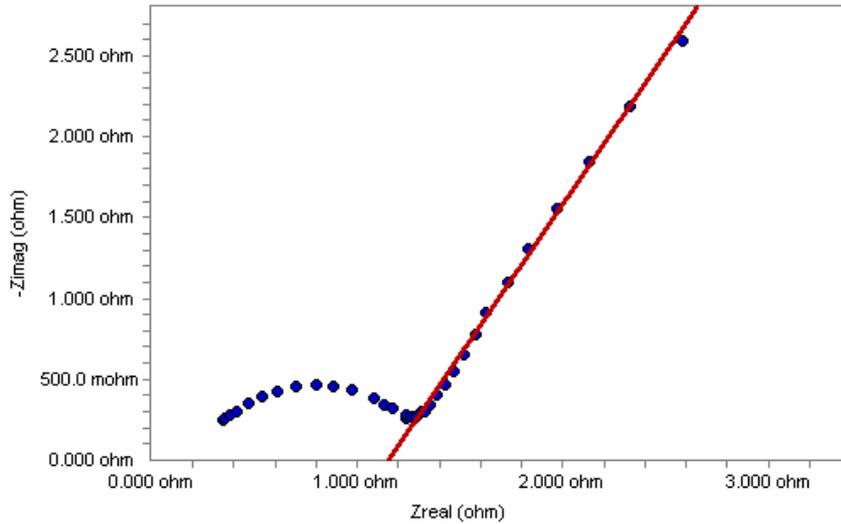


Fig. 7 – The extrapolated line which intersect the real axis at $R_s + R_t - 2\sigma^2 C_d$.

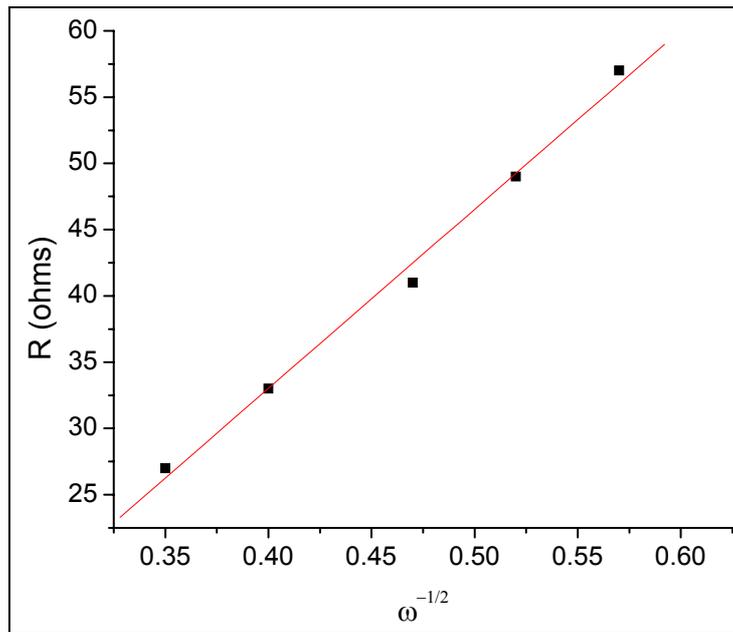


Fig. 8 – Dependence of resistance vs. $\omega^{-1/2}$

Tabel 2

Parameters which were determined at low frequencies

C_d	60 μF
σ	$120 \Omega s^{-1/2}$
D	$6.5 \cdot 10^{-8} \text{ cm}^2/\text{s}$.

On the basis of the values of σ and D it can be concluded that oxidation of phenol is a irreversible diffusion (D) controlled reaction

Adsorption pseudocapacitance

The values of elements of circuit b are analyzed as follows.^{15, 16}

The rate of migration of different active groups within membranes and monolayer on electrodes make necessary to consider the coupling between migration of reactants and electrode process i.e. the electrode process is coupled with a diffusional transport and possible with some reactions preceding, following or in parallel with the electrode process.

A reversible (fast) electrode reaction gives rise to a pseudocapacitance peak at the half wave potential. One defines as adsorption pseudocapacitance the case where only adsorbed constituents participate in the process.

As was shown by¹ pseudocapacitance resulting from a reversible electrode process is independent of frequency below complete surface coverage.

However when the full surface coverage is approached, the size of capacitance peak measured at medium and high frequency starts decreasing *i.e.* the capacitance peak are strongly frequency dependent when saturated monolayers (full coverage) are formed by adsorption.

This phenomenon suggests that the process giving rise to the capacitance peak is impeded at high surface coverage, while there is only little frequency dependence when the surface is only partially covered.

From the frequency dependence of pseudocapacitance it is evident that the electrode process being reversible, slow access of the electroactive groups to the active surface can be responsible for the frequency dependence at high surface concentration (coverage).

It was shown by¹⁵ that one alternative mechanism for approach of the active species to the electrode surfaces is a diffusion process within the adsorbed layer. The diffusion mechanism gives a linear dependence of the pseudocapacitance C_{pc} on

$1/\omega^{1/2}$ at high frequencies with an asymptotical approach to the equilibrium value at low frequencies.

For high frequency the expression for the pseudocapacitance C_{pc} is reduced to the form obtained for the diffusion in a semi-infinite phase, namely:

$$C_{pc} = a_s \frac{K_1}{(1 + K_1)^2} \frac{F^2}{RT} \left(\Delta\delta + \frac{D}{2\omega} \right)^{1/2} \quad (12)$$

where a_s is the concentration of active groups in the layer, K_1 is the equilibrium constant of the electrode process at any polarization, $\Delta\delta$ is the thickness of the electroactive monolayer, D is the internal diffusion coefficient of the active species in the polymeric layer.

As seen in (12) the pseudocapacitance varies linearly with $1/\omega^{1/2}$ through the whole frequency region.

The pseudocapacitance extrapolates to zero for $\omega \rightarrow \infty$ since at all experimental concentrations C_{pc} for $\omega \rightarrow \infty$ becomes extremely small.

Figure 9 presents the capacitance and resistance vs. d.c. potential applied curves, for phenol solution in sulfuric acid medium, on platinum electrode, applying different frequencies of a.c. potential excitation. The Mott Schotky capacitance-resistance curves were recorded at various frequencies corresponding to the three regions from Nyquist plot, at high frequency (90kHz), at small frequency (100Hz), and at 2 kHz frequency.

In Table 3 we present the values of resistance and differential capacitance peak as a function of the frequency of the excitation signal, after five minutes of immersion of the electrode in phenol acid solution.

Table 3
The variation of resistance and capacitance at peak potential with frequency of the excitation signal

Frequency kHz	Resistance Ω	Capacitance μF
0.1	24	15
2	5.5	12
90	1.5	3

As seen from figure 9 and table 3 the above experimental pseudocapacitance values are in

complete concordance with theoretical model of diffusion of active species in an adsorbed layer.

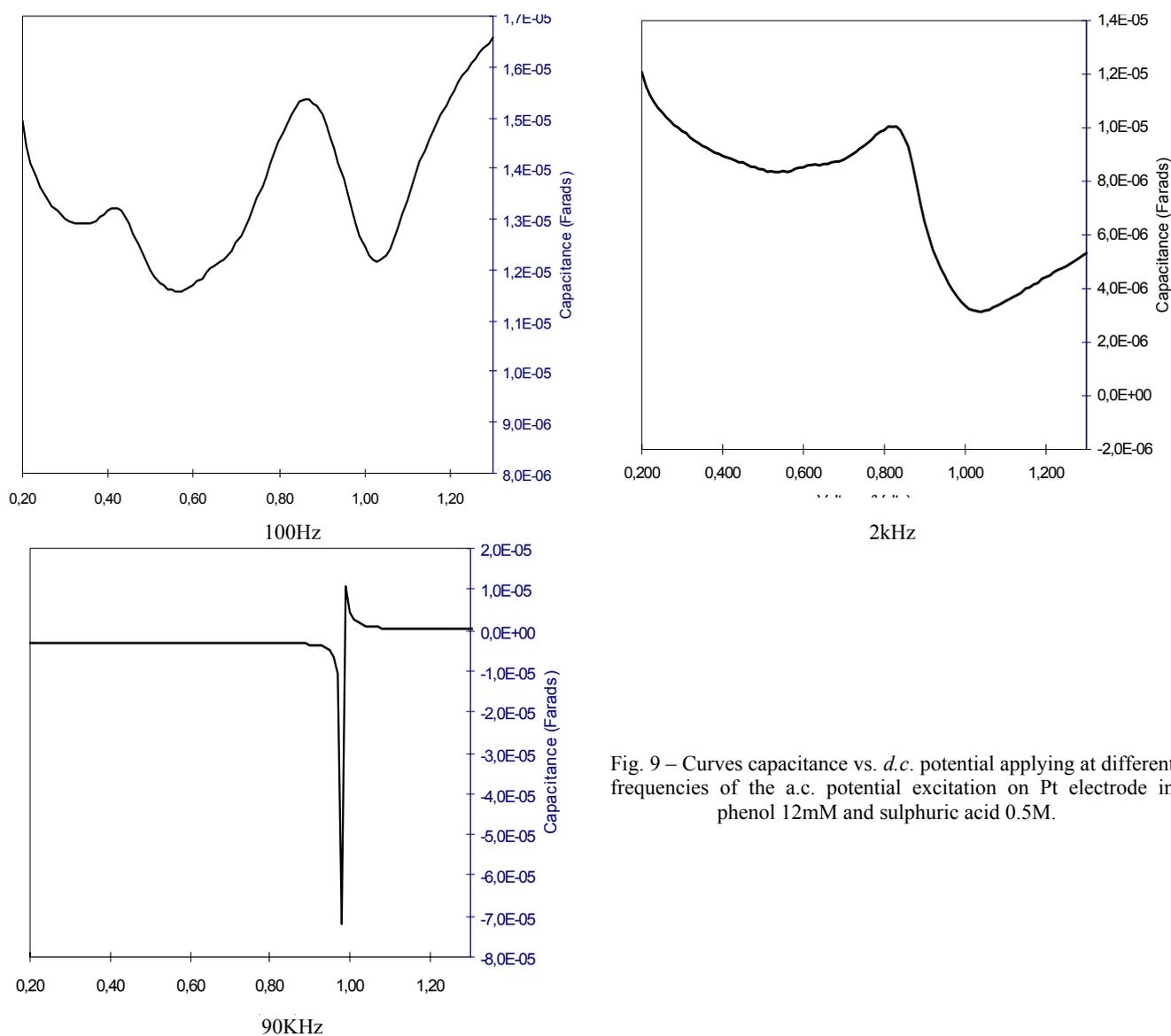


Fig. 9 – Curves capacitance vs. *d.c.* potential applying at different frequencies of the a.c. potential excitation on Pt electrode in phenol 12mM and sulphuric acid 0.5M.

CONCLUSION

Electrochemical oxidation of phenolic species is stopped due to electropolymerisation. Ether- and quinone- type polymeric non-soluble compounds are formed as a result of the coupling of phenoxy radicals generated in the initial oxidation step. These non-soluble solide polymeric compounds block the electrode surface and lead to electrode deactivation and prevent effective total phenol deactivation.

Ortho and *para* linked polyphenol derivatives are formed in the course of electropolymerization of phenol as a result of preferable stabilization of phenoxy radicals via the *ortho* and *para* positions with respect to the original hydroxyl group.

The distribution of electropolymerization products depends on the stability of the radical formed, the structure and reactivity of the monomer molecules, reaction medium (solvent, pH solution), the electrode material, electrode potential and phenol concentration.

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