

Characterization and Stripping Voltammetric Study of Cu (II) Ions on Polypyrrole Incorporating Sulfosalicylic Acid Modified Gold Disk Electrode in Aqueous Medium

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Abstract: *The electrochemical characterization of copper (II)-5-sulfosalicylic acid complex [Cu(II)-SSA] in aqueous trifluoroacetic acid medium was studied by different techniques (linear sweep, cyclic voltammetry, and chronocoulometry) on gold-disk modified with polypyrrole 5-sulfosalicylic acid composite. Addition of 5-sulfosalicylic as a complexing agent during polypyrrole film formation substantially enhances the current signal. The composition of the complexes determined by plotting the peak current versus molar ratio, [SSA]/[Cu(II)] reveals the formation of two types of complex of 1:1 and 1:2 composition. Stripping voltammetric response of [Cu(II)-SSA] complex in aqueous medium was reported and discussed. The optimum conditions, preconcentration potential, preconcentration time and scan rate were investigated and reported.*

Keywords: *Polmerization, Sulfosalicylic acid, voltammetry, preconcentration, electrochemistry*

1. INTRODUCTION

Electroactive conducting polymers, their ease of processing together with their chemically tunable properties, have assumed a great importance in several technologies such as display devices, Solar cells, Gas sensors and Actuators [1]. A great number of sensing applications are designed by exploiting the nature of conducting polymers. Among the conjugating conducting polymers, polypyrrole is the most representative one for its easy polymerization and controllable property of switching it between conducting and insulating states by doping and undoping counter ions into polymer matrix, as well as its chemical and thermal stabilities. Polypyrrole, in the form of films, have been used for sensors for detection of various gases and volatile organic compounds[2, 3].

The utilization of electrochemical techniques for the synthesis and characterization of conducting polymers has become very attractive for sensor development[4-6], and in the electroanalytical application of conducting polymer by modifying the electrode with polymer carrying reagents for selective and sensitive determination of the species of interest.

Conjugated polymers, such as polypyrrole, can be oxidized and reduced in a way that is in principle similar to the redox polymers [7-10]. The oxidation or reduction of polypyrrole can be readily accomplished electrochemically. Polypyrrole films provide a multi-layered, dynamic polymeric coating which has a three-dimensional reaction zone at the electrode surface on which various chemistries such as ion exchange, complexation, precipitation and enzyme reactions can be performed.

Cyclic voltammetry, potential step experiments and coulometry have been used to investigate the electrodeposition of polypyrrole films from acidic, neutral and basic aqueous nitrate solutions and neutral media containing other anions[11]. It is shown that the initial step in the formation of all films is a nucleation process and, indeed, all the electrochemical data resembles that for the nucleation and growth of the metal film. [12-15].

Polypyrrole electrode is used as a substrate for the deposition and stripping of mercury ions from solution[16]. Aspects of the deposition and stripping behaviour, both for the polymer in its underivatized state and for the poly (pyrrole-N-carbodithioate) moiety are compared with the response on bare platinum. The polymer electrodes exhibit significant advantages over the bare platinum surface. The improved stability and reproducibility of surface states has been demonstrated.

The electrochemical polymerisation of pyrrole-substituted cobalt tetraphenylporphine complex on a vitreous carbon electrode has been performed in acetonitrile+ tetrabutylammonium tetrafluoroborate solution[17]. The redox properties of the film have been examined by cyclic voltammetry and compared to those of cobalt-porphyrin monomer in solution.

Electrochemical measurements were undertaken for the investigation of the underpotential deposition-stripping process of copper at bare and modified gold electrodes in 0.11M acetic acid, the first fraction of the European Union's Bureau Communautaire de Références (BCR) sequential extraction procedure for fractionating metals within soils and sediments[18]. Linear correlation of the electrochemical results with atomic spectroscopic results yielded the straight-line equation $y (\mu\text{g L}^{-1}) = 1.10x - 44$ (ppb) ($R = 0.992$, $n = 6$), indicating good agreement between the two methods.

One problem associated with using bare solid metal electrodes, such as gold and platinum, in stripping analysis of heavy metal ions in dilute solutions is that under potential deposition (UPD) gives multiple stripping peaks in the analysis of mixtures. These peaks are often over-lapped and cannot be conveniently used for analytical purposes. In the present investigation, the modified electrode responsible for copper (II) ions, polypyrrole film on gold electrode loaded with 5-sulfosalicylic acid as complexing agent, is used.

2. EXPERIMENTAL

2.1. Chemicals

Pyrrole (Merck) was purified by vacuum distillation and kept in dark under nitrogen atmosphere at 277 K. 5-sulfosalicylic acid (Fluka), copper nitrate (Aldrich) and trifluoroacetic acid (Merck) were used as received without further purification.

2.2. Solutions

A 0.1 mol dm^{-3} solution of 5-sulfosalicylic acid (SSA) was freshly prepared by dissolving the appropriate amount in bidistilled water. Solution of copper (II) nitrate was prepared by dissolving the required amount in trifluoroacetate buffer solution at pH 2.0. The trifluoroacetate buffer was prepared by neutralization of 0.2 mol dm^{-3} trifluoroacetic acid solution by 1.0 mol dm^{-3} NaOH free carbonate solution to obtain the required pH value.

2.3. Apparatus

All electrochemical experiments were carried out on an EG&G PAR Potentiostat / Galvanostat model 263 A. The electrochemical system was interfaced with an IBM computer. The data were captured, stored and manipulated with EG&G M270/500 software which controls the potentiostat via IEEE488 GPIB. A Consort pH-meter model P901 was used to measure the pH of solutions.

2.4. Cell and Electrode

All electrochemical experiments were carried out in conventional one-compartment glass cell at room temperature 298 K under nitrogen atmosphere. The cell contains three electrodes, a working electrode (gold-disk working electrode with area of 0.071 cm^2), a reference electrode (saturated calomel electrode (SCE) as reference electrode) and a platinum counter electrode.

2.5. Preparation of Modified Electrodes

The modified electrodes were prepared on mechanically polished gold disk as bare electrode. The bare electrode was polished mechanically several times and cleaned by thorough rinsing with bidistilled water until seems like mirror image before used. The preparation of modified gold-disk electrode takes place by polypyrrole film and polypyrrole bearing 5-sulfosalicylic acid.

2.6. Measurements

All solutions were freshly prepared, purged with pure nitrogen before measurements and all measurements were carried out at 298 K. An atmosphere of purified nitrogen was maintained above the working solution. A mechanical polishing was made for gold-disk electrode before each run to regenerate the electrodes surface. Scanning in buffer solution regenerates the modified electrode, so one can use it several times without mechanical polishing.

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of Polypyrrole-Modified Electrode Incorporating 5-Sulfosalicylic Acid as a Complexing Ligand

Cyclic voltammogram of degassed aqueous solution of 0.05 mol dm^{-3} freshly distilled pyrrole in 0.2 mol dm^{-3} trifluoroacetate buffer at pH 2.0 is recorded on a freshly polished gold electrode. A

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representative illustration is given in Fig. 1. Generally, the voltammogram shows an irreversible anodic cyclic voltammetric wave, CV. This anodic CV wave appears in the first scan at ~ 1.05 volt versus SCE, and corresponds to the oxidation of pyrrole to its radical cation[19]. The absence of its corresponding reduction CV wave is attributed to the high reactivity of the formed radical cation, which immediately couples with another pyrrole monomer to form a polymeric film on the working electrode, the gold-disk electrode. The positive potential must not be more than the beginning of the oxidation wave of pyrrole to prevent the over oxidation of the produced polymer

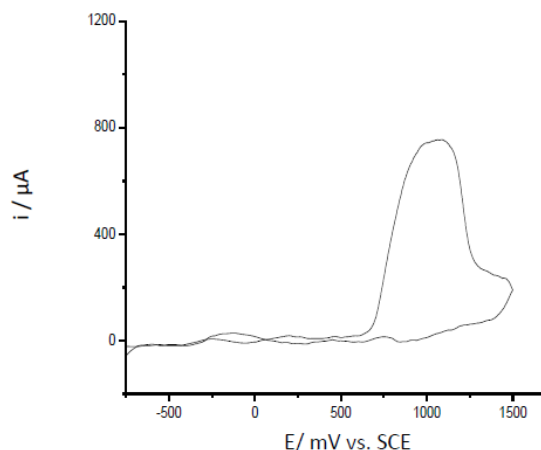
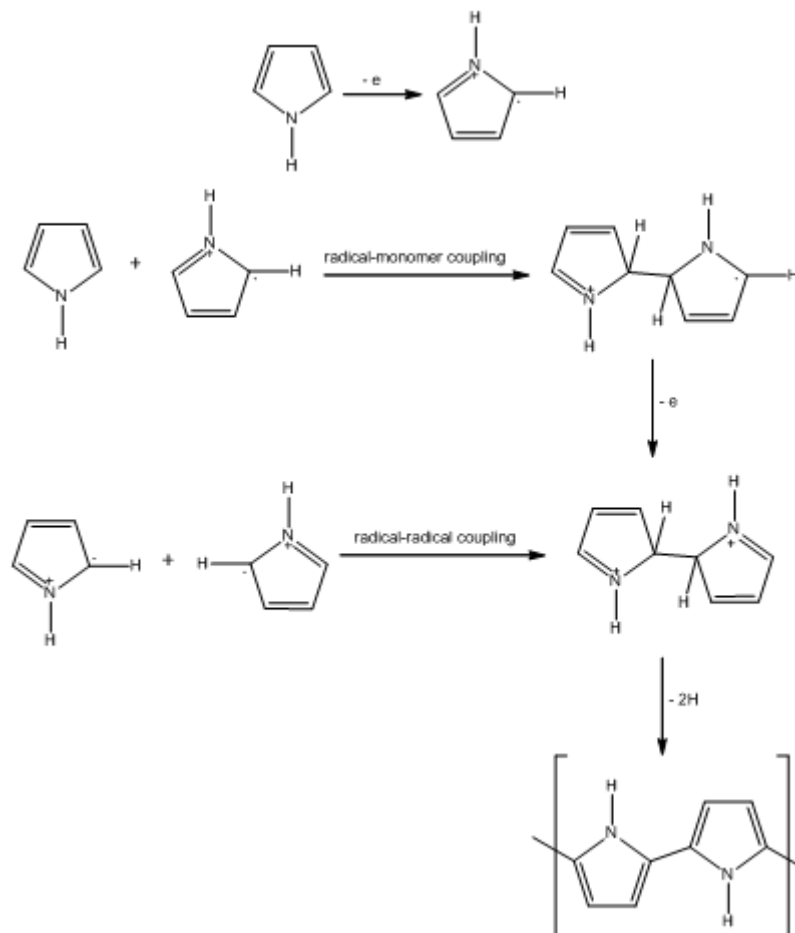


Fig1. Cyclic voltammogram of anodic oxidation for 0.05 mol dm^{-3} pyrrole/ 0.2 mol dm^{-3} trifluoroacetate buffer at pH 2.0 and scan rate of 50 mV/s

The electrochemical polymerization reaction of pyrrole at the working electrode is explained in terms of the following reaction pathway[20](see scheme 1). After the initial oxidation step, which gives the radical cation, a coupling reaction is taken place (radical-monomer or radical-radical coupling).

Scheme 1



Polypyrrole-modified electrode bearing 5-sulfosalicylic acid, SSA, was prepared on a freshly polished gold-disk electrode. The electrode was immersed in a previously degassed aqueous solution of 0.05 mol dm^{-3} freshly distilled pyrrole monomer and 0.01 mol dm^{-3} 5-sulfosalicylic acid, SSA. The modified electrode was obtained potentiostatically at a constant potential of $+0.87 \text{ V}$ for one second. The total charge passing the electrode was measured and ranged from 400 to $500 \mu\text{C}$. Assuming a small contribution from the partial overoxidation of the polypyrrole backbone; this charge was primarily associated with the oxidation of pyrrole and was used as a measure of the polymer coverage. Diaz and Kanazawa[21] who assumed that for every 24 mC.cm^{-2} of charge passed, $0.1 \mu\text{m}$ film resulted from the stoichiometry of the reaction.

A representative illustration is given in Fig. 2. The anodic CV wave appears at 1.20 V versus SCE, corresponds to the oxidation of pyrrole to its radical cation. The small corresponding reduction peak at -0.5 V is attributed to the high reactivity of the formed radical cation, which immediately couples with a pyrrole monomer to form a polymeric film on the working electrode, the gold-disk electrode.

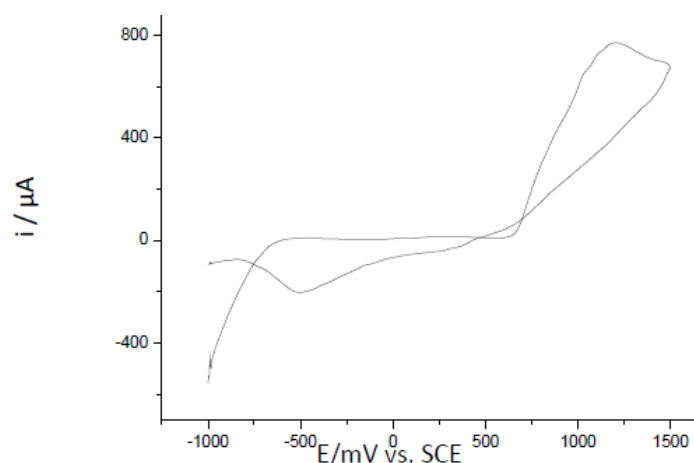


Fig2. Cyclic voltammogram of anodic oxidation for 0.05 mol dm^{-3} pyrrole/ 0.01 mol dm^{-3} aqueous solution of 5-sulfosalicylic acid at pH 2.0 and scan rate 50 mV/s

The electrochemical behaviour of polypyrrole polymer doped with 5-sulfosalicylate anion, (H_2SSA^-), as a large size dopant anion was investigated in 0.2 mol dm^{-3} trifluoroacetate buffer at pH 2.0. Typical cyclic voltammogram for polypyrrole-modified electrode bearing 5-sulfosalicylic acid, SSA, is shown in Fig. 3. It is seen that the shape of the cyclic voltammogram has a different appearance with that of polypyrrole without 5-sulfosalicylic acid. The difference in the shape reveals a dependence of the voltammetric response on the nature of the dopant anion. This would be in accord with the different situation with respect to the counter ion exchange in these films as described elsewhere[22].

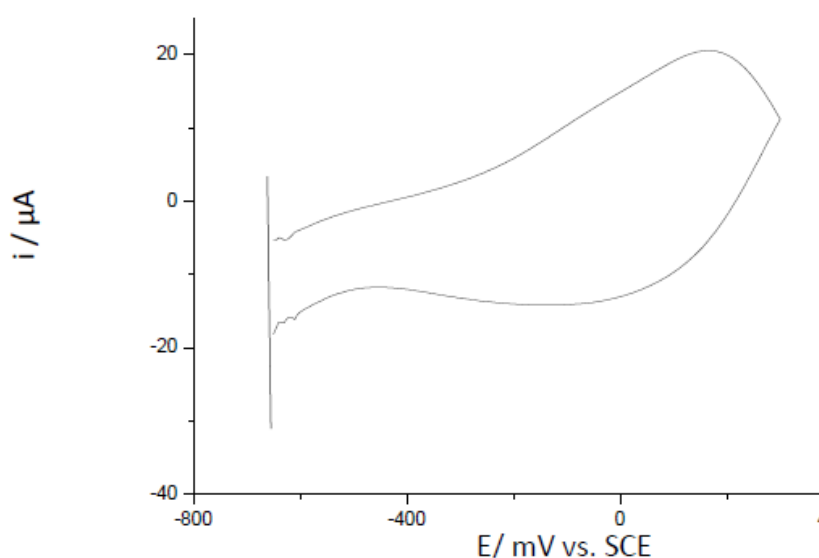
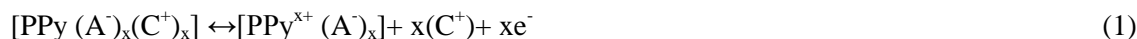


Fig3. Cyclic voltammogram for polypyrrole-modified electrode incorporated 5-sulfosalicylic acid in 0.2 mol dm^{-3} trifluoroacetate buffer solution at pH 2.0 and scan rate of 200 mV/s

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There is a very important observation one can see from the figure that smaller charging current than it observed for [PPy-(CF₃COO)] polymer. This means that the activity of the polypyrrole polymer incorporated 5-sulfosalicylate anion, [PPy-(H₂SSA)] is lower than that of polypyrrole polymer doped with trifluoroacetate anion, (CF₃COO⁻) due to the size of anion is larger in the first case.

Also, the charge/discharge process of the 5-sulfosalicylate doped polypyrrole polymer, [PPy-(H₂SSA)], electrode involves a cation insertion process for compensation. However, the synthesis of polypyrrole polymer, PPy, electrode in the presence of large size dopant anions, the anions are tightly entrapped in polypyrrole polymer backbone and the charge compensation process seems to involve incorporation of cations. This makes it difficult for anions to be involved in the redox reaction with scheme given by equation (9), and the insertion of the electrolyte cations and their ejection occur as shown by the following equation:



Where A⁻ is a dopant anion to compensate positive charges generated in the oxidized polypyrrole polymer, C⁺ is a cation to ensure the electrical neutrality of the film and x is the doping level, which is generally around 0.3.

The electrochemical properties of the polypyrrole-modified electrode bearing 5-sulfosalicylic acid, SSA, depend on the polymerization conditions and the building solution composition as shown below:

3.1.1. Effect of Scan Rate

The effect of scan rate was studied at different scan rates from 100 to 1000 mV/s. Cyclic voltammograms obtained for polypyrrole-modified electrode incorporated 5-sulfosalicylic acid, in 0.2 mol dm⁻³ trifluoroacetate buffer at pH 2.0 are shown in Fig. 4. This electrode was prepared potentiostatically at constant potential of +0.87 volt for one second from aqueous solution of 0.05 mol dm⁻³ pyrrole and 0.01 mol dm⁻³ 5-sulfosalicylic acid.

The relationship between log *i_{pa}* and log *v* is shown in Fig. 4. The result indicates that the log *i_{pa}* is correlates with the log *v* over the entire of 100 to 1000 mV/s. The linear regression line with a correlation coefficient of *r* = 0.996 is obtained with slope of 0.63. Therefore, the anodic peak current is controlled by the mass diffusion, showing a diffusion-controlled process in the solution.

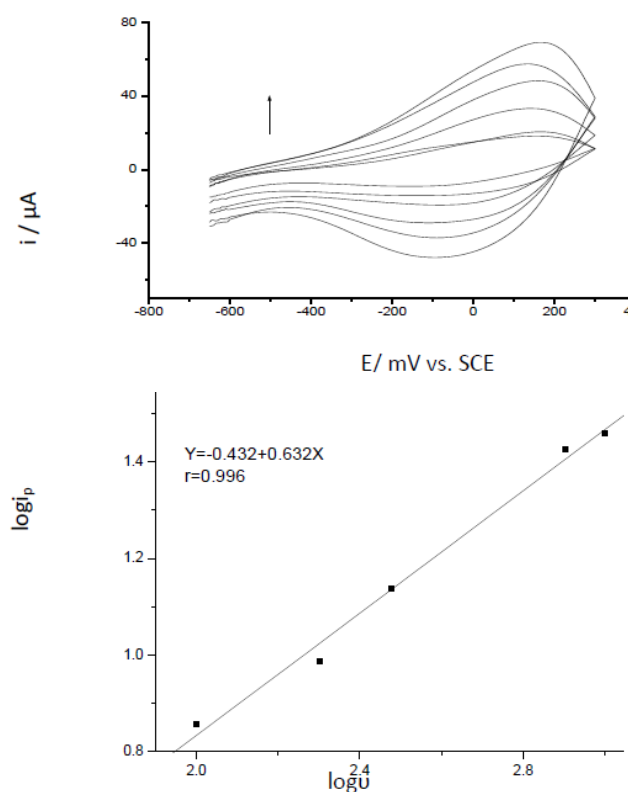


Fig4. Cyclic voltammograms for polypyrrole-modified electrode incorporated 5-sulfosalicylic acid in 0.2 mol dm⁻³ trifluoroacetate buffer at pH 2.0 and different scan rates: (1) 100; (2) 200; (3) 400; (4) 600; (5) 800 and (6) 1000 mV/s

3.1.2. Effect of Layer Thickness

The layer thickness is one of the important factors in the electrosynthesis of polypyrrole polymer electrode incorporated 5-sulfosalicylic acid, which affects the appearance and colour of the film. In general, thick films are black and thin ones are yellow. The layer thickness (as a function of time of polymerization) is studied in the range from 0.5 to 10 seconds at a constant potential of +0.87 volt from aqueous solution of 0.05 mol dm^{-3} pyrrole and 0.01 mol dm^{-3} 5-sulfosalicylic acid.

3.1.3. Effect of Multi Scan

The polypyrrole-modified electrode incorporated 5-sulfosalicylic acid, can be cycled repeatedly between the conducting (oxidized) and nonconducting (neutral) state with no significant decomposition of the polymer layer. It is evident that a negligible change on the voltammogram shape is observed. The switching is also accompanied by a reversible colour change from a pale yellow (neutral) to black (oxidized).

3.2. Stripping voltammetric study of copper (II) ions on polypyrrole-modified electrode incorporating 5-sulfosalicylic acid in aqueous medium

Polypyrrole-modified electrode incorporating with 5-sulfosalicylic acid, SSA, prepared at +0.87 volt for one second from aqueous solution of 0.05 mol dm^{-3} pyrrole/ 0.01 mol dm^{-3} 5-sulfosalicylic acid. Stripping voltammetric behaviour of copper (II) ions on the modified electrode incorporated 5-sulfosalicylic acid in aqueous medium of 0.05 mol dm^{-3} trifluoroacetate buffer solution at pH 2.0 is studied by linear sweep, cyclic voltammetry and chrono-amperometry and coulometry at 298 K. The voltammetric behaviour obtained for the present system will be discussed in detail as follows:

3.2.1. Linear Sweep Voltammetry

Linear sweep voltammetry, LSV, of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II) ions/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 on polypyrrole modified-electrode incorporated with 5-sulfosalicylic acid, SSA, is recorded in the potential range of -0.8 to $+0.3$ volt versus SCE. The effect of preconcentration potential on the response is shown in Fig. 5. As can be seen that, between -0.40 and -2.0 volt range the peak current increases on increasing the potential of the electrode towards the negative values until -1.4 volt then the peak current decreases with further increase in potential value. So at -1.4 volt value was chosen for this study.

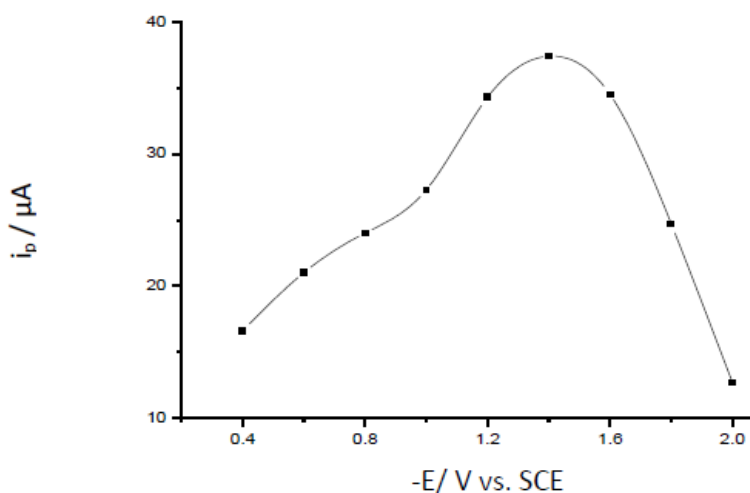


Fig5. Linear sweep voltammograms for $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II)/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 on polypyrrole-modified electrode incorporated 5-sulfosalicylic acid, preconcentration time 20 seconds and scan rate 200 mV/s

The accumulation of copper (II) ions on bare gold-disk, polypyrrole and polypyrrole incorporated 5-sulfosalicylic acid electrodes is shown in Fig. 6. An anodic peak is observed at ~ 0.1 volt versus SCE. This peak is attributed to the anodic stripping of copper (II) ions on bare gold-disk, polypyrrole and polypyrrole incorporated with 5-sulfosalicylic acid electrodes. The peak current increases by modification either with polypyrrole or polypyrrole/ 5-sulfosalicylic acid. In the last case the enhancement in peak current is larger due to the large increase in the complexation sites, the nitrogen pyrrole complexation site in addition to the salicylic acid chelation site.

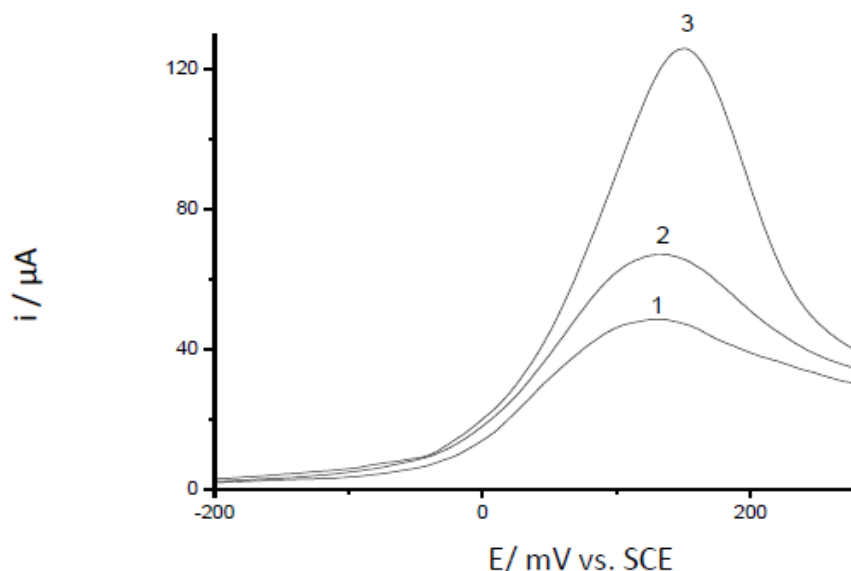


Fig6. Linear sweep voltammograms for $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper (II)/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 on (1) bare gold-disk (2) polypyrrole and (3) polypyrrole incorporated 5-sulfosalicylic acid electrodes, preconcentration time 60 seconds and scan rate 200 mV/s

The dependence of the peak current on the preconcentration time for $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II) ions on polypyrrole incorporated 5-sulfosalicylic acid electrode, preconcentration potential of -1.4 volt is shown in Fig. 7. It is clear from the figure that on increasing the preconcentration time, the LSV peak current increases with increase the preconcentration time. On further increase of time >60 seconds, the peak current decreases.

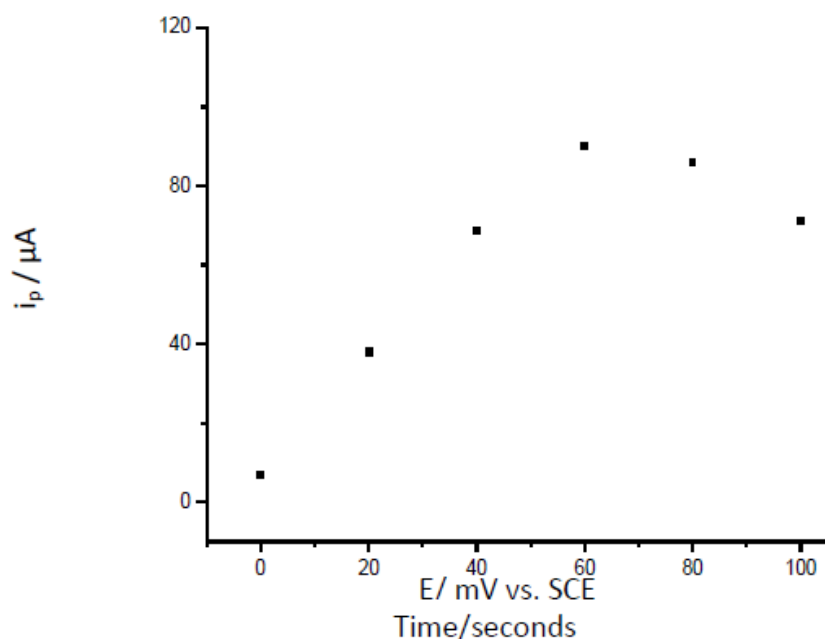


Fig7. Linear sweep voltammograms for $1 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II) ions/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 on polypyrrole-modified electrode incorporated 5-sulfosalicylic acid, preconcentration time: (1) 0, (2) 20, (3) 40 and (4) 60 seconds, preconcentration potential -1.4 volt and scan rate of 200mV/s

The effect of scan rate on the peak current response was studied using different scan rate ranging from 100 to 1000 mV/s. The voltammograms were recorded in Fig. 8. The results show that, the peak current increases with increasing scan rate.

The relation between $\log i_p$ and $\log v$ for $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II) ions on polypyrrole-modified electrode incorporated with 5-sulfosalicylic acid exhibits a straight line appearance over the range of 200 to 800 mV/s with a slope of 0.640 and regression coefficient of 0.991.

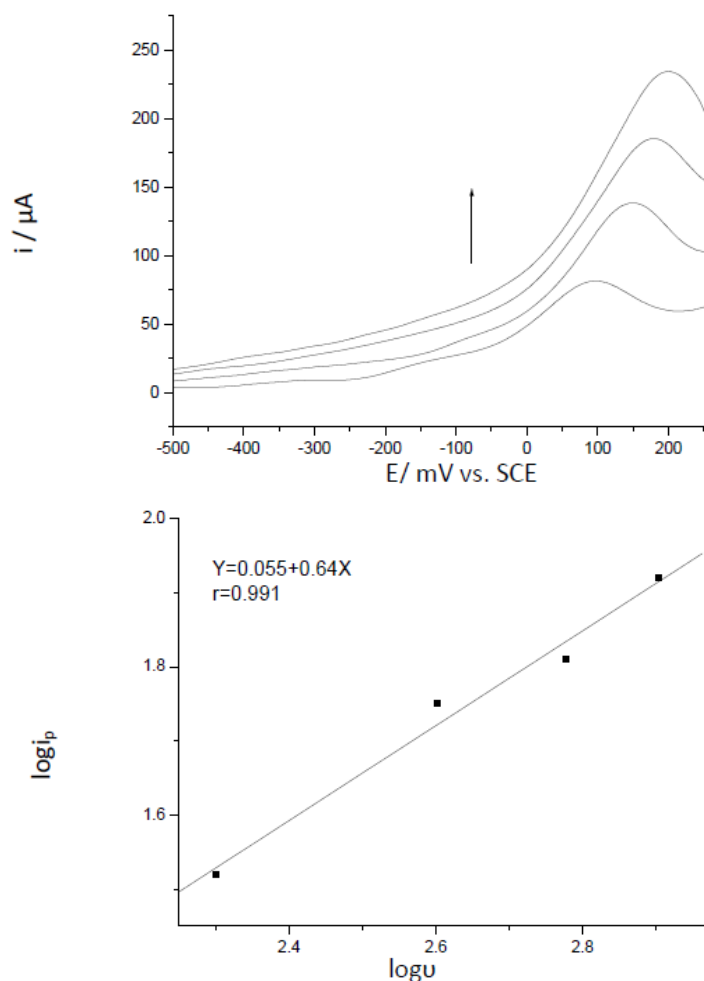
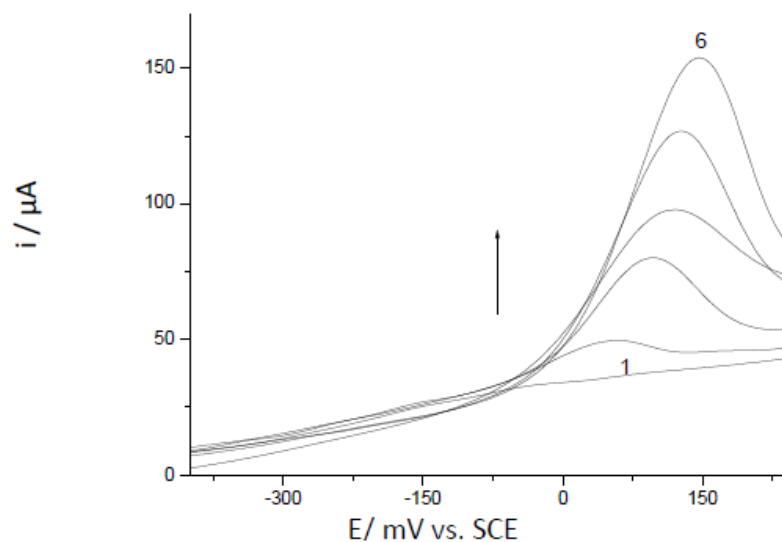


Fig8. Linear sweep voltammograms for $1 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II) ions/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 on polypyrrole-modified electrode incorporated 5-sulfosalicylic acid, preconcentration time 20 seconds, preconcentration potential -1.4 volt and scan rate: 100 (1) 200, (2) 400, (3) 600 and (4) 800 mV/s

From the above results, The optimum conditions of polypyrrole- modified electrode bearing 5-sulfosalicylic acid, for copper(II) determination are: preconcentration potential = -1.4 volt, preconcentration time = 60 seconds and scan rate = 200 mV/s. Fig. 9 shows a typical voltammograms for different copper concentrations on polypyrrole-modified electrode bearing 5-sulfosalicylic acid. It is revealed that with increasing the concentration of copper(II), the peak current response increase. A linear relationship was observed in the concentration range of 1.0×10^{-5} to $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II) with a correlation coefficient of 0.993.



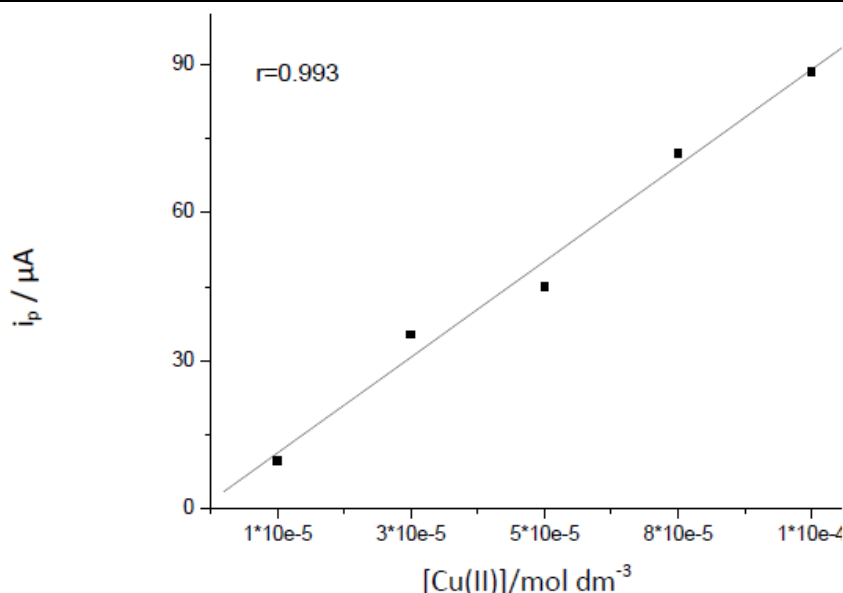


Fig9. Linear sweep voltammograms for different copper concentrations on polypyrrole-modified electrode incorporated 5-sulfosalicylic acid, preconcentration time 60 seconds, preconcentration potential -1.4 volt and scan rate 200 mV/s (1) zero, (2) 1×10^{-5} , (3) 3×10^{-5} , (4) 5×10^{-5} , (5) 8×10^{-5} and (6) 1×10^{-4} mol dm⁻³

On addition of 5-sulfosalicylic acid with concentration varying from 0.5 to 2.5 molar ratio, [SSA]/[Cu(II)], an enhancement of peak current for the two LSV waves is observed. Thus, the reaction between copper(II) ions and SSA is rapid. The LSV voltammograms obtained are recorded in Fig. 10.a The two LSV waves are attributed as above to the anodic stripping of Cu(II) complexed with SSA of different compositions presumably [Cu(II)-SSA] and [Cu(II)-(SSA)₂], respectively. The composition of the complexes were determined by plotting the peak current versus molar ratio, [SSA]/[Cu(II)]. The results are presented in Fig.10.b It is seen that the peak current for the first wave increases on increasing the mole ratio and changes the slope of variation at mole ratio of 1.0. This is indicative of formation of a complex with a composition of 1:1, [Cu(II)-SSA] under such conditions. On the other hand, for the second LSV wave, the peak current increases on increasing the mole ratio [SSA]/[Cu(II)]. The graph obtained has two breaks at mole ratio of 1.0 and 2.0. This reveals the formation of two types of complex of 1:1 and 1:2 composition. As the preconcentration of copper(II) takes place at -0.80 volt, which is far on the negative side of the copper reduction peak, the preconcentration mechanism of copper is mainly based on electrolysis. However, the contribution from the chelating process between 5-sulfosalicylic acid and copper(II) cannot be ignored.

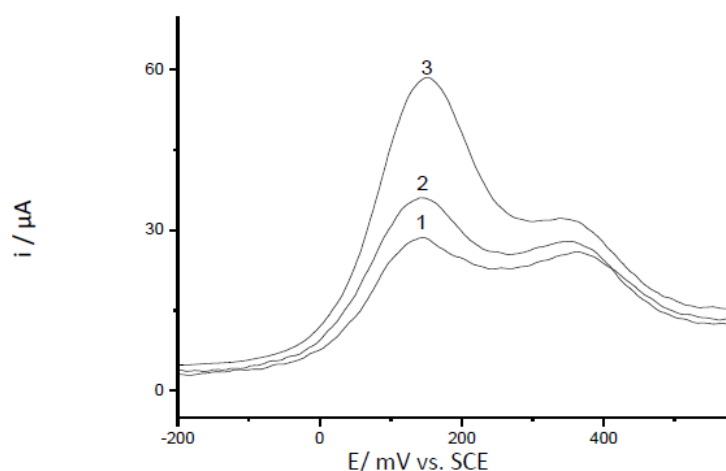


Fig10.a Linear sweep voltammograms for different molar ratio of [SSA]/[Cu(II)] in 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0, where $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ Cu(II) and: (1) zero (2) 0.5×10^{-4} and (3) $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ SSA as a repetitive example, preconcentration time = 50 seconds, preconcentration potential = -0.8 volt and scan rate of 200 mV/s.

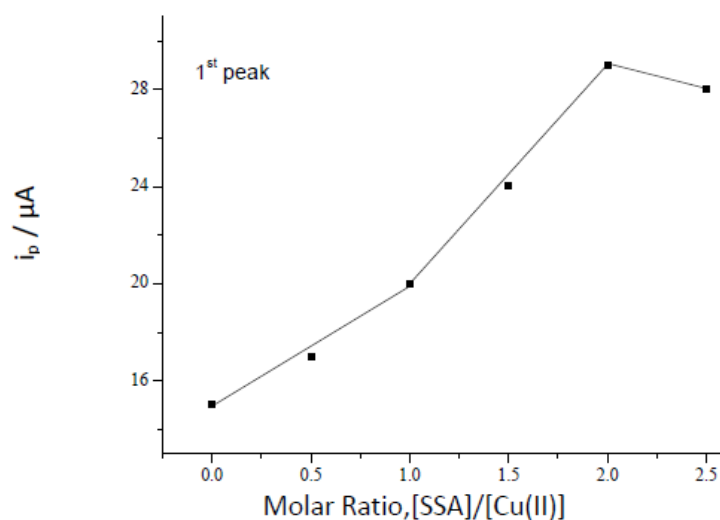
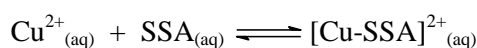
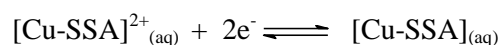


Fig10.b A plot of the peak current versus molar ratio, [SSA]/[Cu(II)]

-In solution:



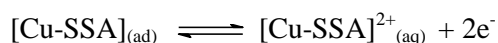
-At preconcentration potential, -0.80 volt:



-On stirring for 50 seconds at pH 2.0:

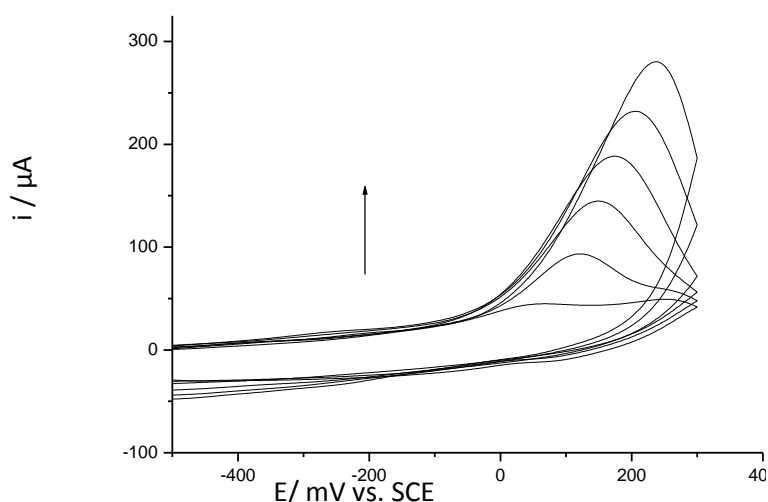


-At stripping peak potential:



3.2.2. Cyclic Voltammetry

Cyclic voltammetric behaviour of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II) ions/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 on polypyrrole- modified electrode incorporated with 5-sulfosalicylic acid was studied and the results are presented in Fig. 11. The stripping cyclic voltammogram, CV, shows an irreversible anodic wave with peak current potential of ~ 0.1 volt versus SCE, since its cathodic counterpart is lacking. This CV wave is, as concluded above, due to the anodic stripping of the copper(II) ions on polypyrrole-modified electrode incorporated with 5-sulfosalicylic acid. On increasing the preconcentration time, the current of the CV wave increase.



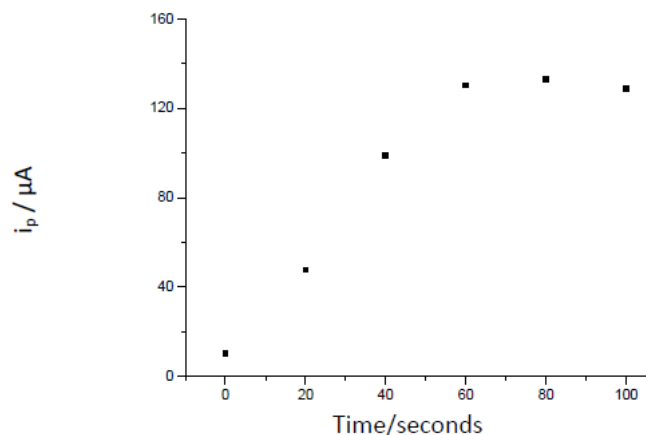


Fig11. Cyclic voltammograms for $1 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II) ions/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 on polypyrrole-modified electrode incorporated 5-sulfosalicylic acid, preconcentration time: 0, 20, 40, 60, 80 and 100 seconds, respectively, preconcentration potential -1.4 volt and scan rate 200 mV/s

Cyclic voltammograms of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ Cu(II) ions at different scan rates, ν , (100 to 1000 mV/s), after preconcentration time 20 seconds and preconcentration potential of -1.4 volt are recorded in Fig. 12. From these cyclic voltammograms, it is clear that the CV wave appear to be electrochemically irreversible, since it lack its cathodic counter-part. The peak current of the CV wave increases on increasing scan rate.

Fig. 12 The relation between $\log i_p$ and $\log \nu$ for the subject system. A straight line was obtained over the entire range of 200 to 800 mV/s with a slope of 0.714 and correlation coefficient 0.969.

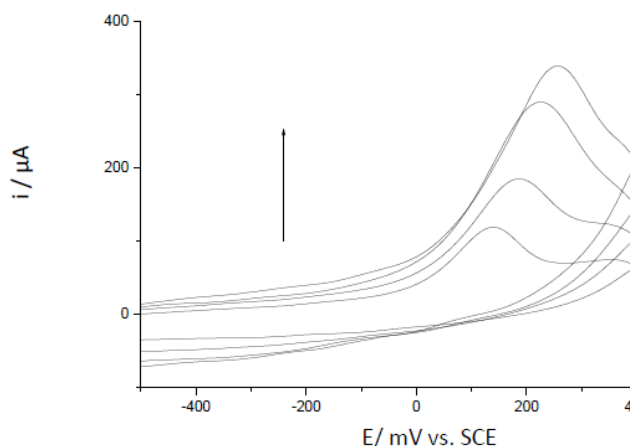


Fig12. Cyclic voltammograms for $1 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II) ions/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 on polypyrrole-modified electrode incorporated 5-sulfosalicylic acid, preconcentration time = 20 seconds, preconcentration potential -1.4 volt and scan rate: (1)200, (2) 400, (3) 600 and (4) 800 mV/s

3.2.3. Chronoamperometry

Chronoamperograms of polypyrrole-modified electrode incorporated with 5-sulfosalicylic acid in $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II)/ 0.05 mol dm^{-3} trifluoroacetate aqueous buffer solutions at pH 2.0 are recorded. A representative illustration is given in Fig. 13. For the entire range of duration time used, the electrode potential is stepped from an initial value $E_i = -0.20$ volt to a final value $E_f = +0.15$ volt. The potential was held at E_f for a time τ after which it was then stepped back to E_i and maintained there for the same time interval. The anodic chronoamperometric data were analyzed using Cottrell equation (2)[23].

$$i(t < \tau) = \frac{nFAD_0^{1/2}C_0^*}{\pi^{1/2}t^{1/2}} \quad (2)$$

Plots of i^a versus $t^{-1/2}$ for each value of the switching time, τ , gave a straight lines with correlation coefficient of 0.999 for all duration times used, which does not pass through the origin as shown in

Fig. 14. This behaviour reveals that, the anodic wave of copper(II) ions on polypyrrole-modified electrode incorporated with 5-sulfosalicylic acid is adsorption-controlled process over the entire range of the duration time (1 to 5 seconds).

Cottrell equation, equation (2) can also be used to identify the nature of the cyclic voltammetric wave. The plot of $it^{1/2}$ versus time, t , does not give horizontal lines parallel to the time axis for all duration times used as shown in Fig. 15 This behaviour supports the above conclusion that, the cyclic voltammetric wave has an adsorption nature.

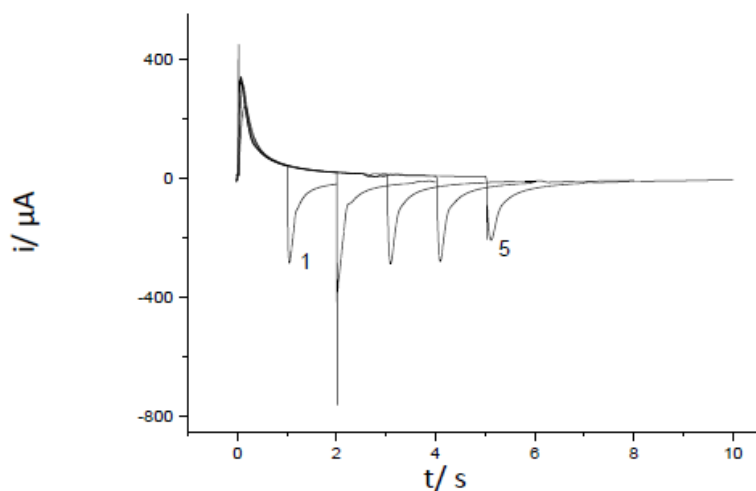


Fig13. Chronoamperograms of polypyrrole-modified electrode incorporated 5-sulfosalicylic acid in 1.0×10^{-4} mol dm^{-3} copper(II)/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0, at different duration times: (1) 1; (2) 2; (3) 3; (4) 4 and (5) 5 seconds

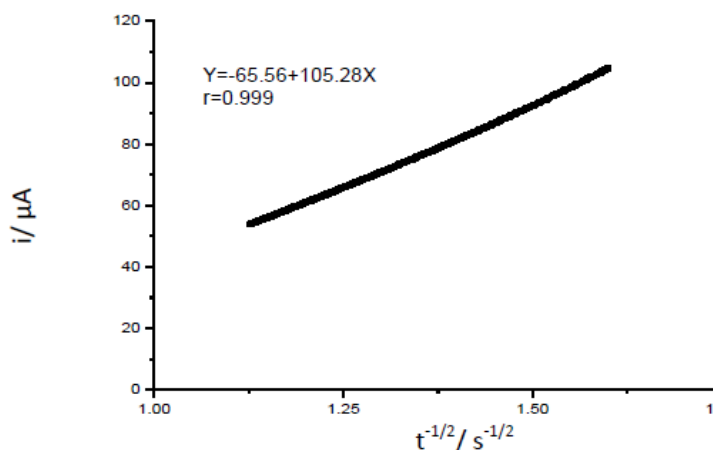


Fig14. Dependence of anodic peak current on $t^{-1/2}$ for polypyrrole-modified electrode incorporated 5-sulfosalicylic acid in 1.0×10^{-4} mol dm^{-3} copper(II)/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 and duration time of 2 seconds

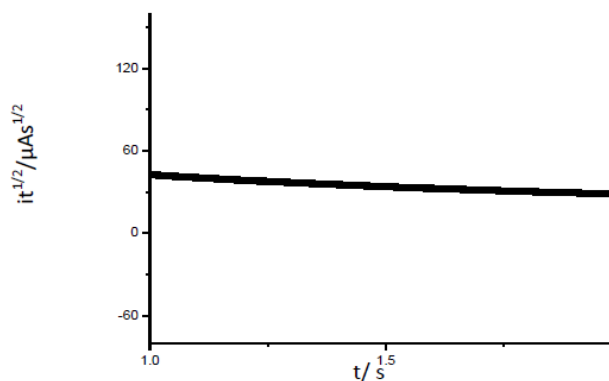


Fig15. Plot of $it^{1/2}$ versus t for polypyrrole-modified electrode incorporated 5-sulfosalicylic acid in 1.0×10^{-4} mol dm^{-3} copper (II)/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 and duration time of 2 seconds

3.2.4. Chronocoulometry

Chronocoulometric data of polypyrrole-modified electrode loaded with 5-sulfosalicylic acid in $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper (II)/ 0.05 mol dm^{-3} trifluoroacetate aqueous buffer solutions at pH 2.0, at different duration times (1 to 5 seconds) are shown in Fig. 16. The electrode potential is stepped from -0.2 volt to +0.15 volt. The potential was held at +0.15 volt for a duration time, τ , after which it was stepped back to -0.2 volt and maintained there for the same time interval. The charge that passes through the electrode during each of the time intervals is measured. On analyzing the anodic chronocoulograms using equation (2), it is seen that the charge $Q(t)$ has a direct proportionality to the square of time, $t^{1/2}$. Linear least-squares lines are obtained for the plots of $Q_c(t)$ versus $t^{1/2}$ with correlation coefficients of $r = 0.9999$ for different duration times (c.f. Fig. 17). The double layer charge of the cyclic voltammetric wave is determined from the intercepts of the obtained lines, according to equation (7), and is found to be $46.896 \mu\text{C}$.

The chronocoulometric data of Cu (II) ions on the subject polypyrrole modified can also be analyzed using equations (3) and (4) [24-27].

$$Q(t < \tau) = \frac{2nFAD_0^{1/2}C_0}{\pi^{1/2}} t^{1/2} + Q_{dl} + nFA \Gamma \tag{3}$$

$$Q_r(t) = \frac{2nFAD_0^{1/2}C_0}{\pi^{1/2}} \theta + Q_{dl} \tag{4}$$

Plotting $Q_f(t < \tau)$ vs. $t^{1/2}$ and $Q_r(t > \tau)$ vs. θ affords good straight lines with regression coefficients: 0.9986 and 0.9995 (c.f. Fig. 18). They have different slopes and intersect each other's above the t-axis. This confirms that Cu (II) ions are adsorbed. Furthermore, the amount of the adsorbate, the surface excess Γ_0 , is determined from the difference in the intercepts for the forward and reverse Anson plots, equations (7) and (8), which is simply, $nFA\Gamma_0$. This difference cancels Q_{dl} and leaves only a net faradiac charge due to adsorbate. The charge obtained for concentration $1 \times 10^{-4} \text{ mol dm}^{-3}$ of Cu(II) ions on the subject electrode is found to be $1.459 \mu\text{C cm}^{-2}$ which is equivalent to surface excess, Γ_0 , of $3.53 \times 10^{-5} \text{ mol cm}^{-2}$.

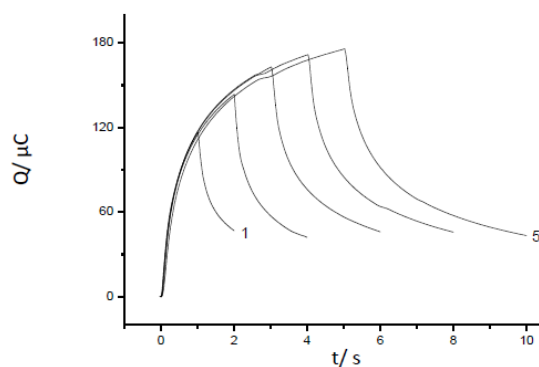


Fig16. Chronocoulograms for polypyrrole-modified electrode incorporated 5-sulfosalicylic acid in $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II)/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0, at different duration times: (1) 1; (2) 2; (3) 3; (4) 4 and (5) 5 seconds

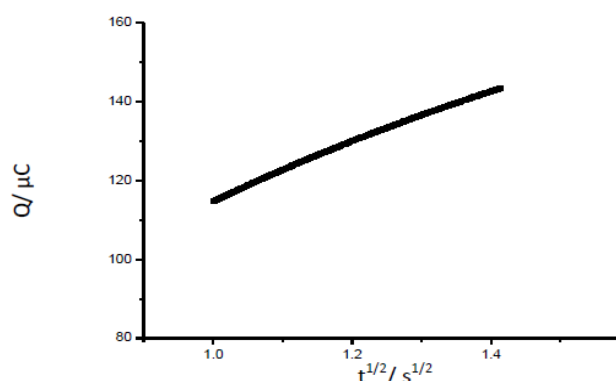


Fig17. Dependence of charge on $t^{1/2}$ for polypyrrole-modified electrode in $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II)/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 and duration time of 2 seconds

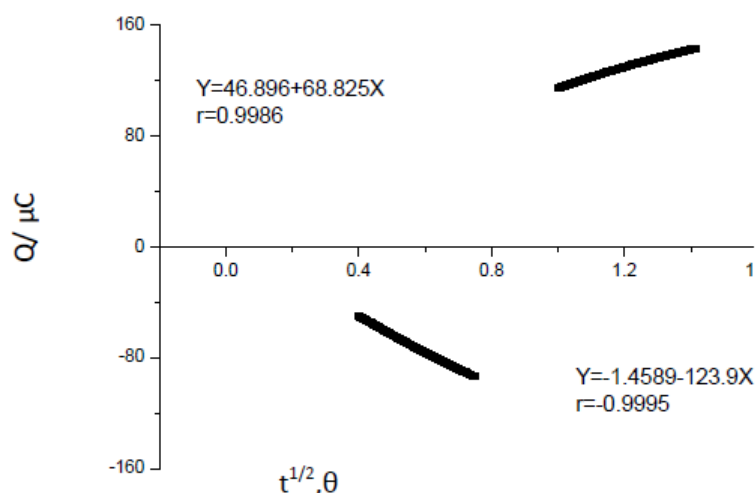


Fig18. Double-potential step chronocoulometric dependence of Q_f on $t^{1/2}$ and Q_r on θ for polypyrrole-modified electrode incorporated 5-sulfosalicylic acid in 1.0×10^{-4} mol dm^{-3} copper(II)/ 0.05 mol dm^{-3} trifluoroacetate buffer at pH 2.0 and duration time of 2

REFERENCES

- [1] Mosayebzadeh Z, Ansari R, Mohammad-khah A, Arvand M. Electrochemical preparation of a copper ion selective electrode based on polypyrrole conducting polymer doped with Ponceau 4R Azo dye. *Anal Bioanal Electrochem.* 2013; 5:109-29.
- [2] Ganjali MR, Ghafarloo A, Faridbod F, Norouzi P. Copper-selective PVC membrane sensor. *Int J Electrochem Sci.* 2012; 7:3706-16.
- [3] Stankovic D, Roglic G, Jovic M, Andjelkovic I, Mutic J, Manojlovic D. New potentiometric sensor for copper determination in waste waters based on a new type of modified GC electrode. *Anal Bioanal Electrochem.* 2012; 4:238-45.
- [4] Pankaj K, Kumar SH, Sukhjeet K. Conducting polymer based potentiometric sensors. *Research Journal of Chemistry and Environment.* 2012; 16:125-33.
- [5] Michalska A. All-Solid-State Ion Selective and All-Solid-State Reference Electrodes. *Electroanalysis.* 2012; 24:1253-65.
- [6] Jeong E-S, Lee H-K, Ahmed MS, Seo H-R, Jeon S-W. Copper (II) selective PVC membrane electrodes based on Schiff base 1, 2-Bis (E-2-hydroxy benzylidene amino) anthracene-9, 10-dione complex as an Ionophore. *Bulletin of the Korean Chemical Society.* 2010; 31:401-5.
- [7] Bredas JL, Street GB. Polarons, bipolarons, and solitons in conducting polymers. *Accounts of Chemical Research.* 1985; 18:309-15.
- [8] Chandler G, Pletcher D. The electrodeposition of metals onto polypyrrole films from aqueous solution. *Journal of applied electrochemistry.* 1986; 16:62-8.
- [9] Nofle R, Pletcher D. The mechanism of electrodeposition of composite polymers including polypyrrole. *Journal of electroanalytical chemistry and interfacial electrochemistry.* 1987; 227:229-35.
- [10] Shen H, Mark JE, Seliskar CJ, Mark Jr HB, Heineman WR. Stripping voltammetry of copper and lead using gold electrodes modified with self-assembled monolayers. *Journal of Solid State Electrochemistry.* 1997; 1:241-7.
- [11] Asavapiriyant S, Chandler G, Gunawardena G, Pletcher D. The electrodeposition of polypyrrole films from aqueous solutions. *Journal of electroanalytical chemistry and interfacial electrochemistry.* 1984; 177:229-44.
- [12] Dong S, Che G. An electrochemical microsensor for chloride. *Talanta.* 1991; 38:111-4.
- [13] Dong S, Sun Z, Lu Z. Chloride chemical sensor based on an organic conducting polypyrrole polymer. *Analyst.* 1988; 113:1525-8.
- [14] Hulanicki A, Michalska A, Lewenstam A. Bifunctionality of chemical sensors based on the conducting polymer polypyrrole. *Talanta.* 1994; 41:323-5.

- [15] Mohadesi A, Salmanipour A, Mohammadi SZ, Pourhatami A, Taher MA. Stripping voltammetric determination of copper (II) on an overoxidized polypyrrole functionalized with Nitroso-R. *Journal of the Brazilian Chemical Society*. 2008; 19:956-62.
- [16] Imisides M, Wallace G. Deposition and electrochemical stripping of mercury ions on polypyrrole based modified electrodes. *Journal of electroanalytical chemistry and interfacial electrochemistry*. 1988; 246:181-91.
- [17] Armengaud C, Moisy P, Bedioui F, Devynck J, Bied-Charreton C. Electrochemistry of conducting polypyrrole films containing cobalt porphyrin. *Journal of electroanalytical chemistry and interfacial electrochemistry*. 1990; 277:197-211.
- [18] Herzog G, Beni V, Dillon PH, Barry T, Arrigan DW. Effect of humic acid on the underpotential deposition-stripping voltammetry of copper in acetic acid soil extract solutions at mercaptoacetic acid-modified gold electrodes. *Analytica chimica acta*. 2004; 511:137-43.
- [19] Heinze J. Electronically conducting polymers. *Electrochemistry IV: Springer*; 1990. p. 1-47.
- [20] Evans GP. The electrochemistry of conducting polymers. *Advances in electrochemical science and engineering*. 1990; 1:1-74.
- [21] Diaz A, Kanazawa K. Polypyrrole: an electrochemical approach to conducting polymers. *Extended Linear Chain Compounds: Springer*; 1983. p. 417-41.
- [22] Diaz AF, Castillo JI, Logan J, Lee W-Y. Electrochemistry of conducting polypyrrole films. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*. 1981; 129:115-32.
- [23] Bard AJ, Faulkner LR, Leddy J, Zoski CG. *Electrochemical methods: fundamentals and applications: Wiley New York*; 1980.
- [24] Alberts GS, Shain I. Electrochemical Study of Kinetics of a Chemical Reaction Coupled between Two Charge Transfer Reactions. Potentiostatic Reduction of p-Nitrosophenol. *Analytical Chemistry*. 1963; 35:1859-66.
- [25] Anson FC. Innovations in the Study of Adsorbed Reactants by Chronocoulometry. *Analytical Chemistry*. 1966; 38:54-7.
- [26] Christie JH, Osteryoung RA, Amson FC. Application of double potential-step chronocoulometry to the study of reactant adsorption. theory. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*. 1967; 13:236-44.
- [27] Anson FC. Patterns of ionic and molecular adsorption at electrodes. *Accounts of Chemical Research*. 1975; 8:400-7.