Nigerian Research Journal of Chemical Sciences (ISSN: 2682-6054)
Volume 12, Issue 2, 2024

# KINETIC STUDIES OF COBALTOCENIUM HEXAFLUOROPHOSPHATE AT BULK BISMUTH ELECTRODES

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***Accepted: October 31, 2024. Published Online: November 6, 2024***

## ABSTRACT

The aim of this study was to estimate the value of standard rate constant for cobaltocenium hexafluorophosphate from reduction of the cobaltocenium cation using bismuth bulk electrodes. Cyclic voltammetry was used to study the cobaltocenium cation/cobaltocene ($CoCp_2^+/CoCp_2$) redox couple in acetonitrile/tetrabutyl ammonium hexafluorophosphate ($AN/TBAPF_6$) electrolyte mixture at bismuth electrodes. The peak current ratio was less than unity just as the potential peak separation was about 130 mV. Estimates of standard rate constants ($k^o$) were made from electrochemical impedance spectroscopy (EIS) measurements but the apparent values of the rate constant varied with concentration. The highest value of $1.39 \times 10^{-3}$ $cms^{-1}$ was observed for the 2 mM concentration and the lowest value of $2.59 \times 10^{-4}$ cm $s^{-1}$ for the 10 mM concentration. The decrease in apparent rate constant with increase in concentration suggests an electrode fouling effect due to adsorbed reaction products. Therefore the potential dependence of the rate of electron transfer in this compound could not be reliably measured at bismuth electrodes and the electron transfer process appeared more complex than an outer sphere reaction. From these findings therefore, the $CoCp_2^+/CoCp_2$ redox couple falls short of being recommended as a reference system at Bi electrodes based on the conditions for a one-electron transfer process. Bismuth electrodes were however used successfully to confirm the quasi-reversible behaviour of cobaltocenium.

**Keywords**: Bulk bismuth electrodes, cyclic voltammetry, electrochemical impedance spectroscopy, Randles circuit, standard rate constants.

## INTRODUCTION

The inclusion of cobaltocenium cation|cobaltocene in the search for reference redox couples followed the IUPAC recommendation [1] that another metallocene, the ferrocene|ferricenium redox couple be used as a reference redox system for non-aqueous solvents. The cobaltocenium cation or bis(cyclopentadienyl)cobalt(III) cation is reported to undergo reversible one-electron reduction at some noble metal electrodes [2]. The reduction equation is represented by

$$[Co(C_5H_5)_2]^+ + e^- \rightleftharpoons [Co(C_5H_5)_2] \qquad (1)$$

In their investigations, Stojanovic and Bond [2] studied the voltammetric behaviour of cobaltocenium cation ($CoCp_2^+$) reduction in the aprotic solvents of acetonitrile (AN) and dichloromethane as well as the protic solvents of ethanol and water, using a variety of supporting electrolytes. They employed the conventionally sized working electrodes of hanging mercury drop electrode (HMDE), gold (Au), platinum (Pt) and glassy carbon (GC); as well as their microelectrodes. The voltammetric reduction behaviour of $CoCp_2^+$ was not similar in the solvents and at the electrodes of investigation. Whereas the peak current ratios approximated to unity at the scan rate of 100 mV $s^{-1}$ for all the electrodes in acetonitrile, dichloromethane and ethanol, values far less than one were recorded for water. In all cases of their investigation, the potential peak separation was in excess of the 59 mV expected of a one-electron reversible process at 298 K. Unlike the measurements carried out in other solvents, much lower concentrations of $CoCp_2^+$ and slow scan rates of the order of 10 mV $s^{-1}$ were recommended if the $CoCp_2^+/CoCp_2$ couple is to be used as a reference system for water. Despite some identified shortcomings, the workers recommended the use of $CoCp_2^+/CoCp_2$ as a redox reference system 'under certain specified conditions'.

Other researchers [3 – 6] have studied the voltammetric reduction of $CoCp_2^+$ in ionic liquids, salts that exist in the liquid phase at and around 298 K. Because the room temperature of most laboratory working environments is about 298 K, these compounds are popularly referred to as room temperature ionic liquids (RTILs). Rogers and co-workers [3] are particularly interested in RTILs because of their very low volatility which makes their working environment relatively safe due to absence of organic vapour, and of their high conductivity which does not necessitate the use of supporting electrolytes, among others. Their main focus in the study of the $CoCp_2^+/CoCp_2$ is on diffusion coefficients and viscosity variations in RTILs in line with Stokes–Einstein equation (2) in which the diffusion coefficient D varies inversely as the viscosity $\eta$.

$$D = \frac{k_B T}{6\pi\eta\alpha} \qquad (2)$$

where:

D = diffusion coefficient; $K_B$ = Boltzmann's constant; T = absolute temperature;

η = dynamic viscosity of the medium, and α = charge transfer coefficient.

All these researchers recommended $CoCp_2^+/CoCp_2$ as a redox reference system based on the results of their investigations.

In this work, cyclic voltammetry was used to study the $CoCp_2^+/CoCp_2$ couple in AN/$TBAPF_6$ and the best voltammograms were obtained at scan rate of 10 mV $s^{-1}$ at both Bi and Pt electrodes. Beyond this scan rate, it became impossible to locate the cathodic and anodic peaks as the peaks disappeared. Interestingly, $TBAPF_6$ which was used as supporting electrolyte here did not feature in any of the research works cited above, for a favourable comparison to be made.

Bismuth bulk electrodes have been chosen for this study in view of their potential replacement for mercury electrodes because of the desirable properties of bismuth outlined elsewhere [7, 8]. The aim of this study is to investigate the potentials of the cobaltocenium/cobaltocene redox couple as a reference system, using bismuth bulk electrodes, with particular focus on standard rate constant of electron transfer.

## MATERIALS AND METHODS

### *Reagents*

Bi powder (purity >99.999%) of particle size 150 mm was obtained from Goodfellow Cambridge Limited, England. Tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) (≥ 99.0% purity), of Fluka analytical, was purchased from Sigma Aldrich, UK, and used without further treatments. Acetonitrile (AN), $CH_3CN$, was purchased from Sigma Aldrich, Gillingham, UK. Cobaltocenium hexafluorophosphate (98% purity) was used as purchased from Sigma Aldrich, UK.

### *Preparation of Reagents and Construction of Bismuth Electrodes*

The supporting electrolyte of $TBAPF_6$/AN was prepared by dissolving 9.6858 g of $TBAPF_6$ (molar mass = 387.43 g) in AN to give 250 mL of the 100 mM concentration. Similarly, 0.3341 g of cobaltocenium hexafluorophosphate (molar mass = 334.08 g) was dissolved in $TBAPF_6$/AN supporting electrolyte to give 100 mL of the 10 mM stock solution. Appropriate volumes of the stock solution were removed and diluted with enough quantities of the supporting electrolyte to the 8 mM, 5 mM and 2 mm concentrations that were used for the experiments. Bismuth electrodes were constructed as has been described elsewhere [8].

### Cyclic Voltammetry

Cyclic voltammetry (CV) measurements were made at Bi as working electrode (WE) using an Ivium Compactstat (model e 1030 (±10 V/±30 mA), Ivium Technologies, The Netherlands) connected to a Dell Precision work station. A platinum (Pt) disc was used as WE for experiments in which comparisons of voltammetry at Bi and Pt were desired. Pt wire was the counter electrode (CE). The non-aqueous Ag/Ag$^+$ (0.01 M $AgNO_3$ in AN) was used as reference electrode instead of Ag/AgCl because AgCl is soluble in AN. All the experiments were performed in a standard three electrode cell containing 18–20 mL of sample solution. The electrochemical cell was purged with a stream of Ar for 15 minutes prior to every experimental run to completely remove traces of oxygen that may otherwise interfere with the electrode reactions. Cobaltocene, the reduced species is very sensitive to oxygen. After each experiment, the electrodes were polished with an aqueous slurry of 0.05 mm alumina powder (Banner Scientific Ltd Coventry, UK) spread over a Buehler microcloth surface and then, rinsed with nanopure water [9].

### Electrochemical Impedance Spectroscopy

As the CV results were promising, with no evidence of electrode fouling/adsorption, attempts were made to determine the electrode kinetics by impedance spectroscopy. Impedance measurements at constant DC potentials, in potential steps of 20 mV were carried out at potential values of 0, ±30, ±60, ±90 and ±120 mV away from the formal potential of each analyte concentration [9].

## RESULTS AND DISCUSSION

Samples of the best cyclic voltammograms of cobaltocenium at Bi and Pt, obtained at the scan rate of 10 mV s$^{-1}$ in the potential range of -0.6 V to -1.1 V are presented in Figures 1 and 2.

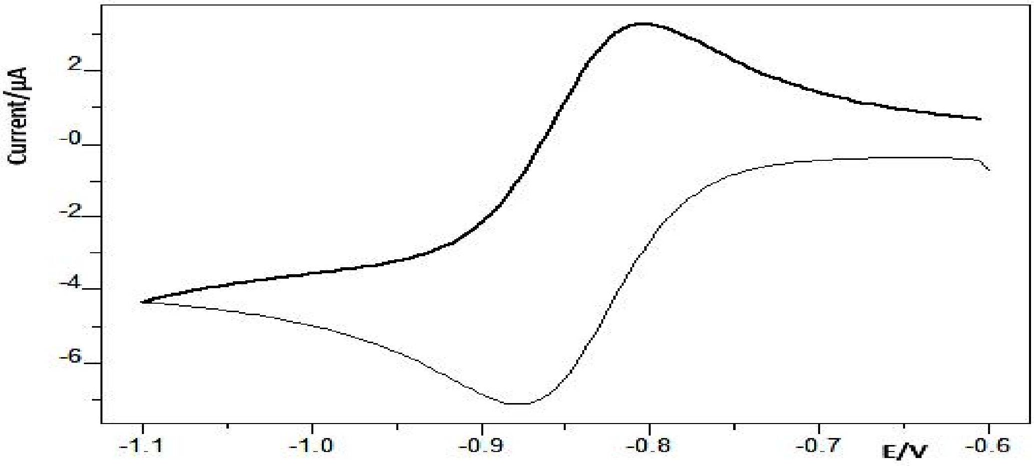

Figure 1: CV of 2 mM cobaltocenium hexafluorophosphate at Bi at scan rate of 10 mV/s in 0.1 M $TBAPF_6$/AN. The non-aqueous Ag/Ag+ (0.01 $AgNO_3$ in AN) reference electrode was used.

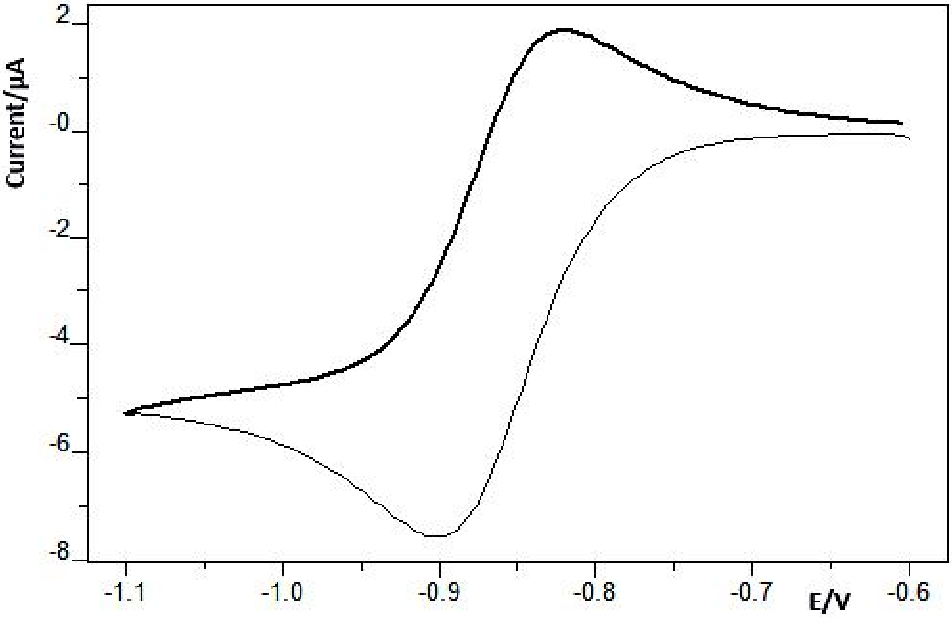

Figure 2: CV of 2 mM cobaltocenium hexafluorophosphate at Pt at scan rate of 10 mV/s in 0.1 M $TBAPF_6$/AN against the potential of a non-aqueous Ag/Ag+ reference electrode.

The asymmetrical shapes of the CVs clearly confirm the quasi-reversible behaviour of the $CoCp_2^+/CoCp_2$ couple in agreement with other reports [10, 11]. The horizontal lines in the cathodic peaks suggest a delay of current flow, hence a delay in electron transfer at the electrode, resulting in a queue.

Some consistent impedance spectra datasets as a function of potential were obtained at the various concentrations. Spectra for the 5 mM concentration are presented in Figure 3.

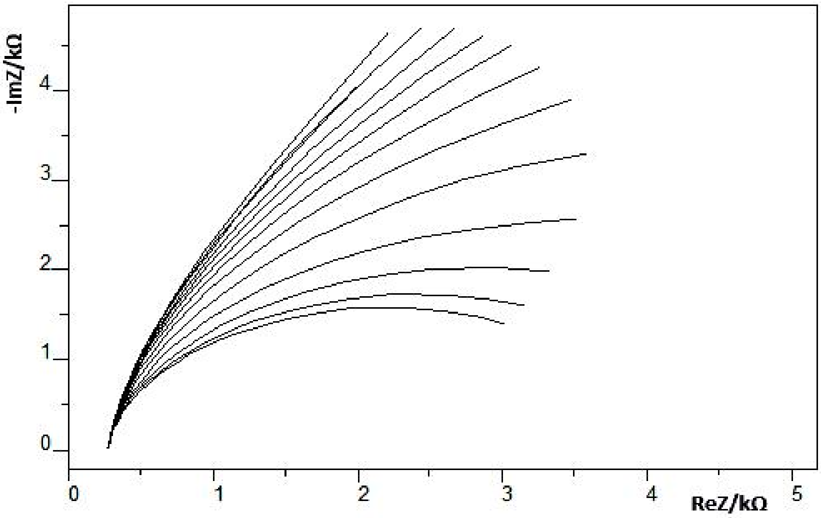

Figure 3: Impedance spectra at different dc potentials for 5 mM cobaltocenium hexafluorophosphate at Bi.The potential range was -0.72 to -0.92 V in steps of 20 mV. The

analyte solution which was prepared in 0.1 M $TBAPF_6$/AN was purged with argon gas for 15 minutes prior to scanning.

A Randles circuit for mixed-kinetics diffusion including a constant phase element (CPE) was simulated to enable measurement of precise values of charge transfer resistance ($R_{CT}$). Some of the values obtained for the 2 mM concentration are presented in Table 1.

Table 1: EIS analysis data for 2 mM cobaltocenium hexafluorophosphate at Bi. The analyte solution was purged with Ar gas for 15 minutes prior to the potential scans.

| E/V | $R_U$/Ω | $R_{CT}$/Ω | AW1/Ω | P1($C_{dl}$)/F x $10^{-7}$ | N1 |
|---|---|---|---|---|---|
| -0.73 | 298.33 | 4688.70 | 203022 | 2.5986 | 0.97608 |
| -0.75 | 300.27 | 14954 | 203710 | 3.9178 | 0.92712 |
| -0.77 | 300.42 | 14006 | 168590 | 3.9032 | 0.92674 |
| -0.79 | 299.96 | 13418 | 128580 | 4.0655 | 0.92154 |
| -0.81 | 299.70 | 12055 | 81667 | 4.2391 | 0.91717 |
| -0.83 | 299.32 | 10346 | 50958 | 4.4637 | 0.91186 |
| -0.85 | 299.27 | 8542.50 | 35568 | 4.615 | 0.90868 |
| -0.87 | 299.66 | 7330.30 | 27454 | 4.7206 | 0.90707 |
| -0.89 | 300.09 | 6933 | 25042 | 4.8807 | 0.90418 |
| -0.91 | 300.01 | 7279.20 | 28054 | 5.0185 | 0.90177 |
| -0.93 | 299.68 | 8339.20 | 35299 | 5.2104 | 0.89819 |
| -0.95 | 300.13 | 9789.50 | 48580 | 5.3281 | 0.89609 |
| -0.97 | 299.48 | 10498 | 63498 | 5.3768 | 0.89521 |

Key: $R_U$ is for uncompensated resistance, $R_{CT}$ is for charge transfer resistance and $C_{dl}$ stands for the constant phase element (CPE) which shows the non-ideality of the double layer capacitance in solution. The Warburg impedance which enables calculation of diffusion coefficients is indicated by W, while N1 is the exponent of the CPE, showing a one-electron transfer.

Impedance spectra fitting by complex non-linear least squares was carried out using EIS analyzer [12]. In general, good fits of the simulated Randles impedance to the experimental data were observed. Examples are given in the spectra of Figures 4 and 5.

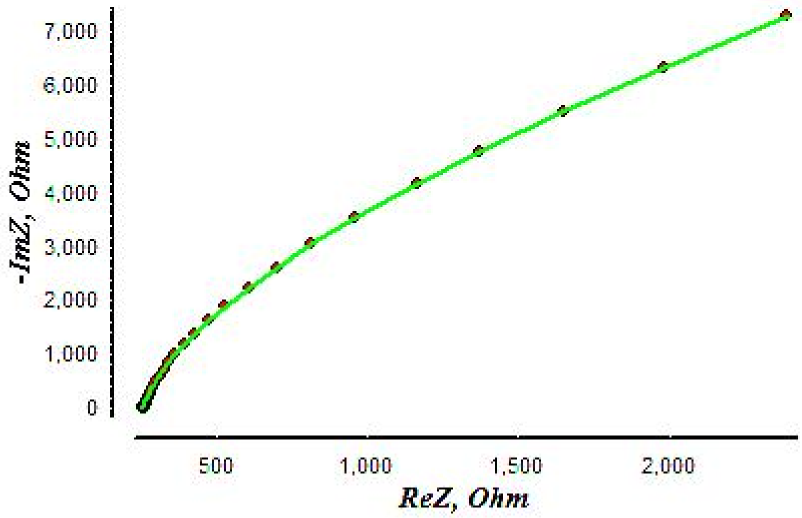

Figure 4: EIS fitted spectrum of 2 mM cobaltocenium hexafluorophosphate at Bi at -0.89 V. The green line is the simulated data while the red points are the experimental data.

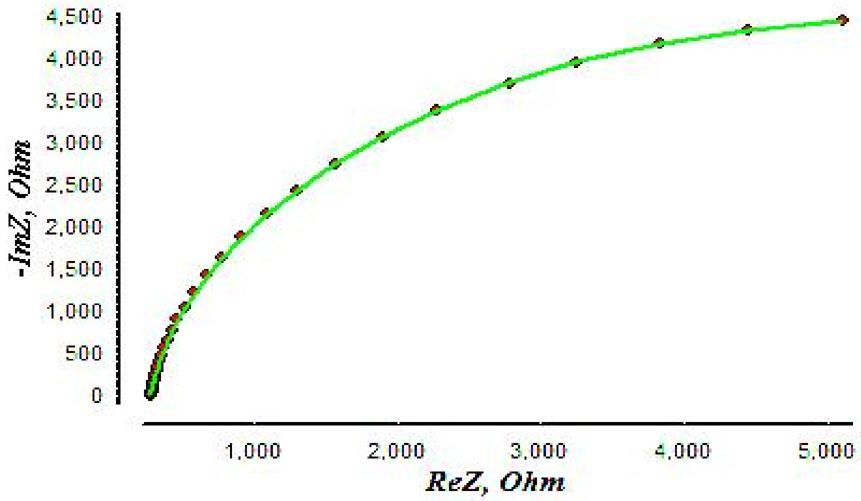

Figure 5: EIS fitted spectrum of 8 mM cobaltocenium hexafluorophosphate at Bi at -0.87 V. The red points are the experimental data fitted into the simulated green line.

Using the Solver Analysis tool, a total of nine estimates for the values of standard rate constants ($k^o$) were obtained for each of the analyte concentrations, in the potential ranges earlier defined by the constant dc potentials of 0, ±30, ±60, ±90 and ±120 mV away from their formal potentials. Values of standard rate constants obtained for the 10 mM concentration are presented in Table 2.

Table 2: Results of Solver Analysis showing values of standard rate constants for 10 mM cobaltocenium hexafluorophosphate at Bi.

| E/V | $R_U/\Omega$ | $R_{CT}/\Omega$ | $C_{dl}$/F x $10^{-7}$ | $k^o$/cm $s^{-1}$ x $10^{-4}$ | SCNLS x $10^6$ |
|---|---|---|---|---|---|
| -0.76 | 304.738 | 20413.53 | 1.62 | 2.56 | 1.93 |
| -0.79 | 310.124 | 20747.69 | 1.52 | 2.52 | 2.01 |
| -0.82 | 312.529 | 20433.21 | 1.43 | 2.56 | 2.11 |
| -0.85 | 311.122 | 19823.73 | 1.36 | 2.64 | 1.98 |
| -0.88 | 306.703 | 19703.14 | 1.30 | 2.66 | 1.86 |
| -0.91 | 301.767 | 19604.22 | 1.26 | 2.67 | 1.67 |
| -0.94 | 298.138 | 20269.42 | 1.24 | 2.58 | 1.64 |
| -0.97 | 294.909 | 20826.50 | 1.23 | 2.51 | 1.62 |
| -1.00 | 289.166 | 20259.76 | 1.23 | 2.58 | 1.54 |

Key: $R_U$ is for uncompensated resistance, $R_{CT}$ is for charge transfer resistance, and $C_{dl}$ represents the double layer capacitance in solution. $k^o$ is for standard rate constant while SCNLS stands for sum of complex non-linear squares.

The mean values of standard rate constants for all the concentrations investigated are presented in Table 3. Ideally, $k^o$ values should not vary with concentration but the data presented in Table 3 clearly indicates that electron transfer does not reflect a simple electrode process.

Table 3. Mean values of standard rate constants for $CoCp_2^{+1/0}$ at bismuth

| Concentration/mM | Standard rate constant $k^o$/cm $s^{-1}$ |
|---|---|
| 10 | $2.59 \times 10^{-4} \pm 5.81 \times 10^{-6}$ |
| 8 | $3.96 \times 10^{-3} \pm 1.98 \times 10^{-3}$ |
| 5 | $6.79 \times 10^{-4} \pm 1.83 \times 10^{-5}$ |
| 2 | $1.39 \times 10^{-3} \pm 1.64 \times 10^{-4}$ |

## CONCLUSION

Electrochemical studies of cobaltocenium hexafluorophosphate using bismuth electrodes revealed the variation of standard rate constants with concentration. This behaviour stems from the lack of chemical reversibility at Bi, occasioned by the very low peak current ratio and high potential peak separation. It also suggests electrode fouling due to adsorbed reaction products. The relative roughness of the bismuth electrode surface as compared to those of the noble metal electrodes point to this. Cobaltocenium hexafluorophosphate has proved to be sufficiently stable in AN/$TBAF_6$ to allow for the collection of impedance spectra at bismuth. However, the quality of data is not sufficient to reveal much about the potential dependence of the rate, as the charge transfer resistance profile of the compound was too complex to analyse. In the light of the foregoing, the $CoCp_2^+$/$CoCp_2$ redox couple falls short of being recommended as a reference system at Bi based on the conditions for a one-electron transfer process.

It is however worthwhile to note that bismuth electrodes have been successfully tested to confirm the quasi-reversible behaviour of cobaltocenium hexafluorophosphate.

### Acknowledgements

A. S. Nomor appreciates Benue State University, Makurdi, and the Nigerian Tertiary Education Trust Fund (TETFUND) for funding. Newcastle University, UK, is appreciated for providing the facilities.

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