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Electrochemical Behaviour of Phenols

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The literature data on the electrochemical behaviour of phenol and its adsorption on various anodic materials (platinum, graphite, gold, and lead dioxide) are surveyed and the influence of the rate of application of the potential, temperature, pH, the rate of rotation of the electrode (stirring) on the maximum oxidation current of phenol and its half-wave potential is examined. The present concept concerning the mechanism of the primary electrode reaction is analysed and the possibility of the extensive oxidation of phenol is considered. The influence of a series of substituents [OH, CH_3, NO_2, Cl, C_6H_4, COOH, C_2H_5, and $C(CH_3)_3$] on the principal characteristics of the potentiodynamic relations is examined and the possibility of a correlation between the half-wave potentials $E_{1/2}$ of substituted phenols and the Hammett constants is analysed.
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I. INTRODUCTION

In connection with wide scale industrial use of phenols, two problems have arisen: the development of convenient and selective methods for their analysis and the removal of phenols from the waste water in industrial undertakings. The latter is related to the high toxicity of phenols and the difficulty of decomposing them by the usual chemical means. Electrochemical methods, especially anodic oxidation, proved to be sufficiently effective for the solution of both problems, which is the reason for the increased interest of investigators in the electrochemistry of phenols.

The aim of the present review is to survey the factual data which have accumulated concerning the oxidation of phenols on anodes.

II. THE PLATINUM ELECTRODE

1. Potentiodynamic Measurements

There is a distinct oxidation wave on the voltage–current curve obtained in the oxidation of phenol on stationary and rotating platinum anodes. A typical form of such curves is illustrated in Fig.1. At a phenol concentration $c_{ph} < 1 \times 10^{-4}$ M under both stationary and dynamic conditions, a single wave is observed with a distinct limiting current and there is a linear relation between the limiting current and c_{ph}. At $c_{ph} > 1 \times 10^{-4}$ M, a decrease of the current is observed on the voltage–current curves, which is due to the inhibition of the electrochemical oxidation process and the linear relation between the maximum current and c_{ph} breaks down—the current increases more slowly than the concentration.[1-3]

It has been noted that during the measurement of the potentiodynamic relation, a readily visible yellow-brown polymeric product is formed on the anode. In order to investigate the kinetics of the growth of this polymer film, ellipsometric measurements have been made in the electrochemical oxidation of phenol in 0.5 M H_2SO_4 solution.[4] Optical studies have shown that, at low potentials (~1 V relative to the reversible hydrogen electrode in the same solution), the rate of growth of the film is low and its thickness is proportional to the square root of the electrochemical oxidation time. The rate of formation of the film increases sharply as the potential shifts towards high positive values (≥2 V) (Fig.2); under these conditions, its thickness reaches on average 1000–10000 Å.

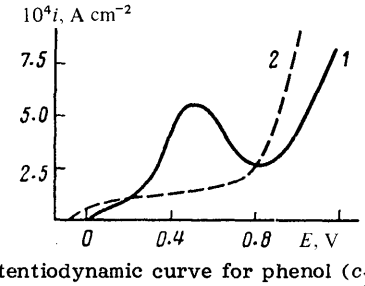


Figure 1. Potentiodynamic curve for phenol ($c_{ph} = 1 \times 10^{-3}$ M) in a saturated borax solution at a platinum anode (i = current density; rate of application of potential $v = 40 \times 10^{-3}$ V s^{-1}; pH 9.5; 20 °C): *1*) supporting electrolyte plus phenol; *2*) supporting electrolyte.[3]

The observed decrease of the current on the potentiometric curve is in fact explained by the strong adsorption of the reaction products and the blocking by the latter of the anode surface.[1-3] Levina et al.[5], who investigated the electrochemical oxidation of phenol in 1 *N* H_2SO_4 solution, assumed that the decrease of the current is caused by the adsorption of oxygen, which cannot occupy the anode surface at low anodic potentials owing to the adsorption of phenol. Such competition for sites on the surface does indeed occur in the case of organic substances and must be taken into account.[6] However, in the study of the electrochemical oxidation of

phenol in aqueous 1 *N* H_2SO_4 and NaOH solutions, the possibility of the formation on the anode surface of a film consisting not only of polymer molecules strongly bound to the surface but also of soluble products has been considered.[7,8] It has been suggested that, at low (<0.2 M) and higher concentrations, products of the second and first types predominate respectively.

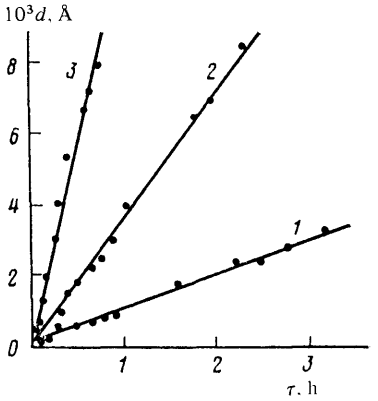


Figure 2. The rate of growth of the polymer film on the platinum electrode (d = thickness of film, τ = time) at three different potentials in a 0.5 M H_2SO_4 + 0.1 M C_6H_5OH solution; potential (V): 1) 2.08; 2) 2.15; 3) 2.28.[4]

Judging from the shapes of the potentiodynamic curves, which have a deep minimum, the process should have ceased in the passivation region as the polymer film grew. Furthermore, it is well known that benzoquinone can be obtained in a satisfactory yield by the preparative oxidation of phenol. It has been suggested[8] that the oxidation of phenol in the passivation region requires that a barrier be overcome, the barrier consisting of the adsorbed polymer film. This phenomenon, involving charged transfer to the adsorbed film, is well known in polarography (the Loshkarev effect†) and involves the electrochemical reaction of a substance which has diffused towards the anode through the adsorbed layer which inhibits the process. In the case of phenol yet another explanation of the process under the conditions of the complete surfave coverage of the polymer film is possible: benzoquinone is formed on oxidation of the polymeric substance and phenol molecules are used to renew this polymer film.

The observed oxidation current depends to a large extent on the state of the surface of the anode, so that identical preliminary treatment of the electrode surface is necessary in order to obtain reproducible results. A positive effect of heat treatment[2] and of electrochemical treatment[1,3] on the surface has been noted. There is no unanimous view concerning the problem of the ratio of the maximum currents on the oxidised and reduced platinum surfaces.[1,7,11]

†M.A.Loshkarev and Yu.M.Loshkarev, in "Vol'tamperometriya Organicheskikh i Neorganicheskikh Soedinenii" (Voltage–Current Measurements for Organic and Inorganic Compounds), Izd.Nauka, Moscow, 1985, p.35.

With increase of pH to 9.0, the oxidation half-wave potential $E_{1/2}$ shifts towards less positive values and, on further increase of pH, remains almost constant.[2] Although the $E_{1/2}$ for irreversible processes lacks the thermodynamic significance of the half-wave potential for reversible processes, its variation nevertheless provides an idea about the range of potentials in which the electrochemical process takes place. The observed shift of the phenol oxidation potential when the pH changes by unity is ~60 mV.[3]

It has been stated that the maximum phenol oxidation current depends on the pH of the medium.[2,3,5,12] However, the published data are exceptionally contradictory. Thus an appreciable change in the maximum oxidation current at pH from 5.0 to 11.0 has not been noted by Hedenburg and Freiser,[2] or Kharlamova et al.[3] and Levina et al.[5] observed in a neutral medium a decrease of the maximum phenol oxidation current compared with the currents in acid and alkaline media, while Zeigerson and Gileadi[12] altogether failed to observe the phenol oxidation current in acid and neutral solutions. They explained[12] the lack of the current by the fact that two reactions take place on the clean electrode surface—the oxidation of phenol and the formation of a layer of adsorbed phenoxy-radicals, and, as soon as the degree of surface coverage approaches unity, the rates of both reactions fall to zero, i.e. complete passivation of the process takes place. Passivation is observed at a fully determined potential, which depends on the concentration of the substance and the pH. In this connection, we may recall that phenol may be oxidised also in the passive region (see above). Evidently the authors[12] did not note the small difference between the supporting electrolyte current and the current in the presence of phenol.

The maximum current is influenced by the rate of application of the potential ν: with its increase, the maximum current rises and the rate of increase depends on the initial phenol concentration. An increase in the rate of application of the potential hardly affects the $E_{1/2}$ for the oxidation of phenol.[1]

An increase in the solution temperature (from 20° to 60 °C) entails a rise in the maximum phenol oxidation current. The temperature coefficient in an aqueous buffer solution is 2.5 to 2.9% per degree,[1,3] which may indicate a non-diffusional nature of the maximum current.

The results examined show that, for a correct interpretation of the anodic process, it is essential to possess quantitative data for the adsorption of phenol on the electrode at different potentials.

2. Adsorption

The dependence of the degree of electrode surface coverage by phenol in 0.1 *N* H_2SO_4 solution on the potential (in the range from −0.3 to +1.0 V) has been determined by the potentiodynamic pulse method (Fig.3).[13] In an analogous solution and in the same range of potentials an extremely weak dependence of the degree of adsorption on the potential in the range from −0.1 to +0.4 V [relative to the normal hydrogen electrode (n.h.e.)] has been found, in agreement with Levina et al.[13], and is described by the Temkin isotherm.[14] According to Levina et al.[13] and Kazarinov et al.[14], the adsorption kinetics obey the Roginskii–Zel'dovich equation.

The dependence of the degree of adsorption of phenol on the potential at different pH has been determined with the aid of rapid galvanostatic pulses taking into account the surface roughness factor and the amount of adsorbed oxygen.[3] It follows from Fig.4 that the degree of adsorption of phenol

on the anode is almost independent of pH. If it is supposed that phenol is oxidised to CO_2 and H_2O, i.e. that the number of electrons involved in the reaction is $n = 28$, then the degree of adsorption per unit true surface is 4×10^{-10} mol cm^{-2}, which agrees with the data of Kazarinov et al.[14]

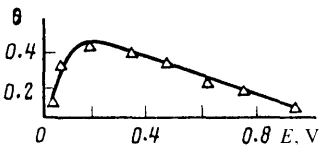


Figure 3. Dependence of the standard surface coverage of the platinum electrode θ in a 1×10^{-4} M solution of phenol on the electrode potential in 0.1 *N* H_2SO_4 solution (the potentials were measured relative to the reversible hydrogen electrode in the same solution).[13]

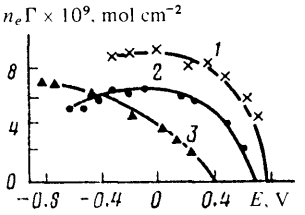


Figure 4. Dependence of the adsorption of phenol (from a 1×10^{-3} M solution) on the platinum anode on the potential at pH 1.6 (curve *1*), 7.5 (curve *2*), and 9.5 (curve *3*) taking into account the roughness factor and the amount of adsorbed oxygen (the potentials were measured relative to the 0.1 *N* calomel electrode) (n_e is the number of electrons involved in the process).[3]

Chronopotentiometric measurements in 0.1 *N* NaOH solution in the presence of 0.05, 0.1, and 0.4 M phenol[8] have shown that the amount of electricity corresponding to the transition time (i.e. the time during which a stationary current is established) falls with increase of the current and reaches a limiting value of 27.2×10^{-3} C cm^{-2} at the high polarising current density of 6×10^{-2} A cm^{-2}. In this case diffusion does not affect the transition time. During this period, the charging process takes place, the amount of charge generated exceeding by a factor of ~60 that necessary for the monolayer coverage of the platinum surface with oxygen. Hence it is concluded that the current is consumed in the formation of polymolecular phenol adsorption layers.

There exist data concerning the adsorption of a substituted phenol (*p*-nitrophenol) on the platinum anode at high anodic potentials (>1.0 V).[15] The dependence of the degree of adsorption of *p*-nitrophenol on the potential, obtained on platinised platinum in 0.1 *N* $HClO_4$ solution by the radioactive tracer method, shows that, starting from 1.3 V, the degree of adsorption rises sharply. This has been explained by the formation of a monolayer in the potential range 0.1 to 0.2 V and the fact that a polymolecular adsorbate layer is produced at $E > 1.0$ V. In determining the intensity of the UV spectra of *p*-nitrophenol and the adsorbed species, the authors[15] calculated the degree of adsorption of *p*-nitrophenol at high anodic potentials taking into account the areas of the electrodes. It was found that it corresponds to the formation of more than 10 adsorbate monolayers. However, judging from the potentiodynamic curve, the inhibition of the phenol oxidation process in acid aqueous solutions begins at a potential of ~1.0 V. For this reason, one cannot rule out the possibility that the observed multilayer adsorption refers not to phenol but to its oxidation product (see above).

Data concerning the influence of chloride ions on the adsorption of phenol are contradictory. It has been stated[16] that phenol is adsorbed more effectively than chloride ions at a concentration of the latter of 0.1 V, but the phenol concentration has not been reported. It follows from the results of an investigation[17] that in 0.1 *N* H_2SO_4 solution the adsorption of phenol (1×10^{-4} M) and the chloride ions (0.1 M) is competitive. The decrease of the degree of adsorption of phenol (1×10^{-3} M) in the presence of chlorides (0.1 M), observed by Kharlamova et al.[3], can also be accounted for by competitive adsorption. Since all the experimental data presented have been determined under different conditions, one cannot obtain a clear idea about the influence of the concentration of chloride ions on the adsorption of phenol.

III. THE GRAPHITE ELECTRODE

1. Potentiodynamic Measurements

On the graphite anode (under stationary and dynamic conditions) in the concentration range 10^{-3}–10^{-6} M, phenol gives rise to a single wave on the voltage–current curve, as on the platinum anode. The phenol oxidation current is greatly influenced by the type of impregnation mass, which, by filling the graphite pores, ensured a constant current density throughout the anode surface.[18,19] A mixture of paraffin with polyethylene is usually employed for impregnation.

The published data make it possible to establish characteristics of the influence of individual factors (the concentration of the substance, the pH of the medium, the rate of rotation of the electrode, etc.) and the appearance of a maximum on the voltage–current phenol oxidation curve. By analogy with the platinum anode, one may expect that the maximum (decrease of the current) will be shown at a specific concentration of the test substance and it does indeed follow from a series of publications[20–22] that, at $c_{pH} = 10^{-4}$ M under stationary conditions, a distinct limiting current is observed, while at $c_{ph} = 10^{-3}$ M there is a maximum. However, the opposite behaviour has also been noted:[23,24] at $c_{ph} = 10^{-4}$ M a maximum was observed, while on raising the concentration to 10^{-2} M and above there was a distinct limiting current. Kharlamova et al.[3] observed a maximum only in 0.1 *N* H_2SO_4 solution at $c_{ph} = 10^{-3}$ M, while in neutral and weakly alkaline medium a distinct limiting current was noted. The appearance of a maximum was probably due to an additional factor which had not been taken into account.

At $c_{ph} \leq 10^{-4}$ M a linear dependence of the maximum current on the phenol concentration is observed, but at $c_{ph} > 10^{-4}$ M the linearity breaks down and the limiting current increases more slowly than the concentration.[20,23,25]

The state of the graphite surface, like that of the platinum anode, influences significantly the phenol oxidation current and a preliminary treatment of the electrode surface is therefore also necessary in this instance. In almost all the

published studies the working electrode surface was treated mechanically (with emery paper, an aqueous suspension of alumina, etc.) before recording each potentiodynamic curve. The favourable influence of a two-stage electrode treatment has been noted: brief boiling in ethanol (0.5 min) followed by anodic treatment at the hydrogen evolution potential in 0.1 *N* H_2SO_4 solution for 2–3 min.[3] If the electrode is not treated again after recording one voltage–current curve, then in the repeated experiment two waves appear on the curve.[21]

The phenol oxidation current depends markedly on the pH of the medium, but, as for the platinum anode, the available data differ greatly. Thus the dependence of the maximum current on the pH was found to have a minimum in a neutral medium,[3,26] which can be explained by a decrease of the concentration of the unionised form of phenol. However, in another study[16] a maximum current was observed at pH 1.2, the current diminishing with increase of pH to 3.2, while on a further increase of the pH it remains almost unchanged. Another investigation established[3,27] that the current in an acid medium is higher than in an alkaline medium, on average by ~40%, while in the study of Korshunov et al.[28] the increment in the same pH range was found to be only ~3%.

The rate of application of the potential influences the maximum current. With increase of ν by a factor of 2 (from 0.62 to 1.24 mV s^{-1}), the current rises, according to Gaylor and co-workers,[20,21] by a factor of 1.5–1.7, which is much greater than could be expected if the current were controlled by diffusion (it would then have increased by a factor of $2^{1/2}$). In our view, this can most probably be accounted for by the diminution of the role of passivating factors with increase of ν, i.e. with decrease of the surface coverage by the polymeric substances.

An increase of temperature (from 20° to 60 °C) entails an increase of the oxidation current. The temperature coefficient in aqueous buffer solution is 0.4% according to Gaylor et al.[20], while according to other data[3,25] it amounts to 1.5–2.0% per degree.

Table 1. The influence of the pH on the half-wave potential for the oxidation of phenol ($E_{1/2}$, V) (relative to the saturated calomel electrode).

pH 1.2	pH 5.6	pH 7.0	pH 8.5	pH 9.0	Refs.
0.93	0.66	0.56	0.55	0.45	[20]
—	0.63	—	—	—	[22]
0.92	—	0.60	—	0.45	[23]
1.05	0.70	0.60	0.60	0.46	[26]

The half-wave potential decreases linearly with increasing pH until the latter reaches the p*K* of phenol, i.e. 9.89. A further increase of the pH does not induce a significant alteration of the half-wave potential.[3,25,26,29–31] Since $E_{1/2}$ for the oxidation of phenol is independent of the composition of the impregnation mass,[15] it is possible to compare its values at different pH obtained by different workers. Table 1 shows that the data agree well with one another.

An increase in the rate of application of the potential leads to a shift of $E_{1/2}$ towards positive potentials.[20]

There are data showing that $E_{1/2}$ is influenced by the phenol concentration. For example, a change in the phenol concentration by a factor of 10 results in a shift of $E_{1/2}$ by 22 mV at pH 5.2.[7,20]

2. Adsorption

The characteristics of the adsorption of phenol on the graphite anode per unit apparent surface at pH from 1.6 to 9.5 have been determined and its degree calculated.[3] Fig. 5 shows that the degree of adsorption changes only slightly as the pH is altered.

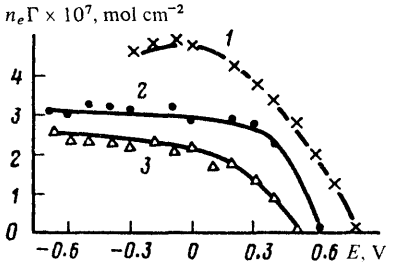


Figure 5. Dependence of the adsorption of phenol (from a 1×10^{-3} M solution) on the graphite anode on the potential at pH 1.6 (curve *1*), 7.5 (curve *2*), and 9.5 (curve *3*) (the potentials were measured relative to the 0.1 *N* calomel electrode).[3]

Comparison of the adsorption and potentiodynamic relations obtained on anodes of the same material has shown that the degree of adsorption of phenol begins to fall at the potential corresponding to the onset of its oxidation and almost ceases when the potential reaches the value corresponding to the maximum rate of oxidation. This is valid for both graphite and platinum anodes.[3]

IV. THE LEAD DIOXIDE AND GOLD ANODES

The electrochemical oxidation of phenol has also been investigated on lead dioxide[32,33] and gold[30] anodes.

On the stationary and rotating lead dioxide anodes in the presence of 0.5 M phenol in sulphuric acid solutions, a distinct anodic wave with a maximum is observed. The inhibition of the anodic process can be explained both by the blocking of the surface by the polymer film[32] and by the adsorption of oxygen.[33] It has been noted that at high positive potentials the film dissolves with the simultaneous evolution of oxygen. This phenomenon, which has not been observed on the platinum electrode (see above), can be evidence in support of the hypothesis that the mechanisms of the oxidation of phenol on platinum and lead dioxide are different.

In order to obtain reproducible results, before recording each anodic curve, the electrode surface was subjected to a preliminary treatment—anodic polarisation at $E = +0.8$ V [relative to the saturated calomel electrode (s.c.e.)] for 2–10 min.[32] The pH dependence of the oxidation current was investigated for a 0.5 M phenol solution in sulphuric acid

at different concentrations (0.5–5 M H_2SO_4).[32] A shift of the current–potential curves of ~250 mV when the pH was altered by unity was then observed. This exceeds by a factor of ~4 the analogous value for the platinum and graphite anodes, which confirms the hypothesis that the phenol oxidation mechanism is different on lead dioxide.

On the gold anode in a solution having the composition $m Na_2SO_4 + n H_2SO_4$, phenol gives rise to a distinct oxidation wave with a maximum. In the pH range 1–14, the dependence of the change in the phenol oxidation half-wave potential on the pH is identical with the dependence obtained for the graphite anode.[30]

V. THE MECHANISM OF THE ANODIC PROCESS

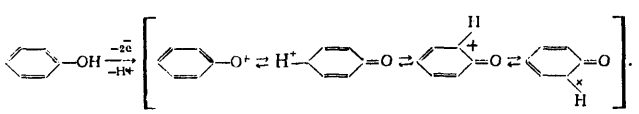
A considerable number of studies devoted to the phenol oxidation mechanism have been published. There exist two sets of views at the present time concerning the mechanism of the primary electrode reaction.[11]

The supporters of the first view believe that the initial stage involves the loss of one electron and the formation of the phenoxy-radical. Calculation based on the dependence of $\lg [I/(I_d - I)]$ on the potential, where I is the instantaneous current and I_d the diffusion current, has shown that the anodic wave corresponds to the transport of one electron.[2] This result apparently refers to a phenol concentration $\leq 1 \times 10^{-4}$ M. However, it is not clear from the above study[2] for which pH the calculation has been carried out. Other evidence in support of the hypothesis that the current is diffusion controlled, apart from the proportionality of the current to the phenol concentration, is not presented in the above publication. However, such a dependence can be observed also for first-order reactions occurring in the kinetic region.

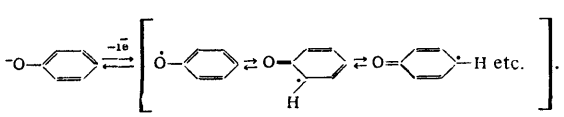
The number of electrons transferred has also been calculated[1] from potentiodynamic curves using the equation relating the electrode potential to the diffusion current. The calculation was performed for a solution with a phenol concentration of 1×10^{-4} M at pH 10.

The supporters of the second view believe that two electrons are transferred in the first oxidation stage and that an intermediate is formed.[21] On the basis of the proportionality of the current to the phenol concentration, it has been concluded that the current is diffusional. These data[21] refer solely to pH 5.2; the range of phenol concentrations employed is not indicated.

It has been shown[11] that the stoichiometry of the phenol oxidation process depends on the pH of the solution. The reaction mechanism has been studied in detail in acetonitrile solution and the results and conclusions have been tested in aqueous buffer solutions. The behaviour of phenol in solution in acetonitrile and water proved to be identical. Thus the oxidation of phenol in an alkaline medium is lower by a factor of ~2 than in an acid medium, which suggests that, in the systems where phenol exists in an unionised state, a two-electron process takes place:



If phenol is fully ionised, a one-electron transition occurs:



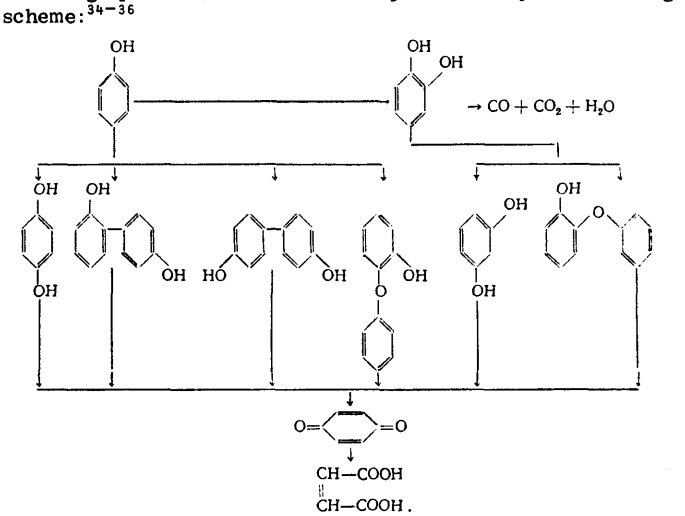
Later publications confirmed the existence of different views on the primary electrode process. In one of them it has been suggested that one hydrogen ion and one electron are involved in the electrode reaction.[26] In another communication[28] it is shown with the aid of the equation for the rotating disc electrode and potentiodynamic relations obtained on the graphite anode in buffer solutions (pH 1–12) that one electron is involved in the phenol oxidation reaction.

However, one should note that the diffusion coefficient was calculated[28] from the Stokes–Einstein equation. The quantity $n = 1$ was obtained for the phenol diffusion coefficient $D = 0.23 \times 10^{-5}$ cm^2 s^{-1}. Since the approximate character of the Stokes–Einstein equation is well known, the value of n calculated in the above study[28] must be treated with caution. Other factors giving rise to doubts about the validity of the calculations in the above investigation should also be noted. Firstly, it is known that the calculations of n and D from the equation for the rotating disc electrode can be performed only in the diffusion region. Furthermore, the above measurements[28] were performed at a single rate of rotation of the disc electrode, which makes it impossible to check in which region the study had been carried out. The conclusion that the measured current is determined by the rate of diffusion was reached solely on the basis of the satisfactory reproducibility of the product $i \cdot \tau^{1/2}$ obtained from chronopotentiometric data for the stationary electrode. Secondly, it has been shown[3] that the electrochemical oxidation of phenol at a concentration of 1×10^{-3} M in acid solutions is partly limited by diffusion, while in an alkaline solution the current is determined by the process kinetics alone. Naturally, in both cases the rotating disc electrode equation is unsuitable for the calculation of n.

The authors[28] were able to observe directly the EPR spectra characteristic of the phenoxy-radicals formed in the first phenol oxidation stage in acid, alkaline, and neutral media.

The mechanism proposed by Gaylor et al.[21] involves the transfer of one electron and one proton in the potential-determining stage and the formation of the PhO$^\bullet$ radical. On the other hand, other investigators[7,8,29] confirmed the dependence of the stoichiometry of the oxidation reaction on the pH of the solution observed by Vermillion and Pearl.[11]

It has been shown[34–36] that the first phenol oxidation stage is followed by the formation of unstable products, which enter into subsequent chemical reactions. The nature of these intermediates has not been discussed, but it can be inferred by analysing the final electrolysis products. It has been established that the electrochemical oxidation of phenol is a multistage process, which can be represented by the following scheme:[34–36]



The formation of hydroquinone and *pp'*-biphenol has been demonstrated by cyclic voltage–current measurements in 25% acetone solution in a Britton–Robinson buffer at a rate of application of the potential of 8.33 V min^{-1}.[35] In the oxidation of phenol in 0.05 M HCl solution (at pH 1.3, $\nu = 0.1$ V s^{-1}, $c_{ph} = 1 \times 10^{-3}$ M) the formation of five reaction products was observed by the same method: *op*- and *pp'*-biphenols, hydroquinone, catechol, and hydroxyhydroquinone.[29] It was shown that all the products are formed as a result of the dimerisation of phenoxy-radicals obtained in the primary one-electron step.

The following mechanism of the total oxidation of phenol on the platinum anode in acid and alkaline media has been proposed:[6,8]

In an alkaline medium	In an acid medium
$PhOH + OH^- \rightleftarrows PhO^- + H_2O$	$PhOH \rightleftarrows PhO^{\cdot} + H^+ + \bar{e}$
$PhO^- \rightarrow PhO^{\cdot} + \bar{e}$	$PhO^{\cdot} + PhOH \rightarrow P_1^{\cdot} + H^+ + \bar{e}$
$PhO^{\cdot} + PhO^- \rightarrow IP + \bar{e}$	$P_1^{\cdot} + PhOH \rightarrow P_2$
$IP \rightarrow$ products $+ n\bar{e}$	$PhO^{\cdot} + PtOH + H^+ \rightarrow$ hydroquinone
	hydroquinone $\rightarrow$ benzoquinone $+ 2H + 2\bar{e}$

Here P_1 and P_2 are dimers and trimers respectively and IP are intermediate products.

Determinations of the total number of electrons participating in the extensive oxidation of phenol under different conditions have been carried out in a series of studies. The study of the adsorption of phenol on the platinum anode (see Section II) at potentials below that corresponding to the onset of oxidation has shown[13] that phenol hinders the adsorption of oxygen when an anodic pulse is applied and the adsorption of hydrogen when a cathodic pulse is applied. From these data and also taking into account the fact that phenol gives rise to a distinct oxidation wave at positive potentials, the authors postulated the presence on the electrode surface of chemisorbed species of one type whose oxidation requires 4 ± 0.5 electrons. This number of electrons is determined by the fact that phenol is oxidised to CO_2 and in this case 4.6 electrons correspond to each adsorption centre. Since the adsorption of phenol is accompanied neither by dehydrogenation nor electron transfer, the authors suggested that it occurs as a result of the dissociation of the double bonds in the benzene ring and the formation of six Pt–C bonds. In this case the plane of the aromatic ring should apparently be arranged parallel to the electrode surface. At the same time, Izumi et al.[8] and Bjerano et al.[37], who support the radical mechanism, suggest that the phenoxy-radical is adsorbed via the oxygen atom, so that the plane of the aromatic ring is more likely to be arranged at an angle with respect to the surface than parallel to it.

It has been suggested that the total number of electrons participating in the oxidation of one phenol molecule varies as a function of the rate of application of the potential from 3 (for $\nu < 1$ V s^{-1}) to 1.5 (for $\nu > 5$ V s^{-1}).[25] It has been found,[25] by means of calculation with the aid of the theoretical equation for the limiting diffusion current, that $n = 3$. The phenol concentration was then 10^{-6}–10^{-7} M and the dependence of the limiting current on the phenol concentration was linear at a flow rate of the solution relative to the electrode of 1×10^{-4} litre s^{-1}.

The influence of the rate of rotation of the electrode (or of the flow rate of the solution) on the maximum phenol oxidation current have been investigated in a number of studies and it has been shown that in an alkaline medium an increase of the rate of rotation of the platinum wire to 1000 rev^{-1} entails a steady increase of the maximum current.[1] However, it is known that the most reliable principal kinetic characteristics can be obtained with the aid of the rotating disc electrode. For this reason, a detailed study has been made[3] of the influence of the rate of rotation of the electrode on the phenol oxidation current on platinum and graphite disc anodes at different pH of the solution. The graphical method was used to calculate the order of the reaction.[38] Using the true kinetic current and the dependence of the oxidation current on the rate of rotation of the electrode, the authors[3] found that in acid and neutral media the oxidation of phenol (at $c_{ph} = 1 \times 10^{-3}$ M) formally obeys a first-order equation. In an alkaline medium (saturated borate buffer solution, pH 9.5) the maximum phenol oxidation current remains constant when the rate of rotation of the platinum anode is raised from 160 to 4000 rev min^{-1}, which formally indicates a zero reaction order. The authors attribute this factor[3] to the formation of a strongly adsorbed polymer film on the electrode.

A dependence of the reaction order P on the initial phenol concentration in the solution has been observed.[8] The values of $P = (\partial \lg i / \partial \lg c_{ph})_e$ were found experimentally at different concentrations in aqueous alkaline solutions (1 *N* NaOH solution) of phenol. It was shown that the order of the reaction is two at $c_{ph} = 0.1$–0.5 M, while at lower concentrations it approaches unity, which is inconsistent with the data of Kharlamova et al.[3]

High reaction orders have been obtained by Levina et al.[5] Calculation of the order of the reaction on a smooth platinum electrode by the equation $i = kc_{ph}^P$, where $P = 2.8$–3.0 showed that P is almost independent of the potential. The authors[5] attribute the anomalously high reaction orders to the anomalous adsorption properties of phenol at fairly high concentrations in solution (from 0.4 to 2 M). Furthermore, it has been noted that, in contrast to the isotherms obtained at potentials such that the oxidation of phenol does not yet occur, the adsorption isotherms in the range of oxidation potentials have a complex character. The degree of surface coverage initially increases slowly with increase of the phenol concentration, in conformity with the Temkin isotherm. However, after the attainment of the critical phenol concentration (~0.4 M), the surface is rapidly filled by chemisorbed species and the slope of the isotherm changes sharply. It has been suggested that this effect is caused by the surface condensation or heterogeneous polymerisation of phenol molecules.

From our point of view, this explanation conflicts with the known electrochemical properties of phenol. In particular, in the range of concentrations employed by Levina et al.[5], polymer layers on the anode surface can be observed even visually. For this reason, the isotherm apparently actually corresponds to the adsorption of not phenol molecules or their fragments but of the polymeric product. The break point then corresponds to the concentration at which polymerisation is particularly vigorous.

The discrepancies between the calculated reaction orders are probably associated with the fact that the authors measured not the true phenol oxidation current but the current distorted by the adsorption of the incomplete oxidation product. For this reason, the reaction orders indicated above are more likely to be purely formal quantities and therefore do not necessarily reflect the real process mechanism.

The maximum phenol oxidation current on the graphite anode in a buffer solution at pH 4.0 and $c_{ph} = 5 \times 10^{-7}$ M is proportional to the rate of movement of the solution u raised to the power 3/4 [$u = (2.1$–$10.5) \times 10^{-5}$ litre s^{-1}].[39] With increase of phenol concentration, a deviation from this relation is observed, which can also be accounted for by the coverage of the surface of the anode by the reaction product.

Levina et al.[5] examined the question of the possible slow stage in the phenol oxidation process. Direct measurement of the rate of adsorption of phenol showed that it exceeds greatly the rate of the electrochemical oxidation and hence cannot be the slow stage.

As shown above (Section II), the half-wave potential for the oxidation of phenol shifts towards more negative values by ~60 mV per pH unit as the pH increases to 9.0. This suggests that the slow stage in the oxidation of phenol in 0.1 *N* H_2SO_4 solution on platinum is the interaction of OH^-_{ads} with the chemisorbed organic species.[5]

The mechanism of the oxidation of phenol on the lead dioxide anode is different from that on platinum and graphite. It has been noted that the phenol oxidation potential is close to the lead dioxide formation potential in these solutions.[32] This observation served as a basis for a new phenol oxidation mechanism on the lead dioxide electrode, according to which the potential-determining stage is the chemical oxidation of phenol by lead dioxide. The latter is regenerated in the electrochemical process, which requires the transfer of four electrons.[33]

VI. THE INFLUENCE OF SUBSTITUENTS ON THE ELECTROCHEMICAL ACTIVITY

We shall consider the influence of the OH, CH_3, NO_2, NH_2, Cl, C_6H_4, COOH, C_2H_5, and $C(CH_3)_3$ groups substituting hydrogen atoms in the benzene ring on the principal voltage–current characteristics of the oxidation of phenol.

1. The Platinum Anode

The influence of the hydroxy-group in the *m*-, *o*-, and *p*-positions in the benzene ring of phenol on the oxidation current in acid and alkaline aqueous media has been investigated[12] and, as noted previously (Section II), appreciable oxidation of phenol in an acid medium (1 M $HClO_4$ solution) was not observed in this investigation. Resorcinol (1,3-dihydroxybenzene) behaves analogously. However, the introduction of the hydroxy-group in the *o*- and *p*-positions renders the corresponding phenols (catechol and hydroquinone) readily oxidisable. The reversible oxidation of hydroquinone, which proceeds at an extremely high rate, is well known.[40] Catechol is apparently also oxidised reversibly. In an alkaline medium (1 M KOH solution), all three substituted phenols are oxidised, giving rise to maxima on the voltage–current relation. The maximum oxidation currents diminish in the sequence hydroquinone > catechol > resorcinol.

As stated above (see Section II), the appearance of a maximum on the voltage–current curve depends not only on the initial concentration of the corresponding phenol but also on the pH of the medium. This is illustrated by the oxidation of hydroquinone in a strongly acid medium (1 M $HClO_4$):[12] the anodic wave with a maximum appears only at a phenol concentration ≥0.2 M and, when the pH is raised to 3.0, the above concentration falls to 0.1 M. It is also noteworthy that the electrochemical oxidation of resorcinol on the anode surface results in the formation of an insoluble polymeric product, as in the case of phenol.[12]

The maximum resorcinol oxidation current increases with increasing pH, but to a much lesser extent than in the oxidation of phenol. When the pH is raised from 12.0 to 13.7, the increase in the maximum resorcinol oxidation current is ~100 times smaller than for phenol.[12]

The introduction of two hydroxy-groups into the phenol molecule in the 2,3- and 2,4-positions permits the oxidation of the resulting compounds in an acid medium and the maximum 2,4-trihydroxybenzene oxidation current is lower by ~30% than for the 2,3-analogue. In contrast to these compounds, 3,5-dihydroxybenzene is not appreciably oxidised in an acid medium, like the initial phenol. However, it is readily oxidised in an alkaline medium and the maximum current for this process is lower than in the oxidation of phenol by ~70%.[12] The substituent $C(CH_3)_3$ reduces somewhat the maximum substituted phenol oxidation current, the decrease of the current being observed in the following sequence as the position of the substituent is altered: *meta* > *ortho* > *para*.[2] It is believed[2] that, when the concentration of the corresponding phenol is 1×10^{-5} M, the current is limited by diffusion, which does not conflict with the experimentally observed independence of the current of the pH. However, a curve with a maximum, typical for diffusion currents at a stationary electrode, was not obtained.[2]

2. The Graphite Anode

Judging from the published data, all substituted phenols, which will be considered below, are oxidised at the anode and give rise to a single wave on the voltage–current curve. 2,6-t-Butylphenol and 6-t-butyl-2,4-dimethylphenol, which give rise to multiwave curves, are exceptions. The appearance of a maximum on the anodic curves for substituted phenols has been related[22] to $E_{1/2}$: if this potential is less than 0.48 V, a maximum may appear. The character of the current was not considered in the above investigation. However, it follows from the analysis of the literature data that a maximum is observed[23,26,27] on the potentiodynamic curves for the oxidation of many substituted phenols having $E_{1/2}$ < 0.48 V (relative to the s.c.e.) at a pH other than in the study discussed above.[22]

The influence of substituents in the *m*-, *o*-, and *p*-positions on the oxidation current of phenols on the graphite anode in an aqueous medium has been examined in a number of studies[20,21,23,26,27,41] and it has been shown that resorcinol, catechol, and hydroquinone are readily oxidised over a wide pH range (1–9). At a catechol concentration of 1×10^{-3} M, a distinct limiting current is observed on the potentiodynamic curve but, with increase of concentration to 1.5×10^{-3} M, a maximum appears.[41]

The data concerning the appearance of a maximum on the voltage–current relations for resorcinol and hydroquinone are contradictory. Results showing the presence of a distinct limiting resorcinol oxidation current at a resorcinol concentration of 1×10^{-4} M [21] and the appearance of a maximum at a concentration of 4×10^{-4} M [26] are available. On the other hand, the presence of a distinct limiting current at a resorcinol concentration of 1×10^{-3} M has been reported.[41] Similar contradictions exist also for hydroquinone. Under identical conditions, and at equal hydroquinone concentrations [$(1.5–0.3) \times 10^{-3}$ M] a maximum has been observed in some studies[20,27,41], while in another[26] it was absent either owing to poor adsorbability or the dissolution of the oxidation product.

Table 2 shows the maximum oxidation current densities for substituted phenols and the initial phenol indicated in different sources differ appreciably from one another.

In the pH range 4–8 the maximum hydroquinone oxidation current hardly changes. The dependence of the resorcinol oxidation current on the pH has been investigated in only

one study[22] and for this reason it is impossible to compare these data with other results.

In a number of investigations[20,21,23] the authors assumed without proof that the oxidation currents of aromatic dihydro-compounds ($c \leq 2.5 \times 10^{-4}$ M) are diffusional in nature. The fact that an increase of the rate of polymerisation increases the maximum current[20] cannot be regarded as unambiguous proof of the diffusional nature of the current, since this can be associated with a decrease of the adsorption of the reaction product. The oxidation currents of catechol and resorcinol in a weakly acid medium are higher approximately by a factor of 2 than the corresponding phenol current.[21] Hence, it was concluded that their oxidation requires twice as many electrons as the oxidation of phenol. However, when the solution is made alkaline up to pH 8.5, the maximum phenol, hydroquinone, resorcinol, and catechol oxidation currents become virtually identical (to within ±3%),[23] which may indicate the same process mechanism.

Table 2. The influence of the hydroxy-group on the maximum density of the oxidation currents of phenols (pH 5.0).

Compound	$10^3 i_{max}$, A cm^{-2}mol^{-1}	Conditions	v, mV s^{-1}	Refs.
Phenol	65	st.*	—	[20]
»	114	dyn.**	1.24	[21]
Hydroquinone	89	st.	—	[20]
»	114	dyn.	1.24	[21]
»	75	st.	8.3	[27]
»	81	st.	3.3	[30]
Resorcinol	207	dyn.	1.24	[21]
»	100	st.	8.3	[27]
»	64	st.	3.3	[30]
Catechol	168	dyn.	1.24	[21]
»	79	st.	8.3	[27]
»	58	st.	3.3	[30]

*Stationary conditions.
**Dynamic conditions.

An approximate calculation of the number of electrons participating in the primary hydroquinone oxidation electrode process has been carried out[20] from the corresponding potentiodynamic curves from the formula $E_{3/4} - E_{1/2} = 0.55n$. It has been noted that the rate of application of the potential influences n; for example, an increase of v by a factor of 2 induces a decrease of n by unity.

The behaviour of trihydroxybenzenes will be examined in relation to pyrogallol. At a concentration of this compound of 2.5×10^{-4} M in a neutral medium, an oxidation wave with a distinct maximum is observed: the maximum current is lower by ~30% than in the case of phenol.[23]

Several studies have been devoted to the influence exerted by the introduction of one methyl group in the *o*-, *m*-, and *p*-positions in the benzene ring of phenol on the oxidation current.[21-23,26] In aqueous buffer solutions at concentrations of cresols of 2.5×10^{-4} M and at pH from 4 to 11, an oxidation wave with a maximum has been observed. Table 3 presents the maximum oxidation currents for the above compounds. Evidently the data from different sources differ markedly.

A fairly complete idea about the dependence of the maximum oxidation currents of *o*- and *p*-cresols on pH can be obtained from Fig. 6 (curves *1* and *2*).[26]

The dimethyl derivatives, namely 2,4-, 2,6-, and 3,4-dimethylphenols, are readily oxidised and distinct anodic waves with maxima are observed.[22,26] The introduction of two methyl groups diminishes the maximum oxidation current compared with phenol on average by 20–30%.[22,26] 3,5-Dimethylphenol, whose oxidation wave has no maximum and the height of the wave does not greatly exceed (by ~5%) the phenol oxidation current, is an exception.[26] The dependence of the maximum oxidation current for 2,6-dimethylphenol on the pH is illustrated in Figure 6 (curve 3).[26]

Table 3. The influence of the position of the CH_3 substituent on the maximum density of the oxidation currents of phenols (pH 5.6).

Compound	Conditions*	$10^6 i_{max}$, A cm^{-2}	Refs.	Compound	Conditions*	$10^6 i_{max}$, A cm^{-2}	Refs.
Phenol	st.	19.0	[21]	*o*-Cresol	st.	10.7	[22]
»	st.	11.6	[22]	»	st.	38.0	[23]
»	st.	45.8	[23]	»	dyn.	16.0	[26]
»	dyn.	14.0	[26]	*p*-Cresol	st.	9.8	[21]
m-Cresol	st.	13.6	[22]	»	st.	9.6	[22]
»	st.	37.0	[23]	»	st.	32.4	[23]
o-Cresol	st.	14.0	[21]	»	dyn.	9.0	[26]

*For the significance of the abbreviations, see the references to Table 2.

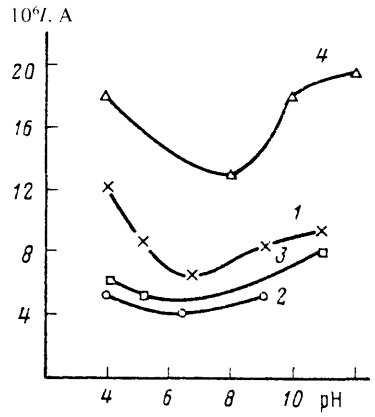


Figure 6. Dependence of the maximum oxidation currents for 4×10^{-4} M solutions of *o*-cresol (curve *1*), *p*-cresol (curve *2*), 2,6-dimethylphenol (curve *3*), and 2,4,6-trimethylphenol (curve *4*) on the pH.[26]

The behaviour of phenol after the introduction of three methyl groups into the benzene ring has been investigated in relation to 2,4,6-trimethylphenol. The absence of a maximum on its oxidation wave in phosphate (pH 7.0), acetate (pH 4.6), and aqueous alcoholic buffer solutions have been noted. The 2,4,6-trimethylphenol oxidation current in the pH range 4–12 exceeds by a factor of almost 2 the maximum phenol oxidation current (Fig. 6, curve *4*).[26]

The introduction of one nitro-group into the benzene ring of phenol reduces the maximum phenol oxidation current at pH 8.5.[23,26] However, the data for the extent of this decrease are extremely contradictory. According to some data,[27] the decrease is on average ~90% at pH 8.5, while according to others[23] it is only ~13%. Similar differences in data persist also at other pH values. For example, it has been stated[22] that the maximum *p*-nitrophenol oxidation current at pH 5.6 is greater than that of phenol, while in another study[26] the opposite relation was observed at the same pH.

The oxidation of *m*- and *o*-aminophenols has been observed to generate a one-electron wave with a maximum, while the oxidation of *p*-aminophenol gives rise to a two-electron wave with a maximum.[23,27,31] The introduction of the amino-group into the *m*-position increases the oxidation current on average by 6%, while the *ortho*-substituent reduces the oxidation current by ~19%.[23]

The question of the mechanism of the electrochemical oxidation of aminophenol has been examined.[31] The character of the dependence of $E_{1/2}$ on pH and the analysis of the maximum current and the parameters $E_{1/2}/\Delta$pH and $\Delta E/\Delta . \lg [i/(i_{\lim} - i)]$ justified the hypothesis that the observed oxidation waves on the graphite anode characterise the oxidation of the phenolic OH group, while the NH_2 group plays the role of an electrochemically inert substituent.

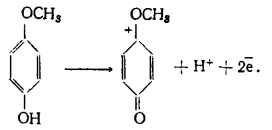
According to the data of Vodzinskii and Semchikova,[23] there is an oxidation wave with a maximum (pH 5.6) on the potentiodynamic curves for the oxidation of monochlorophenol, while other data[22] indicate waves without a maximum (pH 8.5). The difference is probably associated with the difference in the pH of the solution. At pH 5.6 the maximum oxidation currents of *p*- and *o*-chlorophenols are smaller than that of the initial phenol approximately by 15 and 13% respectively, while for *m*-chlorophenol it is greater by ~4%.[22] At pH 8.5 the *p*-chlorophenol oxidation current is lower by ~2% than that of phenol.[23]

A single oxidation wave without a maximum is observed on the potentiodynamic curve for the oxidation of 2,5-dichlorophenol at pH 5.6 and a concentration of 2.5×10^{-4} M, while the maximum oxidation current is lower by approximately 30% compared with phenol.[22]

The maximum oxidation currents for *p*- and *o*-phenylphenols oscillate markedly as the pH is altered: in borate buffer solution (pH 8.5), the current is higher by 6–8%, while in a weakly acid medium (pH 5.6) it is lower by 30–34% than for unsubstituted phenol.[22] The introduction of two phenyl substituents in the 2- and 4-positions lowers the maximum phenol oxidation current by ~31% (pH 5.6).[22]

Phenol with the COOH group in the *o*-position (salicylic acid) has a maximum oxidation current in an alkaline medium (pH 8.5), which is lower by ~31% than that of unsubstituted phenol, while in a weakly acid medium their maximum currents are virtually identical.[22,23] At pH 5.6 *o*- and *p*-ethylphenols have maximum oxidation currents lower by 20–24% than that of unsubstituted phenol, while the maximum oxidation current of *m*-ethylphenol is lower by only ~1.2%.[20,22]

All the monosubstituted methoxyphenols have oxidation currents in a weakly acid medium higher by 8% on average than the maximum oxidation current of the initial phenol.[22] The electrochemical behaviour of *o*-methoxyphenol has been investigated in an acid medium (0.1 M $HClO_4$ solution).[42] Two successive pairs of waves corresponding to the oxidation intermediates 3,3′-dimethoxydiphenoquinone and 3,3′-dimethoxy-4,4′-biphenol, *o*-quinone, and catechol have been observed on the cyclic voltage–current plot. The voltage–current plot for *p*-methoxyphenol (1.13×10^{-3} M) in 2.037 M H_2SO_4 solution shows an oxidation wave with a maximum, which corresponds to a two-electron process:[43]



The introduction of two OCH_3 groups in the 2- and 6-positions in the benzene ring leads to a decrease (at pH 5.6) of the maximum current (by 27%). If the OCH_3 group is introduced in the 2-position in *p*-cresol, the oxidation current increases by ~10%.[22] The influence of the ethoxy-substituents on the oxidation currents of the corresponding phenols was also investigated in the above study;[22] it was found that the *o*-substituent increases the maximum oxidation current of the substituted phenol by ~7%, while the *p*- and *m*-substituents respectively reduce the current by ~2% (this is within the limits of the accuracy of the measurement) and ~19%.

A distinct anodic wave has been observed in the electrochemical oxidation of *p*- and *o*-t-butylphenols in the pH range 5.6–8.5 at a low concentration (~10^{-4} M). The rates of oxidation of these compounds are lower than that of phenol by ~35 and ~55% respectively.[22,23]

The introduction of two and more $C(CH_3)_3$ groups into phenol leads to the appearance on the voltage–current curve of a maximum in aqueous buffer solutions, an example of such behaviour being provided by the oxidation of 2,6-di- and 2,4,6-tri-t-butylphenols.[23] The oxidation current falls in this case (by ~60%). However, it has been reported that 2,4,6-tri-t-butylphenol gives rise to an anodic curve with a distinct limiting current, which is independent of the pH,[44] in conflict with the data of Vodzinskii and Semchikova.[23]

The oxidation of 2,4,6-tri-t-butylphenol at a concentration of 1.11×10^{-3} M in an aqueous ethanol solution (at pH ranging from 0 to 10) at a vitreous carbon anode has been investigated by the cyclic voltamperometric method.[45] A wave with a maximum was observed in an acid medium, while in an alkaline medium two waves with maxima were noted.

After the additional introduction of the t-butyl group into the benzene ring of *o*- and *p*-cresols, the maximum oxidation current in aqueous buffer solutions falls by a factor of ~2.[22]

The appearance of three waves at once without maxima in the oxidation of 6-t-butyl-2,4-dimethylphenol at a concentration of 1×10^{-3} M in an aqueous buffer solution at pH 5.6 has been reported.[20] When the supporting electrolyte is acidified (to pH 1.2), the second wave disappears, while an increase in the alkalinity of the solution (to pH 10) leads to the disappearance also of the third wave. Following an increase of the rate of application of the potential by a factor of 2 (from 0.62 to 1.24 mV s^{-1}), the limiting oxidation current at pH 10 increases by 40–50%, as for unsubstituted phenol. When the temperature is raised by one degree in the range from 20° to 30 °C (at pH 5.6), the maximum currents on all three observed waves increase by 0.8, 2.7, and 5.2%. The temperature coefficients of the maximum currents on the first two waves correspond to the possibility of diffusional control of the oxidation process.

VII. PRACTICAL APPLICATIONS OF THE ELECTROCHEMICAL OXIDATION OF PHENOL AND ITS DERIVATIVES

As shown above, the anodic oxidation of phenol proceeds fairly readily. An important practical application of this process in the purification of phenol-containing waste water arose in this connection. In the solution of this problem, the advantages of the electrochemical method such as efficiency,

reliability, low cost, and also the compactness of the electrolysers and the ease of automating the process have been noted.[47,48] Preliminary calculations have shown that, in the successful solution of this problem, the cost of the removal of phenol from 1 m^3 of water by electrochemical oxidation is lower by a factor of ~2 than the cost of the purification of water by ozonization and by a factor of ~5 than the cost of purification by adsorption on activated charcoal.[49] The above advantages of the electrochemical method have attracted the attention of many investigators, as shown by the numerous publications in this field.

The main bulk of studies have been carried out with graphite anodes. According to a review,[50] most of the studies on the electrochemical purification of waste water containing phenol have been devoted to the study of the oxidation of phenol in solutions containing chloride ions. The optimum oxidation conditions are as follows: alkaline medium (pH 9–11), $i = (4–8) \times 10^{-2}$ A cm^{-2}, and $c_{Cl} \cong 10\%$ for an initial phenol content in the waste water not exceeding 0.5 g $litre^{-1}$. The consumption of electrical energy on the oxidation of 1 g phenol using the electrochemically generated hypochlorite of the corresponding metal is 0.03–0.09 kWh.

The design of the electrolyser is important for the effective electrochemical oxidation of phenol. Electrolysers of the box or filter press types without a diaphragm are normally employed. The latter are preferable, since they make it possible to increase the electrode surface area to the maximum extent in a given volume by reducing the interelectrode gap and the dead space.

A report has been published[51] on the purification of factory waste water containing 2.5 g $litre^{-1}$ of phenol, 201 g $litre^{-1}$ of sodium chloride, and 4.6 g $litre^{-1}$ of sodium hydroxide on apparatus consisting of six BGK-12 baths connected in series. However, according to Sakharnov,[49] the purification was not carried out under optimum conditions.

There are also data indicating the employment of electrolysers with a powdered anode, made up of carbon-graphite materials, for the electrochemical purification of phenol-containing water.[52] The waste water was passed through the pre-polarised powdered anode, which made it possible to prevent the blocking of the pores by phenol and the oxidation products.

Industrial waste water contains as a rule several compounds of organic and inorganic origin; for this reason, an individual approach to the purification of each waste is necessary. Furthermore, the purification conditions developed on artificial solutions are not always suitable for the purification of real waste water. A comparison has been made[53] of the rates of oxidation of phenol in an artificially prepared solution and in industrial tar water. It was shown that the rate of oxidation of phenol in the tar water is close to the rate of its oxidation in the artificial solution, but, when identical amounts of chloride ions are added to the two solutions, the rate of oxidation of phenol in the industrial water increases more slowly than in the artificial solution.

We shall consider examples of the purification of industrial phenol containing waste water in electrolysers with insoluble anodes. In a study[54] of the electrolysis of the waste from the chemical coke industry, the simultaneous removal of oil (to the extent of 96%) by electroflotation and of phenol (to the extent of 30–40%) and cyanides (to the extent of 100%) by electrochemical oxidation was observed. The water was treated on a laboratory electrolyser with a horizontal cathode under which vertically arranged graphite anodes were placed. The electrolyser operating conditions were as follows: $i = 0.01$ A cm^{-2}, $\tau = 40$ min, and $t = 60–70$ °C. According to preliminary calculations, the cost of the purification of 1 m^3 of the waste water was 10–12 kopecks.[54] The low degree of removal of phenol from water, probably as a result of constructional deficiencies of the electrolyser, is noteworthy.

In the waste water from the Kherson petroleum processing works, it has been possible to reduce simultaneously by electrolysis the concentration of petroleum hydrocarbons from 0.29 to 0.016 g $litre^{-1}$, of phenols from 2×10^{-3} to 6.5×10^{-4} g $litre^{-1}$, of surfactants from 1.8×10^{-2} to 6.1×10^{-3} g $litre^{-1}$, and of inorganic substances from 5.5 to 3.8 g $litre^{-1}$.[55] The experiments were performed in a laboratory electrolyser with a vertical graphite anode and a zinc cathode under static conditions: $i = 8.5 \times 10^{-2}$ A cm^{-2}, $\tau = 40$ min, and $t = 40$ °C. The salt composition of the purified waste in the area of the anode and its design were not indicated in the relevant study,[55] but, judging from the figure quoted, the anode consisted of a rod placed in a spherical flask at a comparatively large distance from the analogous rod cathode. In our view, such design of the electrolyser is unsuitable for the practical electrochemical purification of waste water.

The purification of tar waters in an electrolyser with a cylindrical graphite anode has been reported;[53] at $i = 0.2$ A cm^{-2}, $c_{Cl} = 40$ g $litre^{-1}$, and $t = 60$ °C, the phenol concentration was reduced from 5.2 to 0.75 g $litre^{-1}$, i.e. by 85%, after the operation of the electrolyser for 1 h. However, at such high phenol concentrations it is more useful to employ the regenerative purification procedures.

The electrochemical oxidation of phenols, cyanide, and thiocyanates in the waste water from the enrichment works of the Zyryanovsk Lead–Zinc Combine has been investigated.[56] The experiments were performed in an electrolytic bath without a diaphragm containing graphitised carbon anodes. Before electrolysis, sodium chloride was introduced into the water to be purified; the purification was carried out at $i = 0.35 \times 10^{-2}–0.80 \times 10^{-2}$ A cm^{-2} and 20 °C. The waste water investigated[56] was characterised by a very low initial concentration of phenols, which diminished by only about 30% during the purification process.

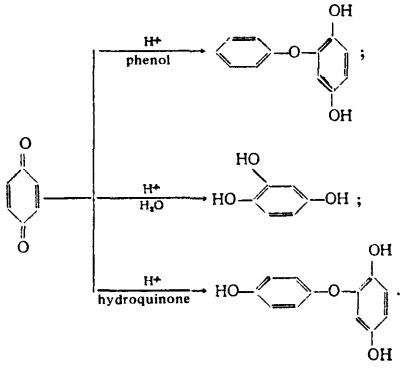
It has been suggested[53] that waste water containing phenols, thiosulphates, thiocyanates, and chlorides be purified by being passed downwards from above through a vertical cylindrical electrolyser with a platinum plate anode and an iron grid cathode. The electrolysis was carried out at $i = 0.8–0.12$ A cm^{-2} and the duration of the treatment ranged from 5 to 8 h. Under these conditions, the biological consumption of oxygen (BCO) in the waste water was reduced by 95%. However, the necessity to employ platinum as the anode material makes the process significantly more expensive.

The detoxication of the waste water from the coke chemical works by electrolysis at $i = 0.7–1.0$ A cm^{-2} has been investigated;[56] after electrical treatment for 5 h, the phenol concentration fell from 1.25 g $litre^{-1}$ (1.3×10^{-2} M) to 0.07 g $litre^{-1}$ (7.4×10^{-4} M). The consumption of electrical energy was 165 kWh m^{-3}. It is noteworthy that the process was performed at pH < 7.0, i.e. the conditions were not optimal for the oxidation of phenol by a hypochlorite.

An electrochemical method for the degradation of phenol by electrolysis at anodes with an active magnetite coating has been described.[57] Waste water containing 0.5 g $litre^{-1}$ of phenol and exhibiting a chemical consumption of oxygen (CCO) of 0.229 g $litre^{-1}$ was electrolysed at pH 7 and $i = 1.5 \times 10^{-2}–3.0 \times 10^{-2}$ A cm^{-2}. After electrical treatment for 2–5 min, the degree of elimination of phenols reached 95% and that with respect to the CCO was 77.8%; the consumption of electrical energy was 37 kWh m^{-3}. It is noteworthy that the use of the magnetite anode is technologically disadvantageous—it is brittle and has a relatively high electrical resistance.

In view of the requirement for large amounts of hydroquinone and alkylhydroquinones, especially in the photo- and cine-industry, the method of their synthesis by oxidising the corresponding phenols is of great practical interest. Such attempts have already been made for a long time,[58-62] but the required substance was obtained in a low yield and was impure. The oxidation process and the composition of the reaction products depend to a large extent on the phenol concentration, the electrolyte temperature, the pH of the solution, and other parameters. Depending on the electrolysis conditions, many compounds are formed, some of which may prove useful.

Under ideal conditions, quinone is formed on the anode and, after reduction at the cathode, is fully converted into hydroquinone. In reality ring-opening products (oxalic and maleic acids) as well as compounds obtained as a result of the total degradation of phenol (carbon dioxide and monoxide) are formed together with the required substance. Tarry substances are also formed in a considerable amount, apparently as a result of secondary reactions,[63,64] which may involve the interaction of *p*-benzoquinone with phenol. In the presence of hydrogen ions, this leads to the formation of phenoxyhydroquinone; under analogous conditions, the interaction of *p*-benzoquinone with hydroquinone affords hydroxyphenoxyhydroquinone. The interaction of *p*-benzoquinone with water in an acid medium leads to the formation of hydroxyhydroquinone:



The above side reactions not only reduce the current and material yield of phenol but also hinder the isolation and purification of the required substance.

An appreciable reduction of the amount of side products formed can be achieved by carrying out the electrolysis of aqueous sulphuric acid solutions (acid concentration 1 to 5 wt.%) in a diaphragm electrolyser with added phenol at a concentration of 0.5–4.0 wt.%.[64,65] During electrolysis, the pH was maintained at <4.0, the anodic potential was 0.9 V (relative to the s.c.e.), the cathodic potential was <−0.4 V, i = 0.2–0.4 A cm^{-2}, and t = 50–60 °C. Under these conditions, the material yield of hydroquinone was ~50% and the current yield was ~85%.[64] An apparatus which makes it possible to isolate fairly pure *p*-benzoquinone from the reaction mixture has also been described in detail. If conditions optimal for the preparation of *p*-benzoquinone are used, the material yield of alkylquinones is only 20%.

It has been shown[66] that, in acetonitrile solutions, dimethylphenol is oxidised to dimethylquinone. However the attempts to reduce this substance to the corresponding hydroquinone were unsuccessful. Alkylhydroquinones having the general formula $C_6H_{(6-x)}R_xO_2$ (where R is an alkyl group containing up to four carbon atoms and x ranges from 1 to 3) can be obtained in satisfactory yields by oxidising the corresponding phenols.[66]

The electrochemical oxidation of 2-methyl-, 2,6-dimethyl-, 2,3,6-trimethyl-, and 2,3,5-trimethyl-phenols has been carried out[66] in an electrolyser with a cation-exchange diaphragm. The anode was made from lead dioxide and the anolyte employed consisted of a 1:1 water–acetone mixture containing 0.5 M sulphuric acid; the cathode was made of lead, the catholyte consisted of a 0.5 M aqueous sulphuric acid solution, and i = 0.12–0.15 A cm^{-2}. Under these conditions, the material yield of 2,6-dimethyl-*p*-benzoquinone was 86% and the current yield was 55%. At the end of the reaction, the anolyte was transferred to the cathodic compartment and the quinone was reduced to hydroquinone; the yield of 2,6-dimethylhydroquinone (purity 90%) with respect to the phenol which had reacted was 65%. Other alkylhydroquinones were obtained in similar yields.[66] Thus the process leads to the possibility of obtaining hydroquinone also from waste water containing phenol at a fairly high concentration.

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Thus the kinetics of electrode processes in the electrochemical oxidation of phenol have been investigated in detail on the basis of extensive experimental data on this subject. It has been shown that phenol-containing waste water can be purified electrochemically and alkylhydroquinones can be obtained; however, some of the problems arising in the practical application of this procedure have not as yet been satisfactorily solved.

In the first place, in the majority of applied studies there has been no scientifically based approach to the selection of optimum process conditions, in particular the current density; for this reason, as regards experimental data, many parameters are selected at random. There is a clear gap between theoretical studies on the kinetics of the oxidation of phenol and practical electrolysis. There is insufficient information about the adsorption of phenol on platinum and graphite anodes and contradictory data have been obtained for the influence of chloride ions on the rate of oxidation of phenol. The cause of the inhibition of the oxidation of phenol observed in kinetic studies has not yet been established. If this could be done, the problem of the activation of the electrode under continuous conditions could be solved.

In the study of the waste water purification processes, little attention has been devoted to the analysis of the electrolysis products; the necessary conditions guaranteeing the complete oxidation of phenol to carbon dioxide and water have not been established. Relatively unproductive and difficult to service electrolysers of the box type are as a rule recommended for the purification of waste water. The question of the application of highly effective electrolysers with bulk electrodes in the purification process has so far been little studied.

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