Cathodic Stripping Differential Pulse Voltammetric Determination of Poly(8–Hydroxyquinoline) Matrix

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ABSTRACT: Cathodic stripping differential pulse voltammetric (CSDPV) procedure was successfully used for the determination of poly(8-hydroxyquinoline) (PHQ) matrix. The linearity range for the determination of PHQ in the presence (1 mmolL-1) of copper (Cu(II) ion was found to be more sensitive ten times of magnitude higher than the determination of PHQ alone. The lower detection limit was found to be as low as 10 nmolL-1. While, in the case for the determination of Cu(II) ion as a PHQ–Cu(II) chelate, the linearity range is (0 – 4 µmolL-1). The determination of PHQ chain and/or Cu(II) ion was successfully applied in the presence of variety of anions, cations and in an insulating poly(vinyl alcohol) (PVA) matrix. The PVP matrix enhanced the absorbability at the mercury electrode surface which caused increased in the peak high of the chelated Cu(II)

Keywords: Poly(8-Hydroxyquinoline), copper (II) ion, anions, cations, CSVD, PVA, PVP, determination

INTRODUCTION

Cathodic stripping voltammetry (CSV) of metal ions is one commonly used of the main electrochemical stripping techniques, which is suppressing considering the potential benefit of CSV, including high specificity, mercury free and oxygen insensitive analysis. CSV is effectively the electrochemical inverse of ASV, where the analyte of interest is accumulated as an oxidizing species on the electrode surface at positive potential, and then quantified during the stripping step as the electrode potential is swept cathodically. Often, CSV techniques also involve complexation of the metal ions of interest, and the use of a hanging mercury drop electrode (HMDE) (Zhang H., 1989; Zhang J., 1994). Various CSV methods for directly analyzing aqueous metal have also been developed previously (Viltchinskaia, 1995). These all methods employ the technique of first accumulating metal from solution by electro depositing (M₂n⁺On) on anodically on the working electrode and then stripping of the reduced M⁺ ions by sweeping the potential cathodically.

Cathodic stripping voltammetry has proved suitable for a number of organic compound including drugs as thiopurine and thiopyrimidine derivatives at hanging mercury dropping electrode were investigated (Temerk, et al. 1992; 1993) in solutions of varying pH.

Although not exhaustive, the above list contains the best of the recently developed CSV techniques for metals determination, and this is also evident in various review (Goyal, 2005; Esteban, 1994) with such a limited range of applications for CSV existing at, an investigation of new electrode materials and electrochemical techniques in this area is easily justified, in order to extend the range of CSV – based electroanalytical techniques.

The Hanging Mercury Drop Electrode (HMDE) has been used as a model surface for the physicochemical study of adsorption phenomena of hydrophobic molecules such as aliphatic fatty acids (Ulrich, 1988), tri-n-butyl phosphate (Dogie, 2003) and the study of fractal properties of adsorbed linoleic acid (Risovic, 2001), to study surface adsorption of mitomycin (Pérez, 2002), the insecticide imidacloprid (Giannakopoulos, 2008). Also, HMDE was previously used to study the mechanism of the reduction and breaking of the S–S bonds in proteins (Heyrovsky, 1994; Honeychurch, 1997), dithiocarbamate pesticides (Giannakopoulos; 2007) and cysteine (Stankovich,
1977; Florence, 1979), using Cathodic Stripping Voltammetry. HMDE has been employed for the analytical determination of the redox states of phosphonic acid derivatives, amino-(4-dihydroxyphenyl) methyl phosphonic acid, and 3-(3,4-dihydroxyphenyl)-alanine (Dopa) by cyclic voltammetry (CV). The theoretical electrochemical aspects of Cathodic Stripping Voltammetry (CSV) have been applied for the adsorption of monophenols (Gasowska, 2002) and polyphenols (Giannakopoulos, 2011; Oliveira Brett, 2002; Ghica, 2005) on a HMDE and a glassy carbon mini-electrode respectively.

The electrochemical interfacial adsorption of a series of polyphenolic molecules (i.e. polyhydroxybenzoic acids) at the Hanging Mercury Drop Electrode (HMDE)–electrolyte interfaces were investigated using Square Wave-Adsorption Cathodic Stripping Voltammetry (SW-AdCSV) at pH7.5. Polyhydroxybenzoic acids bearing one 4-hydroxybenzoic acid, two 3,4-dihydroxybenzoic acid (protocatechuic) or three 3,4,5-trihydroxybenzoic acid (gallic) OH-groups at positions C3, C4 and C5 on the benzene ring were studied. The complex interfacial electrochemical behaviour of these molecules has been deconvoluted to (i) adsorption events and (ii) redox formations at the HMDE interface. The approach presented is based on the comparative analysis of the SW-AdCSV signals in conjunction with the molecular structure of the molecules. Accordingly, theoretical calculations, involving nonlinear-fit, resulted in the identification of the interfacial reaction mechanism of adsorbed gallic acid on the HMDE (Giannakopoulos, 2012).

EXPERIMENTAL

8-Hydroxyquinoline (8-HQ) was obtained from Aldrich (chemical co., US.). poly (vinyl alcohol) (PVA; Mwt =2.2x10^4; degree of hydrolysis, 88%) was purchased from chemical co., Japan). A copper nitrate Cu(NO₃)₂ was obtained from chemically pure of Merck. All Materials employed in the present study were of analytical reagent products from their Aanalar grade nitrates salts (BDH): Cu(NO₃)₂·3H₂O, Ni(NO₃)₂·6H₂O, Co(NO₃)₂, CaCl₂, MgCl₂·6H₂O, NH₄Fe(SO₄)₂·12H₂O, Al₂(SO₄)₃·16H₂O, ZnSO₄·7H₂O, Cd(NO₃)₂·4H₂O, and Pb(NO₃)₂.

Cathodic stripping differential pulse voltammetric (CSDPV) measurements were carried out with a PAR model 303A hanging mercury electrode (HMDE) and a PAR model 305 magnetic stirrer. Voltamograms were recorded on advanced X–Y recorder model RE0089 after automated deareation of the electrolyzed solutions.

The pH measurements were made using Jenway 3305 pH-meter accurate to ± 0.01 pH unit.
with glass calomel electrode assembly. The pH-meter was standardized against pH values 4.0 and 10.0 buffers (prepared by dissolving buffer capsules in definite amount of second deionized water).

Magnetic stirrer Jenway 1000 was used for stirring the solutions.

The cell used for the voltammetric studies is a thermostated PAR cell equipped with a three electrodes system. This system contained a hanging mercury drop electrode (HMDE) as the working electrode, Ag / AgCl, Saturated KCl as the reference electrode and platinum wire as a counter electrode. The surface area of the hanging mercury drop electrode was 1.2 x 10^-2 cm^2.

2.3- Preparation of Solutions

Poly(8-Hydroxyquinoline), PHQ, was prepared based on the homo-oxidative polymerization technique of the corresponding monomer, 8-HQ (Kamal, 2002; Ahmed, 2003).

A solution of copper (II) was prepared by dissolving a known amount of chemically pure Cu (NO_3)_2 (Merck) in twice-distilled deionized water and was standardized complexometrically (Vogel, 1989). Solutions (1 mmol L^-1) of the metal solutions of anions such as CO_3^{2-}, NO_3^{-1}, SO_4^{2-}, B_4O_7^{2-}, PO_4^{3-}, CH_3COO^{-1} were prepared from their Analar grade sodium salts.

A modified universal buffer series derived from that of Britton (Britton, 1952) was prepared. The constituents of this series of buffer were prepared as follow:-

(a) A solution of 0.4 M of each phosphoric and acetic acids were prepared by accurate dilution of the A.R.concentrated acids.

(b) A solution of 0.4 M boric acid was obtained by dissolving the appropriate weight of the re crystallized acid in bi distilled water.

(c) A stock acid mixture was prepared by mixing equal volumes of the three acids in a large bottle. The total molarity of the acid mixture was thus mentioned at 0.4 mol L^-1.

A series of buffer solutions (pH 3–12) were prepared as follow: 150 ml of the acid mixture was placed in a 250 ml measuring flask followed by the appropriate volume of 0.4 M NaOH solution with stirring and measuring pH values.

10 ml of the supporting electrolyte (universal buffer containing 15% ethanol) was placed in the electrolysis cell, followed by an appropriate volume of the solution of the depolarizer. The solution was deareated by passing a slow stream of pure nitrogen through it for 20 minutes. Sequential addition of mM stock solution of the investigated compound of PHQ or metal nitrates were used.

Metal ions such as Cu(II), Ni(II), Co(II), and Fe(III) were prepared by dissolving a known amount of chemically pure metal nitrate (Merck) in twice-distilled deionized water and were standardized complexometrically (Vogel, 1989). The working standard solutions in the syntheses were prepared in 10-ml volumetric flasks in aqueous ethanol (60% ethanol). The solutions were then diluted to an appropriate volume with doubly distilled water. Solutions of the anions; e.g., Cl^-, Br^-, I^-, NO_3^{-1}, PO_4^{3-}, B_4O_7^{2-}, CH_3COO^-, CO_3^{2-}, HCO_3^-, C_6H_5COO^-, citrate, and tartarate, were prepared from their Analar grade sodium salts.

2.4. Procedure for the CSVD of PHQ Matrix

The differential pulse cathodic stripping voltammetry (DPCSV) were carried out at: scan rate 5 mVs^-1, modulation amplitude 100 mV, deposition time 120 sec., plus 15 sec quiescent period. All measurements were performed at 22±0.5 oC. Nitrogen was bubbled through the solution in the cell for 20 min. to remove oxygen to an undetectable level, and the corresponding voltammetric curves were recorded.

RESULTS AND DISCUSSION

CSDPV of PHQ at Different pH Value

The chathodic stripping differential pulse voltammetric (CSDPV) behavior of PHQ matrix at the hanging mercury dropping electrode (HMDE) in various pH media was shown in Fig. 1. In acidic and neutral media (pH < 7.10), the reduction response of the adsorbed PHQ was not observed and the cathodic reduction peak is completely overlapped with the background discharge. This behavior is due to the highly catalytic effect of the adsorbed PHQ molecules on the hydrogen ion (H+) discharge potential. However, In alkaline media (pH > 7.1), the voltammograms display a relatively weak signal at the negatively charged electrode potential (E_p = −1.55 V, pH 11.20) which is highly affected by the background discharge. Under these conditions
the DPCSv peak of PHQ can not be used as a sensitive signal for its analytical determination of PHQ chain using such technique.

It was observed that the more sensitive CSDPV signal for the reduction of PHQ–Cu(II) matrix observed at pH 7.10 and the peak height decreases with increasing or decreasing the pH. This signal is strongly Cu(II) and/or PHQ concentration dependent. Hence, pH 7.10 is chosen as the optimum pH medium for the trace determination of Cu(II) and/or PHQ matrix.

**Effect of operating parameters**

**3.3.1- Effect of alcohol percentage on the CSDPV of PHQ – Cu(II) system**

The CSDPV of PHQ–Cu(II) system at pH 7.1 was recorded in solutions containing different ethanol percent. The maximum response of the chelated Cu(II) peak is recorded at 15 % ethanol. With increasing or decreasing the ethanol percent, the signal decreased by about 10 – 20 %. This behavior is due to the solubility effect at lower ethanol percent as well as at higher percentage, ethanol may be compete with the adsorption of the PHQ–Cu(II) system. Therefore, 15 % ethanol at pH 7.1 was used in our subsequent experiments.

**3.3.2. Effect of Scan Rate**

The effect of scan rate on the CSDPV peak of the chelated PHQ–Cu(II) system was investigated at pH = 7.1 containing 15% ethanol, t_{acc}, 120 sec., E_i = 0.0 V, and pulse amplitude 100 mV. The peak height increases by 15% with increasing the scan rate from 2 to 5 mV s^{-1}. At higher scan rates 10 and 20 mV s^{-1} the peak height decreased. Then, the scan rate 5 mV s^{-1} was selected as an optimum one for the analytical determination of Cu(II) and/or PHQ experiments.

**Effect of Pulse Amplitude**

The pulse amplitude dependence of the i_p of the CSDPV peak height of complexed Cu(II) increases with changing the pulse amplitude from 25 to 100 mV. At pulse amplitude 100 mV the peak height is 200 % of the height at 50 mV and the peak potential slightly shifted to less negative value.

The effect of accumulating time (dipping time) (t_{acc}) on the maximum response of the CSDPV of the chelated Cu(II) was examined using the concentration of 2.0 µmolL^{-1} of PHQ (Fig. 3). The peak height increases with increasing the pre-concentration time. This behavior is consistent with a process that is limited by adsorption of the
investigated system. At higher accumulation time \((t > 180 \text{ sec})\) the electrode surface becomes saturated, since, the peak current reaches a constant value at adsorption longer than 120 sec., which was used in our subsequent experiments.

The cathodic stripping differential pulse voltammetric (CSDPV) behavior of PHQ chelates with copper ion \([\text{PHQ} – \text{Cu(II)} \text{ matrix}]\) was recorded over a wide pH range \((1.4–11.25)\) as shown in (Fig. 2). This behavior shows a very sharp, sensitive and resolved cathodic reduction peak at potential \(-0.45 \text{ V (pH-dependent)}\). This peak corresponding to the reduction of the chelated Cu(II) ion of the strongly adsorbed and accumulated PHQ–Cu(II) matrix at the dropping mercury electrode surface. The optimum solution and operation conditions for determination of Cu(II) and PHQ matrix at HMDE using CSDPV technique were studied and recorded as follows: pH 7.10, alcohol percentage 15 %, pulse amplitude 100 mV, scan rate 5 mVs\(^{-1}\), deposition time 120 sec., and starting potential 0.0 V. The sensitivity of the CSDPV signal of the PHQ–Cu(II) matrix are fully investigated by variation of concentration of PHQ on 1 \((\mu\text{molL}^{-1})\) of Cu(II) shown in (Fig. 4). The variation of the peak height of CSDPV response with the concentration of PHQ is linearly, and the linearity range for determination of PHQ in the presence \((1 \mu\text{molL}^{-1})\) of Cu(II) is the range \((0.01 – 0.2 \mu\text{molL}^{-1})\).

It should be mentioned that, under the optimum conditions for determination of PHQ by using CSDPV, the detection limit was \(1 \times 10^{-8} \text{ molL}^{-1}\). While, in the case of determination of Cu(II) as PHQ–Cu(II), the linearity range for determination of Cu(II) in presence of \((10 \mu\text{molL}^{-1})\) of PHQ is the range \((0 – 4 \mu\text{molL}^{-1})\), and the detection limit was \(1 \times 10^{-7} \text{ molL}^{-1}\).
Effect of Interfering Ions on PHQ–Cu(II) Chelates

The effects of interference of cations, anions, organic additive and/or insulating matrix on the response of the peak height of the DPCSV of the chelated Cu(II) with PHQ matrix were examined. The recovery percentage (%) of the peak height relative to the peak height of (1 µmolL⁻¹) of Cu(II) and (2 µmolL⁻¹) of PHQ was recorded and plotted as (Fig. 5). It was found that, in the presence of 1.0 and 10.0 µmolL⁻¹ mixture of K(I), Na(I), Ca(II), Ba(II), Mg(II), Mn(II), Pb(II), Cd(II), Co(II), Ni(II), and Zn(II), the peak height decreases by 6.25% and 9.37% respectively. The results indicated that the degree of recovery of 0.1 µmolL⁻¹ PHQ–Cu(II) system in the presence of metals ions mixture is in the range of 90.63 and 93.75% in presence that metals ions mixture. The degree of recovery of 0.1 µmolL⁻¹ PHQ–Cu(II) system in the presence of 100 µM mixture of CHCOO⁻, BO₄²⁻, PO₄³⁻, SO₄²⁻, NO₃⁻, and CO₃²⁻ is about 98.65%. This result refers that all of these anions does not competitor with the adsorpbability of the investigated species at the mercury electrode surface. Addition of 10 and 100 µmolL⁻¹ of glutaric acid, as an example for amino acids, to 0.1 µmolL⁻¹ of PHQ–Cu(II) system the response current due to the reduction of Cu(II) chelated is decreased about 2.13%

Although the addition of amino acid (1000 times), the degree of PHQ recovery is about 97.61%. It is interesting to note that the addition of Triton X-100 does not highly affected on the cathodic reduction peak height (iₚ) of the chelated Cu(II) ion, whereas the degree of the recovery about 97.25%. However, in the presence of EDTA (10 mmolL⁻¹), the iₚ of the chelated Cu(II) signal is almost diminishes and the degree of the recovery of PHQ is ~ 24.14%. This dramatic effect is due to the very strong chelating efficiency of EDTA towards Cu(II) than PHQ matrix.

Effect of Insulating Matrix

In the presence of insulating matrix such as poly (vinyl alcohol) (PVA) in the concentration range 10 ~100 µmolL⁻¹, the degree of the recovery of PHQ–Cu(II) system (0.10 : 0.05 µmolL⁻¹) was found to be closed 93 %, as shown in (Fig. 6) and peak potential of the CSDPV peak of the chelated
Cu(II) is almost constants in the presence of PVA matrix. While, in presence of poly (vinyl pyrrolidine) (PVP) with the concentration (100 µmol L⁻¹) the reduction peak height (iₚ) of chelated Cu(II) with PHQ was higher than the reduction peak height (iₚ) of PHQ–Cu(II) system alone. This means that the PVP matrix enhanced the absorbability at the mercury electrode surface which caused increased in the peak high of chelated Cu(II), The calibration plot of reduction peak height (iₚ / mA) was increased with increasing the PHQ concentration.

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References


