

Electrochemical Study of Iodide in the Presence of Phenol and o-Cresol: Application to the Catalytic Determination of Phenol and o-Cresol

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Abstract: The electrochemical oxidation of iodide in the presence of phenol and o-cresol was investigated at a glassy carbon electrode in buffered media by cyclic voltammetry, linear sweep voltammetry and controlled-potential coulometry. The experimental results indicate that the phenol and o-cresol convert to their derivatives after participating in a halogenation coupled reaction (quasi-catalytic reaction) following the oxidation of iodide to iodine. The concentrations of phenol and o-cresol have been determined in aqueous solutions according to the linear dependence of quasi-catalytic peak currents with the concentration. The calibration graphs show two linear sections of 0.0 to 1.0×10^{-4} M and 2.0×10^{-4} to 1.0×10^{-3} M for phenol and 4.2×10^{-5} to 1.0×10^{-4} M and 2.0×10^{-4} to 1.0×10^{-3} M for o-cresol. The theoretical detection limits and the relative standard deviations for ten measurements of phenol and o-cresol are 1.125×10^{-5} M, 1.06% and 4.201×10^{-5} M, 1.44%, respectively.

Keywords: Electrochemical study, determination, phenol, o-cresol.

Introduction

Phenol and related compounds are used extensively in industry in the manufacture of a large variety of aromatic compounds including rubber, fertilizer, paints, drug preparations, petroleum, and agricultural industries [1-3]. Phenol is reported to be carcinogenic and exposure to phenol results in several symptoms such as convulsions, dizziness and irregular respiration [1, 4].

Some typical phenols as atmospheric pollutants are phenol, o-cresol, m-cresol, and p-cresol; however, phenols are noted more as water pollutants than as air pollutants [5]. It is frequently pollutant in industrial waste and occurs in soil and drinking water supplies [6]. In the food industry, phenols are of interest because they are essential compounds of fruit juices, beer, and wines [7].

Since many phenolic compounds can cause bad taste and undesirable odor contamination and are highly toxic and hazardous to human health [8], their analysis at low concentrations is very important [9, 10]. As the manufacture and use of phenols requires qualitative and quantitative control, a wide variety of methods have been developed to determine phenolic compounds. The range of available methods extends from distillation [11], membrane extraction [12], liquid-liquid extraction [13, 14] and gas chromatography [15, 16] to more sophisticated techniques such as microwave-assisted extraction [17, 18], ultra sonication and supercritical fluid extraction [19, 20].

Recently, some achievements in the field of enzyme electrode [21, 22] and biosensors [23, 24] have been reported. Tyrosinase-based biosensors for the determination of phenolic compounds in the organic phase have been reported extensively [25-27]. Regarding electroanalytical techniques, procedures involving phenol oxidation at solid electrodes [28-29] have been reported. In addition, chemically-modified carbon paste electrodes have proven very useful for analytical applications [22, 30].

In the previous works [31, 32], the electrochemical oxidation of iodide in the presence of barbituric acid was investigated and barbituric acid was determined by a quasi-catalytic method and coulometric titration. In this paper, we describe the electrochemical behavior of iodide in the presence of phenol and o-cresol. Here, we present a simple and sensitive method of determination of these compounds based on their reaction with electrogenerated iodine.

Experimental

Reagents and solutions

Phenol and o-cresol were prepared from the highest purity grade chemicals purchased from Aldrich. A stock Britton-Robinson buffer solution, which was 0.04 M with respect to boric, orthophosphoric and acetic acid, was prepared from analytical-reagent grade. From this stock solution of buffer, solutions of various pHs were prepared by the addition of 0.2 M sodium hydroxide solution. The solutions of various pHs of Walpole acetate buffer were prepared by mixing the appropriate amounts of 0.2 M acetic acid and 0.2 M sodium acetate. The solutions of 0.2 M disodium phosphate and 0.1 M citric acid were used for preparing the McIlvaine buffer solutions. All other reagents were of analytical grade and used without further purification.

Apparatus

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out with Metrohm model 746 VA Trace Analyzer connected to a 747 VA Stand. Coulometry was performed with Autolab model PGSTAT20 potentiostat-galvanostat. A glassy carbon (GC) electrode (0.2 mm diameter) was used as working electrode, which was sequentially polished with alumina powder. A platinum wire and a commercial saturated Ag/AgCl-electrode from Metrohm were used as an auxiliary and a reference electrode, respectively. Coulometry at controlled potential was performed at a platinum electrode (4 cm²). Cyclic voltammetric measurements were conducted at room temperature under nitrogen.

Analytical procedure for calibration curves

Phenol and o-cresol stock solutions were prepared by dissolving the right amount of pure substance into McIlvaine buffer solution (pH 5.4). At first, the cyclic voltammogram of 3×10^{-3} M sodium iodide in McIlvaine buffer (pH 5.4) was recorded between 0.0 and + 0.7 V. Then, different volumes of phenol or o-cresol solutions were added to the sodium iodide solution. After each addition, a cyclic voltammogram was taken for each addition. Scan rate was chosen 50 mVs^{-1} as optimum scan rate.

Results and discussions

The cyclic voltammogram of 1×10^{-3} M of sodium iodide in aqueous solution containing 0.2 M acetate buffer (pH 4.8) is shown in Fig. 1. As it can be seen from the Fig. 1a, iodide shows an anodic peak at 0.537 V and a cathodic peak at 0.457 V corresponding to the oxidation of iodide (I⁻) to iodine (I₂) and vice versa. Fig. 1b shows the cyclic voltammogram of 1×10^{-3} M solution of iodide in the presence of 1×10^{-3} M phenol.

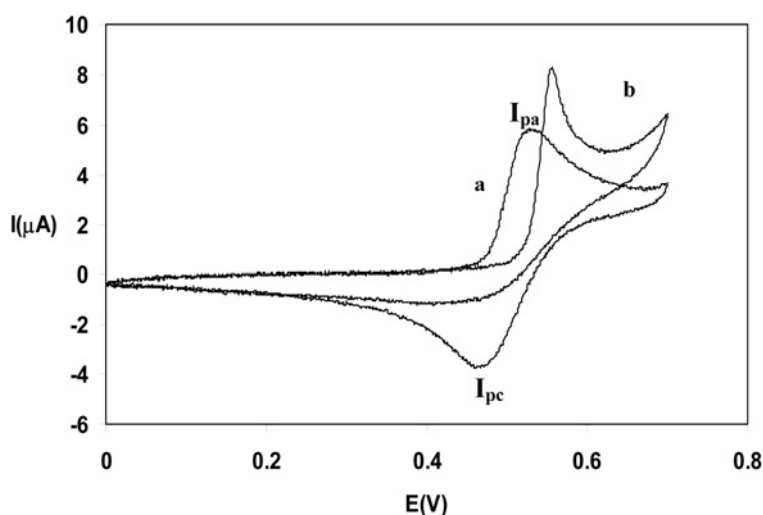


Figure 1. Cyclic voltammograms of 1×10^{-3} M sodium iodide: (a) in the absence and (b) in the presence of 1×10^{-3} M phenol, at GC electrode in aqueous solution containing 0.2 M acetate buffer (pH 4.8), scan rate 20 mVs^{-1} .

The cyclic voltammogram exhibits an increase in the anodic current and the disappearance of the cathodic current in reverse scan. The anodic peak potential is shifted to more positive potential (from

0.537 V to 0.559 V) in the presence of phenol, which is due to the deposition of the product on the surface of the electrode inhibiting to a certain extent the performance of the electrode process [33].

A typical cyclic voltammogram of sodium iodide (1×10^{-3} M) in the presence of 1×10^{-3} M phenol at different scan rates at pH 4.8 is shown in Fig. 2. Under these conditions, proportional to the increase of sweep rate, the cathodic peak (C) appears and the height increases progressively with scan rate. As it can be seen from Fig. 2 (inset, left) the I_{pc}/I_{pa} ratio increases toward unity by increasing the scan rate (I_{pc} and I_{pa} are the cathodic and anodic peak currents of iodide, respectively). The current function ($I_{pa}/v^{1/2}$) also decreases by increasing the scan rate (Fig. 2, inset, right). This diagnostic citation fulfills the requirement for irreversible chemical reaction following a reversible electron transfer (EC process) [34].

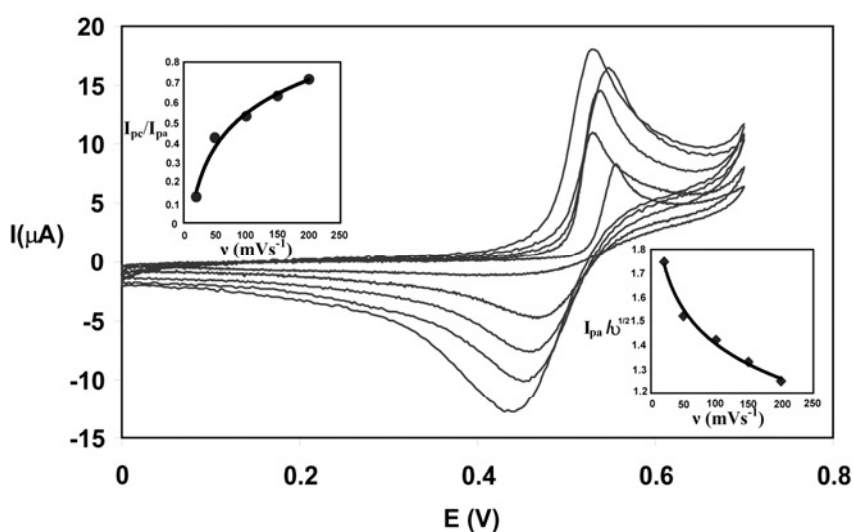


Figure 2. Cyclic voltammograms of 1×10^{-3} M sodium iodide in the presence of 1×10^{-3} M phenol at GC electrode, at various scan rates: 20, 50, 100, 150, 200 mVs^{-1} . Inset: variation of peak current function ($I_{pa}/v^{1/2}$) (right) and peak current ratio (I_{pc}/I_{pa}) (left) as a function of scan rate.

Coulometric experiments were carried out to determine the number of electrons transferred in the oxidation of 1×10^{-3} M iodide solution in the presence of 1×10^{-3} M phenol at 0.550 V vs Ag/AgCl. The monitoring of the electrolysis process by cyclic voltammetry shows that as the electrolysis proceeds, the anodic peak decreases and disappears when the charge consumption becomes about two electrons per sodium iodide. However, the coulometry of the solution containing only sodium iodide consumes one electron per mole of iodide, which indicates that the number of electrons increases in the presence of phenol. This is a good indication of regeneration of iodide in the following chemical reaction, which shows an EC mechanism (quasi-catalytic reaction, see eq. (1) and (2)). The anodic peak current of iodide in the absence of phenol, which is diffusion controlled, I_p^d , increased in the presence of phenol. On this basis, the increasing anodic peak current in the presence of phenol (Fig. 1b) that is related to the regeneration of iodide at the surface of the electrode [34] is presented as a quasi-catalytic current (I_p^{cat}). Thus, the most probable mechanism is as following:



The proposed mechanism was also confirmed by a positive test for iodine in the product obtained from the bulk electrolysis in the solution containing sodium iodide and phenol. Such a mechanism is also in good agreement with the results already proposed about electrochemical iodination and bromination of dibenzoylmethane [35].

The cyclic voltammograms of sodium iodide in the presence of *o*-cresol are shown in Fig. 3. The similar behavior is observed for *o*-cresol. The anodic peak current of NaI in the absence of *o*-cresol (I_p^d) was increased in the presence of *o*-cresol (I_p^{cat}). The decreasing current function ($I_{pa}/\nu^{1/2}$) and increasing current ratio (I_{pc}/I_{pa}) with scan rate shows EC mechanism. Coulometry and positive test of iodine in the product of bulk electrolysis of *o*-cresol and sodium iodide indicate the similar quasi-catalytic reaction in the same manner to phenol.

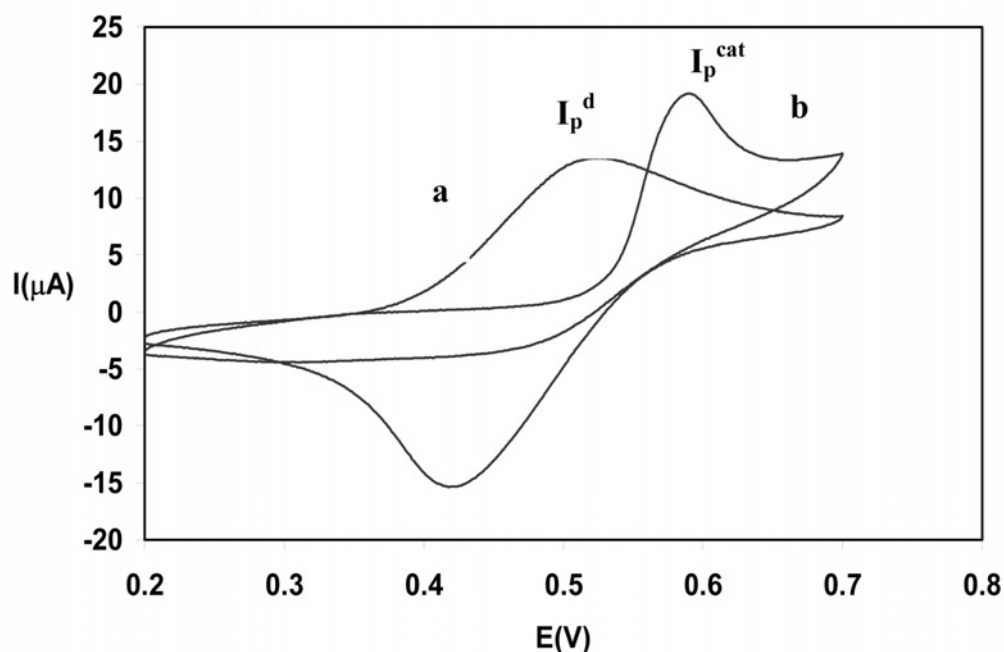


Figure 3. Cyclic voltammograms of 1×10^{-3} M sodium iodide: (a) in the absence and (b) in the presence of 1×10^{-3} M *o*-cresol, at GC electrode in aqueous solution containing 0.2 M acetate buffer (pH 4.8), scan rate, 20 mVs^{-1} .

Analytical aspects

Optimization of the solution pH

In order to investigate the effect of pH on the cyclic voltammogram of sodium iodide in the presence of phenol and *o*-cresol, various types of buffer solutions were chosen. In each buffer at different pH values, the cyclic voltammograms of sodium iodide and phenol or *o*-cresol were recorded and the I_p^{cat}/I_p^d ratios were calculated. I_p^{cat} is the anodic peak current of iodide in the presence of phenol or *o*-cresol, and I_p^d is the anodic peak current of iodide in the absence of these compounds.

Among three different buffer solutions of Britton-Robinson, Walpole acetate and McIlvaine, the best results were obtained in McIlvaine buffer. The typical current ratios of I_p^{cat}/I_p^d of phenol and *o*-cresol were plotted against pH in McIlvaine buffer in Fig. 4. As it can be observed from Fig. 4, both ratios I_p^{cat}/I_p^d increased by increasing the pH. At pH higher than 6, the peaks became ill-defined and in

pH lower than 5 the ratio $I_p^{\text{cat}}/I_p^{\text{d}}$ is low. The best value of pH 5.4 is chosen for determination of both compounds.

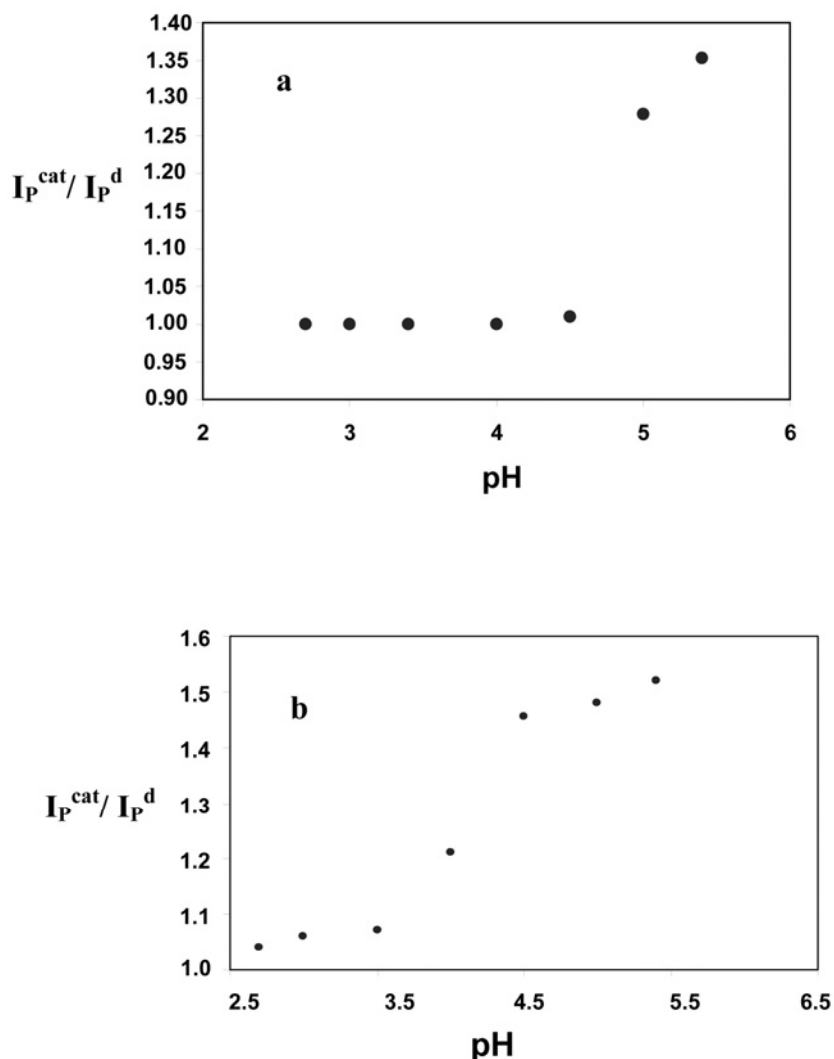


Figure 4. Plot of $I_p^{\text{cat}}/I_p^{\text{d}}$ vs pH in McIlvaine buffer solution of (a) phenol and (b) o-cresol.

Optimization of scan rate

The influence of scan rate, ν , on the anodic peak current of iodide in the presence and absence of phenol and o-cresol was examined in the range of 20–200 mVs^{-1} . Fig. 5 shows cyclic voltammograms (CV) of 1 mM sodium iodide in buffered medium (pH 5.4) and linear sweep voltammograms (LSV) of NaI in the presence of 2 mM phenol at various scan rates. As it can be seen by increasing the scan rate, both currents, I_p^{d} and I_p^{cat} (the anodic current of iodide in the absence and presence of phenol, respectively) were increased. The plot of the ratio $I_p^{\text{cat}}/I_p^{\text{d}}$ vs scan rate for phenol is shown in Fig. 5f. As shown in this figure, the maximum of $I_p^{\text{cat}}/I_p^{\text{d}}$ is obtained at 20 mVs^{-1} . Since the difference of ratio values of 20 and 50 mVs^{-1} is small in this method, a scan rate of 50 mVs^{-1} is preferable due to increasing the rate of analysis. The voltammograms of o-cresol were recorded at similar conditions. The same trends with increasing scan rate were observed for this compound (Fig. 5g). The scan rate 50 mVs^{-1} was also chosen for o-cresol.

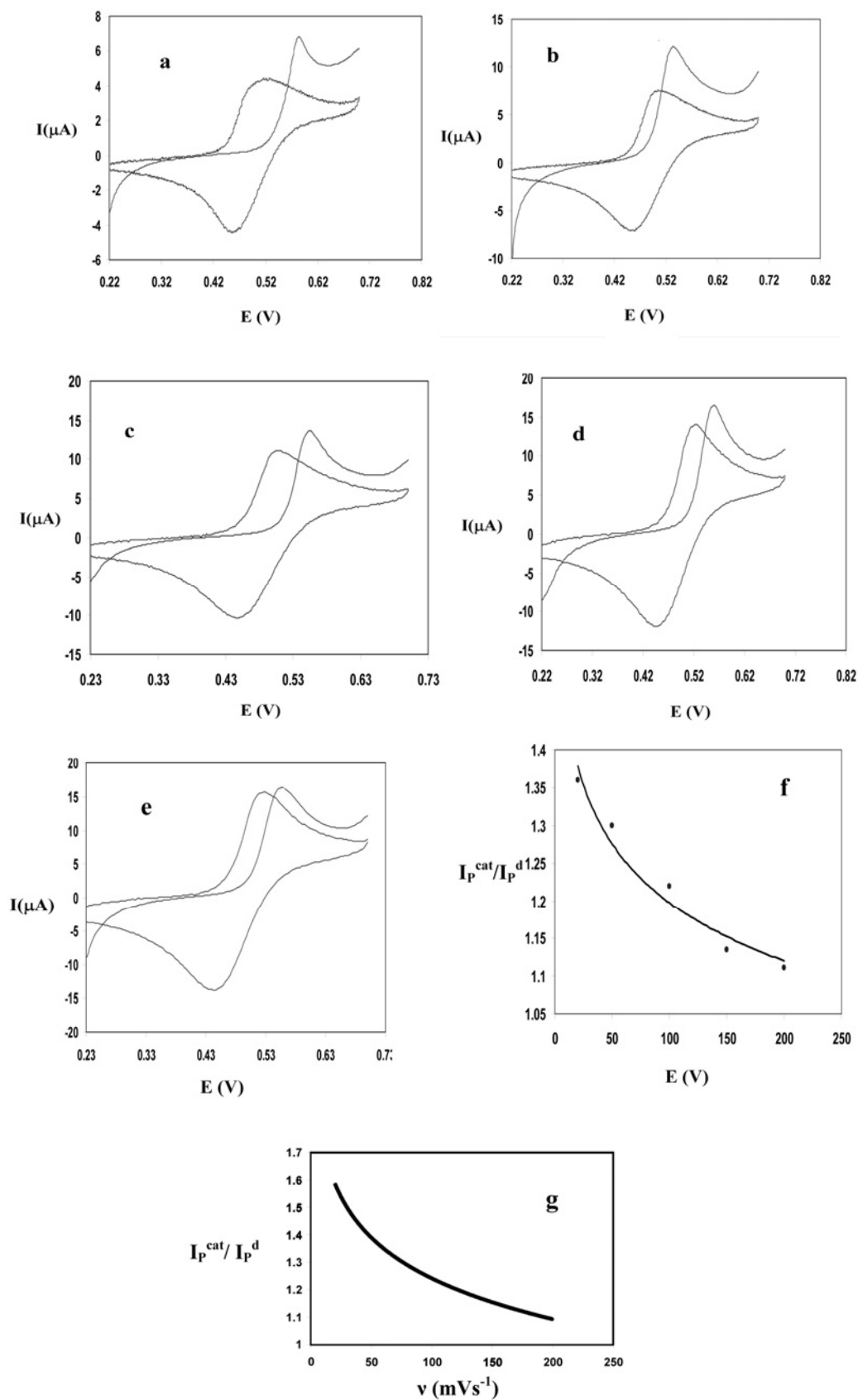


Figure 5. Voltammograms of 1 mM sodium iodide, CV in the absence and LSV in the presence of 2 mM phenol at GC electrode, at various scan rates. Scan rates from (a) to (e) are: 20, 50, 100, 150, and 200 mV s^{-1} , respectively. Curves f and g show the variation peak of the current ratio ($I_P^{\text{cat}}/I_P^{\text{d}}$) as a function of scan rate for phenol and o-cresol.

Optimization of sodium iodide concentration

The cyclic voltammograms at different concentrations of sodium iodide in the presence of phenol or o-cresol were recorded, and the best value of 3×10^{-3} M for sodium iodide concentration was obtained.

Calibration graphs

The cyclic voltammograms of phenol at different concentrations under the optimum conditions described above such as 3×10^{-3} M sodium iodide, pH 5.4, in McIlvaine buffer and a scan rate of 50 mVs^{-1} were shown in Fig. 6. The calibration graph of phenol shows two linear sections of 0.0 to 1.0×10^{-4} M ($r = 0.993$, $y = 66.71x + 25.78$) and 2.0×10^{-4} to 1.0×10^{-3} M ($r = 0.996$, $y = 6.25x + 32.53$) of phenol. The calibration graph of o-cresol shows two linear sections, 4.2×10^{-5} to 1.0×10^{-4} M ($r = 0.999$, $y = 143.5x + 18.28$) and 2.0×10^{-4} to 1.0×10^{-3} M ($r = 0.998$, $y = 14.85x + 40.7$). The theoretical detection limit (DL) was calculated from $DL = X_b + 3S_b$ equation, in which, X_b and S_b the are average value and standard deviation (SD) of blank for nine measurements. Theoretical and experimental detection limits, relative standard deviations and recoveries of phenol and o-cresol are reported in Table 1.

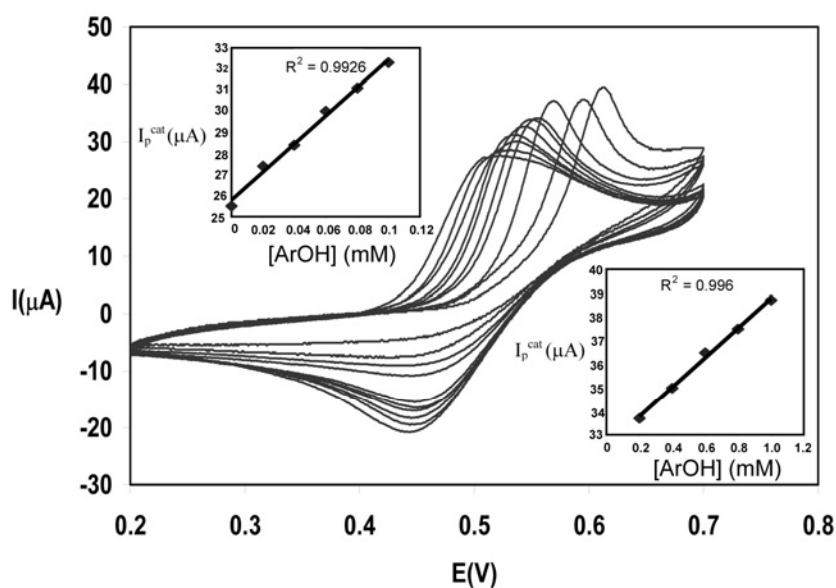


Figure 6. Voltammograms of phenol at different concentrations, 0 , 2×10^{-5} , 4×10^{-5} , 6×10^{-5} , 8×10^{-5} , 1×10^{-4} , 2×10^{-4} , 4×10^{-4} , 6×10^{-4} , 8×10^{-4} , 1×10^{-3} M. Inset: the calibration graphs of phenol in two different concentration ranges, GC electrode, scan rate 50 mVs^{-1} , McIlvaine buffer (pH 5.4) and 3×10^{-3} M sodium iodide.

Table 1. Detection limits, relative standard deviations and recoveries of phenol and o-cresol determination by cyclic voltammetry.

Compounds	Theoretical DL (M)	Experimental DL (M)	SD Relative	Recovery
Phenol	1.16×10^{-5}	1.125×10^{-5}	1.06	97 %
o-Cresol	4.56×10^{-5}	4.201×10^{-5}	1.44	95 %

Interferences

In order to assess the possible analytical application of the catalytical method described above, the effect of some organic and inorganic substances was tested. It was found that many organic compounds such as ascorbic acid, acetaldehyde, cyclohexane, methanol, ethanol, acetone, carbon tetrachloride and inorganic ions such as Mg^{2+} , Co^{2+} , Cu^{2+} , Ca^{2+} , Li^{+} and K^{+} do not interfere, even in large amounts. As a real sample, phenol was determined in tap water under optimum conditions, in which phenol can be recovered by 5 % relative error in tap water.

Conclusions

The results of this work show that iodide is oxidized to iodine. The iodine then, reacts with phenol or o-cresol in a quasi-catalytic chemical reaction. In addition, the results of this work show that iodide can be used as a mediator in the determination of these compounds. The calibration graphs, relative standard deviations and recoveries are reported for the determination of phenol and o-cresol. Comparing the proposed determination of phenol and o-cresol with the methods previously reported [36-38], one may conclude that it is characterized by a simple cell and electrode, short analysis time, simple procedure, and commonly available reagents. And determination over a wide order of magnitude in the sample is possible.

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