International Journal of Natural and Engineering Sciences 8 (2): 25-29, 2014
ISSN: 1307-1149, E-ISSN: 2146-0086, www.nobel.gen.tr

Voltammetric Analysis of Hydroquinone and Catechol at Iodine-Coated Polycrystalline Platinum Electrode

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Received: June 11, 2014
Accepted: July 24, 2014

Abstract
The present work has been devoted to application of iodine-coated polycrystalline platinum electrode to separate and simultaneous analysis of hydroquinone and catechol. For a relatively short potential range, -0.2 – 0.9 V, the iodine-coated platinum electrode exhibits remarkable inertness towards adsorption and surface processes. The voltammogram of hydroquinone at iodine-coated electrode shows an anodic peak centered at 0.55 V and a cathodic peak centered at 0.33 V. Catechol voltammetric features are manifested by an odic peak centered at 0.70 V and a cathodic peak centered at 0.45 V. Excellent linearity between anodic or cathodic peak currents and hydroquinone concentration within a concentration range of $8.5x10^{-6}$ – 0.01 M was demonstrated. Similarly catechol also showed an excellent linear relationship between the peak currents and the concentration within the concentration range $5x10^{-5}$ and 0.01 M. Simultaneous determination of a mixture of hydroquinone and catechol by the developed method was applicable to analysis of mixtures of the two compounds as proved by analysis of standard mixtures of both compounds. Determination of hydroquinone in pharmaceutical bleaching creams with excellent accuracy provides an evidence for applicability of the developed method for analysis of real pharmaceutical samples.

Key words: analysis of hydroquinone, analysis of catechol, iodine-coated platinum electrode, analysis of bleaching creams

INTRODUCTION

Analysis of hydroquinone and catechol receives considerable attention because of the importance of its analysis as a component in pharmaceutical preparations and as an environmental pollutant[1-3]. The two isomeric benzenediol compounds are artificially found in cosmetic preparations for depegmenting and whitening of small areas of hyperpegmented skin[2]. They also find use in developing solutions in black-and-white photography[4], paper and rubber industries[5]. From these industrial routes, in addition to some other natural sources [6] , hydroquinone and catechol find their way to the environment. These industrial applications of the two compounds in addition to its toxicity in the environment demand simple, accurate, precise simultaneous analysis of the two compounds. Spectrophotometric [3,7] and chromatographic methods [8] for analysis of these compounds do exist but development of voltammetric method for analysis of the two compounds is attractive in terms of simplicity of instrumentation and methodology.

Iodine-coated platinum electrodes, on the other hand, demonstrate a remarkable inertness towards molecular adsorption and surface processes[9]. The suppression of the chemistry at the surface of platinum electrode renders iodine-coated platinum electrode suitable for voltammetric analysis in a limited potential range[10].

In an earlier work, we have reported the applicability of iodine-coated platinum electrode to analysis of some ions whose reduction potentials are accessible within the iodine-coated inertness and stability range[11]. On the premise that iodine-coated platinum electrode can be used for analysis of some molecules whose reduction potentials are accessible within the iodine-coated platinum range we have undertaken the present work.

MATERIALS AND METHODS

Cell, Instruments and Materials

A potentiostat (362, Princeton Applied Research) interfaced to a computer via GPIB interface (IEEE). A locally modified LabView® (IEEE) software was used for data acquisition. A conventional H-shape electrochemical cell equipped with a multiple inlet system for admission of supporting electrolyte, purging and blanketing the solution with oxygen-free nitrogen was used. The reference electrode was an Ag/AgCl/ $[Cl^-]$ = 1.0 M, and all the reported potentials were measured and referenced to this electrode. The working electrode was a 1.0 mm diameter platinum wire (certified reagent 99.99% minimum purity, Aldrich). The immersed part of the wire was curved in order to provide a mark for obtaining a consistent surface area.

All reagents used were highly pure analytical reagent (A.R.) chemicals and used as received from the suppliers without further purification. Sulfuric acid (Aldrich, USA), hydroquinone, catechol, sorbitol, methylhydroxy benzene and phenol were supplied by Fluka (USA). Polyethylene glycol and citric acid were purchased from BDH (England). The auxiliary electrode was made of platinum (Certified Reagent, 99.99% minimum purity, Aldrich). The purging nitrogen was G5 Grade , 99.999% minimum purity supplied by the International Gas Company and coupled with Oxisorb® cartridge (Supelco, USA) to remove, if any, residual traces of oxygen. All solutions were made from the above mentioned reagents dissolved in Millipore-Q water (Merck Millipore).

Procedures

Preparation of iodine-coated electrode

The polycrystalline platinum electrode was polished with alumina powder, rinsed with water, sonicated for 5

minutes, and dipped for ten minutes in freshly prepared chromic acid solution. After that the electrode was generously rinsed with Millipore-Q water, placed in the cell and conditioned between -0.25 V and 1.3V until the characteristic voltammogram for polycrystalline platinum electrode was reproduced. Reproducing the well-known characteristic cyclic voltammogram was considered a verification of the electrode cleanliness.

The iodine-coated electrode was prepared by potentiostatic exposure of the electrode in the double layer potential region (ca. 0.2 V) to a solution composed of 0.50 M H_2SO_4 + 0.010 M KI for 5 minutes. The iodide - containing solution was drained and the working electrode compartment and the working electrode was extensively rinsed with the iodine-free 0.50 M H_2SO_4 solution. The working electrode compartment was filled with 0.5 M H_2SO_4 solution and the electrode potential was cycled between -0.25 V and 0.8 V. The absence of hydrogen adsorption/desorption features is an indication of the complete coating of platinum surface.

Voltammetric measurements in hydroquinone and catechol containing solution and all the other investigated compounds were carried out at the above-mentioned iodine-coated electrode in 0.5 M H_2SO_4 supporting electrolyte environment. All measurements were carried out at ambient pressure and temperature.

RESULTS AND DISCUSSION

Voltammetric determination of Hydroquinone at Iodine-Coated Platinum Electrode

Figure 1 shows a representative voltammogram for iodine coated-platinum electrode along with the voltammogram of the corresponding clean platinum electrode. The voltammogram of the iodine-coated electrode shows nearly complete absence of the voltammetric features of platinum which are attributed to oxygen adsorption/desorption and hydrogen adsorption/desorption at the platinum surface. This suppression of the surface electrochemistry background and the remarkable inertness towards molecular adsorption is the most important feature of the iodine-coated electrode. Stability of iodine coating at the surface is evidenced by absence of any change in the voltammogram of the iodine-coated electrode upon cyclization of potential between -0.25 V and 0.8 V potential limits. This stability was traced for more than three months by cyclic voltammetry and the stability of iodine-coated electrode was manifested by the persistence of the voltammogram of iodine-coated electrode as far as the electrode potential was not allowed to exceeded 0.90 V. The simplicity of preparation of the iodine-coated platinum electrode, however, allowed starting with a new coating at the onset of every set of experiments.

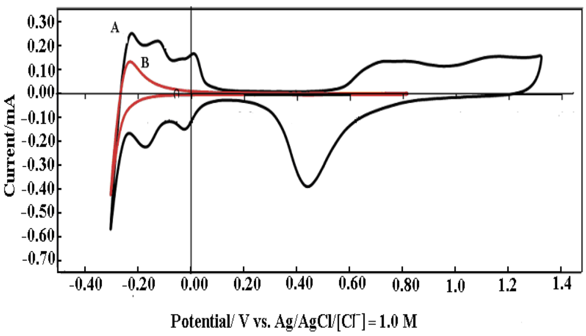

Figure 1. (A) Cyclic voltammogram of the polycrystalline platinum electrode and (B) iodine-coated polycrystalline platinum electrode recorded in 0.5M H_2SO_4. Both voltammograms were recorded in 0.50 MH_2SO_4 at a scan rate of 100 mV/s. (M. Hourani and B. Hijaz)

Figure 2 shows a set of representative cyclic voltammograms for iodine-coated platinum electrode in a 0.5 M H_2SO_4 containing different concentrations of hydroquinone. The cyclic voltammogram shows two peaks, one anodic peak for oxidation of hydroquinone and another peak for reduction of the hydroquinone oxidation product. The anodic peak is centered at 0.55 V while the cathodic peak is centered at 0.33 V. The potential difference between the anodic and cathodic peaks is about 220 mV. This indicates that the system is irreversible and iodine as expected does not catalyze electrooxidation of hydroquinone at the platinum surface. The ratio of the cathodic current to the anodic current, i_c/i_a is about 0.95 which is very close to unity amounting to the stability of the hydroquinone oxidation product in the solution.

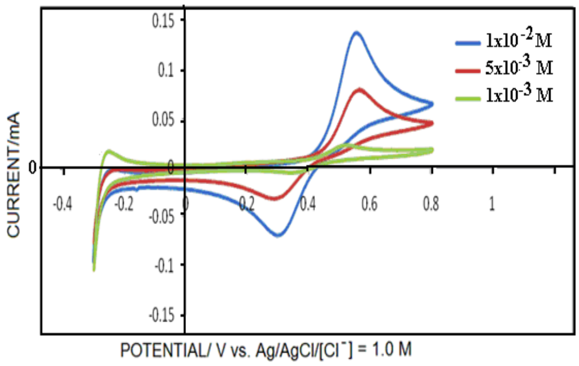

Figure 2. Voltammograms of iodine-coated electrode in 0.5 M H_2SO_4 + variable concentration of hydroquinone. The concentrations are shown in the legend. Scan rate for both voltammograms = 100 mV/s. (M. Hourani and B. Hijaz)

Calibration curve was established by plotting the anodic and cathodic peak currents versus the concentration of hydroquinone in the solution. The relationship between the concentration of hydroquinone and the anodic peak current indicated a linear relationship (R^2 = 0.999) with a calibration equation given by equation 1.

$i_{pa} = 1.2928x10^4\ C_{HQ} + 0.11$ …………………………....….(1)

Where i_{pa} is the anodic peak current in units of milliampers and C_{HQ} is the molar concentration of hydroquinone. The lowest detection limit based on S/N ratio of 3 is $2.55x10^{-6}$ M and the limit of quantitation (LQ) is $8.5x10^{-6}$ M (based on S/N =10).

The cathodic peak also showed a linear relationship between the hydroquinone concentration and the cathodic peak current, i_{pc} (R^2 = 0.988). The calibration equation is given by equation 2.

$i_{pc} = 7.233x10^3\ C_{HQ} + 0.01$ …………………………….(2)

The lowest detection limit for determination of HQ from the cathodic peak current is $4.01x10^{-6}$ M (S/N=3) and the limit of quantitation, LQ is $1.38x10^{-5}$ M (based on S/N=10). These results indicate that the anodic or the cathodic peak, can be used for determination of HQ.

The effect of scan rate on the anodic peak current was investigated by variation of the scan rate for the cyclic voltammograms produced for 0.01 M hydroquinone. The anodic peak current showed an excellent linearity between the anodic peak current and the square root of the scan rate, $\nu^{1/2}$ (R^2 = 0.998). This indicates that the peak is due to diffusion controlled process not complicated by surface processes [12] . Similarly the cathodic peak current shows linearity with the square root of the scan rate leading to the same conclusion of absence of surface processes and that the oxidation/reduction of hydroquinone system is a diffusion-controlled process characterized by absence of surface processes or coupled homogeneous reactions [12].

Voltammetric Determination of Catechol at Iodine-Coated Platinum Electrode

Figure 3 shows a set of representative voltammograms for the iodine-coated platinum electrode in 0.5 M H_2SO_4 solutions which contained different concentrations of catechol. The general appearance of the voltammogram is similar to that of hydroquinone. Electrooxidation of catechol is manifested by appearance of an anodic peak centered at 0.70 V and a counter cathodic peak for reduction of the oxidation product centered at 0.45 V. The potential difference between the anodic and the cathodic peaks is 250 mV which indicates that the catechol also shows irreversible behavior upon oxidation at iodine-coated platinum electrode. This behavior is not unexpected because iodine is known to passivate platinum surfaces rather than enhancing their electrocatalytic properties. The ratio of i_c/i_a is nearly 1 which presents an evidence for the stability of the oxidation product of catechol under our experimental conditions and the absence of any coupled homogenous chemistry to the oxidation or reduction processes. The anodic peak currents extracted from the voltammograms were found to display a linear relationship with catechol concentration.

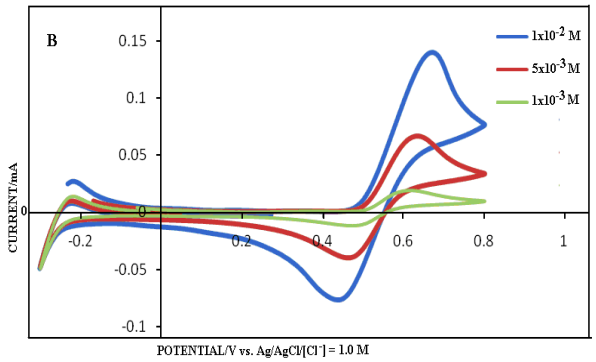

Figure 3. Cyclic voltammogram of iodine-coated electrode in 0.5 m H_2SO_4 + variable concentration of catechol. The concentration are shown in the legend of the figure. Scan rate = 100 mV/s. (M. Hourani and Bushra Hijaz)

The calibration equation for the anodic peak currents is given by equation 3.

$$i_{pa}(mA) = 1.3838x10^{4}C_C + 0.011 \quad \text{.....(3)}$$

The coefficient of determination, R^2, for the range between $5x10^{-5}$ M and $1x10^{-2}$ M is equal to 0.999. The lowest detection limit based on S/N ratio of 3 is $2.3x10^{-6}$ M and the limit of quantitation is $7.7x10^{-6}$ M. The cathodic peak current was also found to display a linear relationship with concentration of catechol. The calibration equation for the cathodic peak current vs. the concentration of catechol is given by equation 4.

$$i_{pa}(mA) = 1.0084x10^{4}Cc + 0.01 \quad \text{.....(4)}$$

The coefficient of determination is 0.997 for the concentration range of $5x10^{-5}$ M – $1x10^{-2}$ M attesting to the excellent linearity within this range.

Simultaneous determination of hydroquinone and catechol

Figure 4 shows a representative voltyammogram for the iodine-coated platinum electrode in a 0.5 M H_2SO_4 solution containing 0.01 M hydroquinone and 0.01 M catechol. The voltammogram shows two poorly resolved anodic peaks and two less poorly resolved cathodic peaks for the two compounds. The cathodic peaks resolution is better than the anodic peaks and for this reason the cathodic peaks were considered for simultaneous determination of the two compounds. The background level for the cathodic peak was established by extrapolation of the linear segment of the voltammogram immediately after the switching potential from 0.8 V to 0.6 V. Based on the voltammograms of the pure components, the peak currents for catechol and hydroquinone were labeled as A and B respectively (Figure 4). A set of four solutions containing hydroquinone and catechol with a variable combination within the range of $1.0x1^{-3}$ - $1.4x10^{-2}$ M for the two compounds were prepared and analyzed by cyclic voltammetry. The concentrations were calculated from the peak currents and the results are given in Table 1. The correlation coefficient for hydroquinone analysis results is 0.9930 while the correlation coefficient is 0.9990 for catechol analysis results. This excellent linearity between the nominal concentrations of hydroquinone and catechol in the mixture and their corresponding values determined by cyclic voltammetry at iondine-coated platinum electrode provides a strong evidence for the applicability of the present method for simultaneous determination of the two compounds in real samples containing the two compounds.

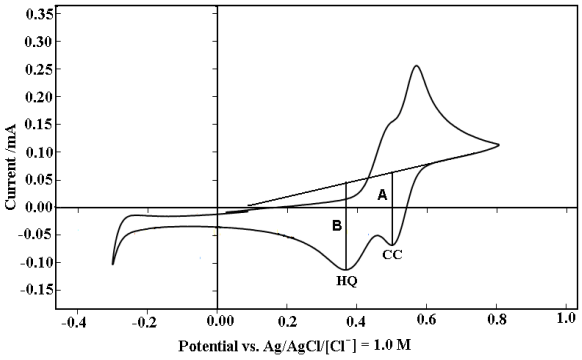

Figure 4. Cyclic voltammogram of iodine-coated platinum electrode in 0.5 M H_2SO_4 + $1.0x10^{-2}$ M hydroquinone + $1.0x10^{-2}$ M catechol. dE/dt = 100 mV/s. (M. Hourani and Bushra Hijaz)

Recoveries

Recovery studies for spiked synthetic matrix similar to the commercial cosmetic creams are given in Table 2. The average recoveries for hydroquinone and catechol from the synthetic cream samples were 100.1% and 97.4% respectively. These results attest to the accuracy of the method.

Table 1. Actual concentrations versus determined concentrations by cyclic voltammetry at iodine-coated platinum electrode in mixtures of hydroquinone and catechol. Peak currents were measured as in Figure 4.

Mixture sample Number	Hydroquinone		Catechol	
	Analytical Concentration, mol.L^{-1}	Determined Concentration, mol.L^{-1}	Actual Concentration, mol.L^{-1}	Determined Concentration, mol.L^{-1}
1	1.0x10^{-2}	1.1x10^{-2}	1.0 x10^{-2}	1.0x10^{-2}
2	7.5x10^{-3}	7.7x10^{-3}	7.5x10^{-3}	7.2x10^{-3}
3	5.0x10^{-3}	4.2x10^{-3}	5.0x10^{-3}	4.9x10^{-3}
4	3.0x10^{-3}	2.8x10^{-3}	1.0x10^{-3}	1.2x10^{-3}

Table 2. Percent recoveries of hydroquinone and catechol in cosmetic cream synthetic matrix samples* spiked with standard hydroquinone and catechol standard solutions.

Sample No.	HQ or CC nominal* concentration, mol.l^{-1}	HQ or CC* determined concentration, mol.l^{-1}	% recovery
1	1.0x10^{-3} HQ	1.03x10^{-3}	103%
2	5.0x10^{-3} HQ	4.88x10^{-3}	97.6%
3	1.0x10^{-2} HQ	9.97x10^{-3}	99.7%
4	1.0x10^{-3} CC	9.82x10^{-4}	98.2%
5	5.0x10^{-3} CC	4.75x10^{-3}	95%
6	1.0x10^{-2} CC	9.91x10^{-3}	99.1%

Synthetic HQ denotes hydroquinone while CC denotes catechol

Interferences

Some potential interferences were investigated at the iodine-coated platinum electrode. Three standard solutions; 1.0x10^{-3} M, 5x10^{-3} M and 1.0x10^{-2} M of resorcinol, phenol, 2-methoxy phenol, citric acid, polyethylene glycol were prepared and analyzed by cyclic voltammetry at iodine-coated platinum electrode. Voltammetric measurements for resorcinol, phenol, and citric acid showed absence of any voltammetric response within the scanned range, -0.2 V and 0.8 V. These results indicate that these compounds are not potential interferences for the developed method. Polyethylene glycol and 2-methoxy phenol, however, show observable peaks at concentrations equal or greater than 5x10^{-3} mol l^{-1}. These results indicate that these compounds are potential interferences and their existence in the analyzed solutions must be taken in consideration.

A group of metallic ions comprising Al^{3+}, Cr^{3+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Cu^{2+} and Ag^{+} which may interfere with analysis was also investigated. All of these ions showed no response except Ag(I) and Cu(II) as indicated in our earlier work [10,11].

Analysis of real samples

Two commercial skin bleaching creams, Eldoquin Forte (ICN Pharmaceuticals, USA) and Philaquin Forte (Philadelphia Pharmaceuticals, Jordan) were analyzed for their hydrquinone contents. Each gram of the cream nominally contains 40.0 mg of hydroquinone (4.0% hydroquinone). The matrix includes stearic acid, propylene glycol, polyoxyl 40 stearate, polyoxythylene, propylene glycol stearate, glycerol monostearate, light mineral oil, squalane, propylparaben and sodium metabisulfite dissolved in purified water.

An accurately weighed amounts of the above-mentioned creams ranged from 0.20 to 3.0 g were separately dissolved in 100.00 ml of 0.5 M H_2SO_4 aliquots with efficient stirring until complete dissolution. Cyclic voltammograms were recorded at the iodine-coated platinum electrode for the above-mentioned solutions within the potential range -0.3 and 0.8 V at scan rate of 100 mV/s.

The concentrations were determined from the measured anodic peak currents and compared with the expected concentrations calculated from the nominal percentage of hydroquinone in the analyzed cosmetic creams (4.0%). The results for the analyzed samples are given in Table 3. The relative error for the two commercial brands ranged from 0.0 to 2.0% and the correlation coefficient between the expected values and the determined values is 0.9969. These results present a strong evidence for the applicability of the developed method for determination of hydrquinone in real samples.

Table 3. Analyzed samples of two cosmetic reams; Eldoquin Forte (ICN Pharmaceuticals, USA) and Philaquin Forte (Philadelphia Pharmaceuticals, Jordan). Both creams nominally contains 4.0% hydroquinone.

Sample No.	Eldoquin			Philaquin		
	Expected Concentration, mol l^{-1}	Determined concentration, Mol l-1	Relative percent error	Expected Concentration, mol l^{-1}	Determined concentration, Mol l-1	Relative percent error
1	7.2x10^{-4}	7.3x10^{-4}	1.3	8.6x10^{-4}	8.64x10^{-4}	0.46
2	1.4x10^{-3}	1.4x10^{-3}	0	1.5x10^{-3}	1.53x10^{-3}	2
3	3.7x10^{-3}	3.69x10^{-3}	0.27	3.7x10^{-3}	3.72x10^{-3}	0.54
4	7.3x10^{-3}	7.31x10^{-3}	0.13	7.6x10^{-3}	7.5x10^{-3}	1.3
5	0.010	0.010	0	0.011	0.011	0

CONCLUSIONS

The present study demonstrates the applicability of iodine-coated polycrystalline platinum electrode to analysis of hydroquinone, catechol and mixtures of the two compounds. Preparation of the electrode simply involves immersion of a verified-clean platinum electrode in 0.5 M H_2SO_4 + 0.010 M KI solution at 0.2 V. The electrode is stable and survives rinsing and cyclization of potential within -0.2 V and 0.8 V. Exceeding a potential of about 0.9 V oxidizes the adsorbed iodine from the surface.

The limited potential range of the iodine-coated platinum electrode implies selectivity in analysis where limited number of chemical species show electroactivity in this limited range. In fact, few chemical species were found to interfere with voltammetric analysis of these compounds. Recorcinol, the third isomer of the dihydroxybenzene did not show any response within the stable range for iodine-coated platinum electrode. The components of placebo in commercial hydroquinone preparations were found to display no voltametric response with the stable potential range of iodine-coated platinum electrode.

The linearity of the voltammetric response , the peak current, i_p, with the concentration of hydroquinone or catechol may provide the basis for using the iodine-coated platinum electrode as a voltammetric sensor for analysis of hydroquinone and catechol.

Analysis of hydroquinone and catechol at iodine-coated electrodes showed moderate sensitivity where the detection limits are 2.55×10^{-6} M (0.28 ppm) and 2.3×10^{-6} M (0.25 ppm). This sensitivity is much higher than that needed for analysis of hydroquinone in cosmetic creams.

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