International Research Journal of Natural Sciences

Vol.8, No.2, pp.52-59, July 2020

Published by ***ECRTD-UK***

Print ISSN: ISSN 2053-4108(Print)

Online ISSN: ISSN 2053-4116(Online)

CYCLIC VOLTAMMETRIC (CV) EVALUATION OF ELECTRO CHEMICAL BEHAVIORS OF K_3 [FE (CN) $_6$] AND URIC ACID

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ABSTRACT: *Cyclic Voltammetry has a multipurpose electroanalytical technique for the study of electroactive species, the method displays redox behaviour of chemical species inside a wide range potential. The current at the working electrode is observed as a three-cornered excitation potential is applied to the electrode. The purpose of this paper was to determine the diffusion coefficient (D) of the* $K_3[Fe(CN)_6]$ *and uric acid; electrochemical nature of* $K_3[Fe(CN)_6]$ *and uric acid, effects of varying the concentrations analytes on peak currents and peak splitting and scan rate CV on peak currents and peak splitting. All the reagents used for this experiment were analytical grade.* $K_3[Fe(CN)_6]$ *and uric acid solutions were prepared. The experiment has been implemented with the principles of cyclic voltammetry. The relationship between the scan rate and the peak current were investigated and the result shows that there is a direct relationship between scan rate and peak current that is* $I_p \alpha\ V^{1/2}$*. As articulated on the above voltammograms, the peak current increases with the augmentation of the concentrations of* $K_3[Fe(CN)_6]$*, So that, the researcher conclude the manifestation of direct relationship between peak current and concentration of analytes. The experiment of this research shows that the increasing of diffusion coefficient (D) with increasing of concentrations /and scan rate.The peak currents and peak splitting fluctuate with variation of scan rate of CV. Similarly, the peak currents and peak splitting vacillate with variation of concentration of the analytes.CV therefore can be used as an indication of major analytical tool for the determination of the trace elements which are electro active in nature. The electrochemical nature of* $K_3[Fe(CN)_6]$ *and uric acid were determined; reversible and irreversible respectively.*

KEY WORDS: Ferricyanide, Cyclic Voltammetry, Uric Acid, Electrochemical Behaviour.

INTRODUCTION

Cyclic voltammetry is a method used for investigating of the electrochemical behaviour of a system [1]. It was first described in 1938 and pronounced theoretically by Randies [2]. Cyclic voltammetry is the most broadly used technique for obtaining qualitative information about electrochemical reactions [1]. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes, on the kinetics of heterogeneous electron-transfer reactions and on coupled chemical reactions or adsorption processes [1, 3, 4]. Cyclic voltammetry is frequently the first experimental approach performed in an electroanalytical study, since it offers rapid location of redox potentials of the electro active species and convenient evaluation of the effect of media upon the redox process [1, 3- 6]. A cyclic voltammogram is obtained by applying a linear potential sweep (that is, a potential that increases or decreases linearly with time) to the working electrode [1]. As the potential is swept back and forth past the formal potential, E°, of an analyte, current flows through the electrode that either oxidizes or reduces the analyte. The magnitude of this current is proportional to the concentration of the analyte in solution, which allows cyclic voltammetry to be used in an analytical determination of concentration [1, 4].

CV has become a very popular technique for electrochemical studies of new systems, and has proved as a sensitive tool for obtaining information about fairly complicated electrode reactions [7]. CV methods have found to have extensive applications for the evaluation of thermodynamic and kinetic parameters such as number of electrons change (n), heterogeneous rate constant (ko), entropy (S), Gibb's free energy (G) and diffiision coefficient (Do) etc., of a number of redox reactions and associated chemical reactions[1]. These methods are especially useful in both oxidation and reduction process and to study the multiple electron transfer in an electrochemical reaction [8].

Potassium ferricyanide is a bright red salt with a chemical formula $K_3Fe\ (CN)_6$ [1]. The salt contains the octahedral coordinated $[Fe\ (CN)\ _6]^{3-}$ ion [1, 9]. It is soluble in acetonitrile-water media (1:1) and its solution shows some green yellow fluorescence [1]. Like other metal cyanides, solid potassium ferricyanide has a complicated polymeric structure [1]. The polymer consists of octahedral $[Fe(CN)_6]^{3-}$ centres cross linked with K^+ ions that are bound to the CN ligands[1,10]. The K^+---NCFe linkages break when the solid is dissolved in water-acetonitrile media [1]. The $Fe(CN)_6^{3-}$ / $Fe\ (CN)_6^{4-}$ redox couple is used as an example of an electrochemically reversible redox system used to study some basic concepts of Cyclic Voltammetry[1]. $[Fe\ (CN)_6]^{3-}$ consists of a Fe^{3+} centre bound in octahedral geometry to six cyanide ligands [1]. The complex has Ohsymmetry [11]. The iron is low spin and easily reduced to the related ferrocyanide ion $[Fe(CN)_6]^{4-}$, which is a ferrous (Fe^{2+}) derivative[1,11]. This redox couple is reversible and entails no making or breaking of Fe-C bonds: $[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$ [1].

For the reasons above, potassium ferricyanide redox is a standard in electrochemistry [1]. This redox couple is also used in: preparation of Prussian Blue (the deep blue pigment in blue printing), as a chemical reducer in photographic processing to remove silver from negatives and positives (dot etching), in wine production potassium ferricyanide has been used to precipitate out copper if copper has been used as a fungicide on the grapes [12].In histology, it is used to detect ferrous iron in biological tissue [13].

The main objective of this experiment was to illustrate the basics of cyclic voltammetry by studying the one-electron reversible redox system. The properties of the reaction: $Fe^{3+}(CN)_6^{3-}\ Fe^{2+}\ (CN)_6^{4-}$ were investigated. The parameters of greatest interest for a reversible CV are the peak cathodic Potential (E_{pc}), the peak anodic potential (E_{pa}), the peak cathodic current (i_{pc}) and the peak anodic current (i_{pa})[14]. The peak currents of a reversible process are given by the Randless Sevick equation: $i_p = (2.69 \text{ x } 105)n^{3/2}AD^{1/2}\ V^{1/2}$, Where A is the electrode surface area (cm^2) obtained using geometrical measurements, D is the diffusion coefficient (cm^2/s), C is the concentration of the electroactive species in the bulk solution (mol/cm^3) and V is the scan rate (v)[1, 14]. Therefore, i_p is proportional to C and proportional to $V^{1/2}$ [14]. If A is known, then D can be calculated from the slopes of the linear [15].

Uric Acid (UA) (2, 6, 8-trihydroxypurine) is electroactive biomolecule, a white crystalline powder, soluble in water and is one of the important final end products of purine metabolism in the human body [16]. In healthy persons the concentration of uric acid in urine is around 2mM and in the blood it is in the range of 120mM to 450mM [16]. Normally, healthy human beings excrete about 400 to 700 mg through urine per day [17]. Abnormal levels of uric acid are symptoms of several physiological disorders [18]. High levels of uric acid cause hyperuricemia, excess serum accumulation of uric acid in the blood can lead to arthritis (gout) [16]. The low concentration of uric acid leads to hyperuricemia and other diseases such as Lesch-Nyhan syndrome and heavy hepatitis [18]. Uric acid is also a marker for the renal failure [16]. Its quantitative determination in body fluids is necessary for the treatment of diseases [19].

The purpose of this paper is to determine the diffusion coefficient (D) of $K_3Fe(CN)_6$ and uric acid; electrochemical nature of $K_3Fe(CN)_6$ and uric acid; the effects of fluctuating concentrations of $K_3Fe(CN)_6$ and uric acid on peak currents and peak splitting and the effects of shifting scan rate of the CV on peak currents and peak splitting.

EXPERIMENTAL

Reagents

All the reagents used for this experiment were analytical grade, a 100ml stock solution of 10mM $K_3Fe(CN)_6$ in 0.1 M KNO_3 was prepared. Successive dilutions of this solution were done. 0.1 M $HClO_4$ was made for cleaning the working electrode during analysis of $K_3Fe(CN)_6$, 1m M EtOH was made for cleaning the working electrode during analysis ofuric acid , 5mM uric acid and deionized water were used.

Apparatus

In the experiment underneath, cyclic voltammeter, Arrangement of a three electrode glass cell was used together, glassy carbon working electrode (Diameter of glassy carbon= 0.3cm, radius =0.15cm) was used, the Ag/AgCl reference electrode, and the platinum wire as a counter electrode.

Analytical procedure

The glassy carbon working electrode was refined using a solution of 0.1 M $HClO_4$ and cleaned with distilled water beforehand experimentation to have renewed working surface and to ensure good electron transfer. The solutions that prepared above was added to the cell and carefully eliminated with Oxygen-free Nitrogen 15 minutes before running a CV. In addition, the solution was stirred between experiments in order to restore initial conditions, but it was not stirred during the experiment. 0.1M KNO_3 supporting electrolyte was to control electrode potentials, eradicate the transport of electroactive species from travelling in the electric field gradients, preserve persistent ionic strength and keep constant pH, this guaranteed a diffusion controlled electrode process. The glassy carbon working electrode was rinsed very well between experiments. The CV was run from -0.2 to 0.8 V, the CV was completed at different scan rates. In addition, the CV was run from -0.2V to 0.8 V by varying the concentration of $K_3Fe(CN)_6$.

To realize electrochemical nature of uric acid, a cyclic voltammetry was run for 0.005 M uric acid with different scan rate, from -0.2 to 1.4 V. The glassy carbon working electrode was rinsed very well between experiments and immersed in 0.001 M EtOH for 30minutes. The electrode was removed from the solution and rinses it thoroughly; the experiments were conducted at room temperature (25°C). Finally, the voltammograms of the analytes ($K_3Fe(CN)_6$ and uric acid) were fashioned and interpreted .

Experimental results and discussions

a. Effects of scan Rate

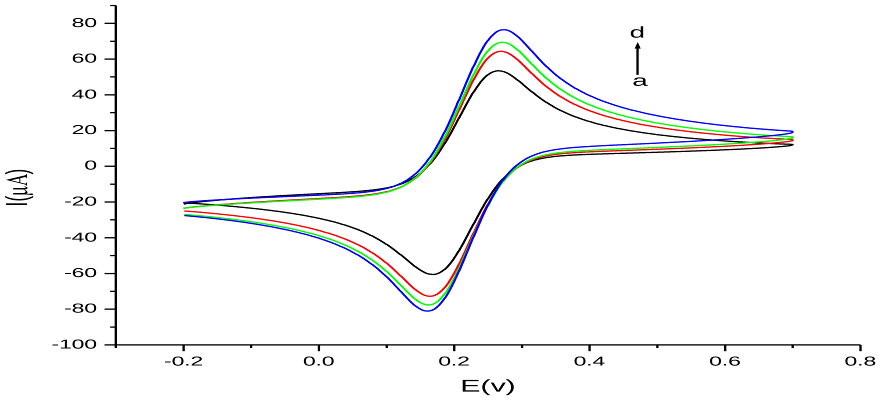

Fig1. Voltammograms of 5 mM $K_3Fe(CN)_6$ at different scan rate

Table1. Voltammetry results of 5mM $K_3[Fe(CN)_6]$ at different scan rate

Scan Rate (mVs^{-1})	Ia(μA)	Ic(μA)	Ea(V)	Ec(v)
100	63.4	-63.36	0.265	0.169
150	76.31	-77.1	0.268	0.164
175	81.64	-82.31	0.271	0.162
200	87.1	-87.2	0.273	0.161

b. Effects of concentration

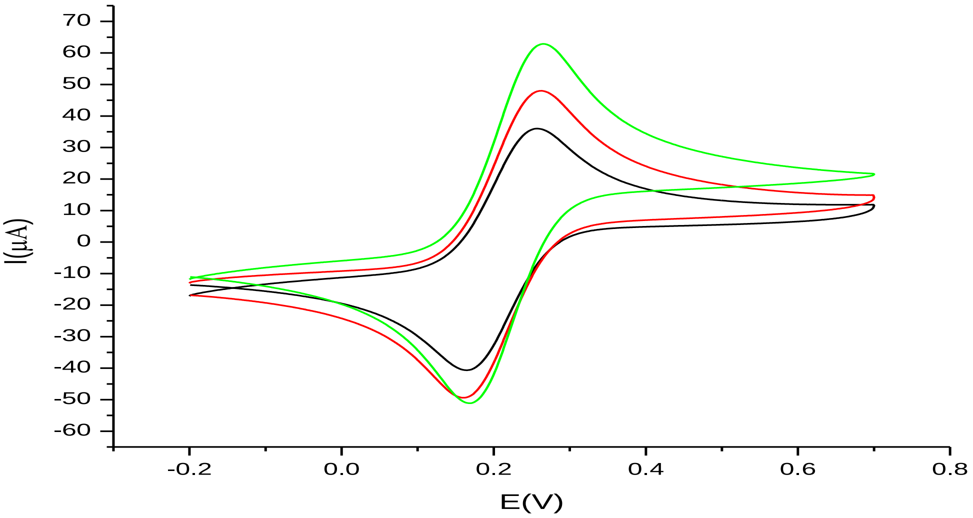

Fig.2. Voltammograms at scan rate100 mVs^{-1} and different concentrations of $K_3Fe\ (CN)_6$

Table2. Voltammetry results of $K_3\ [Fe\ (CN)_6]$ at scan rate100 mVs^{-1} and different concentration

Conc.(mM)	Ipa	Ipc	Epa	Epc
2	42.46	-43.9	0.257	0.164
3	53.7	-53.7	0.263	0.161
5	63.4	-64.3	0.265	0.169

C. Uric Acid at different scan rate

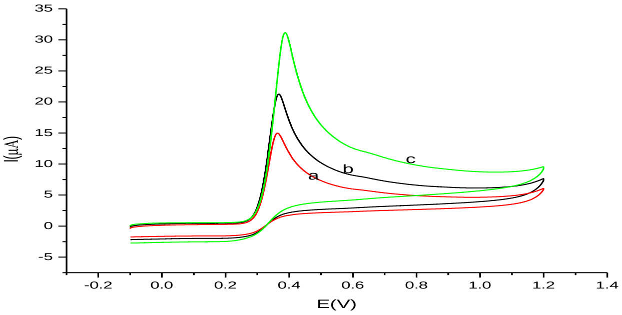

Fig.3. Voltammograms of 5mM Uric Acid at different scan rate

Table3. Voltammetry results of 5mM Uric Acid at different scan rate

	Scan rate in mVS^{-1}	Current(μA)	E(v)
A	100	13.5	0.363
B	125	20.2	0.367
C	150	29.1	0.387

1.1. Calculations

Electrode area (A) = πr^2= 3.14x $(0.15cm)^2$ = 0.07065 cm^2; Δ Epeak= 59mV/n, n=59mv/ (0.265-0.169) =0.89= 1; I p= Ic-Ia= (63.4-63.36)μA = 126.76μA

Determination of diffusion coefficient (D) (cm^2/sec)

For K_3Fe (CN) at 5 mMK_3Fe $(CN)_6$ and 100mv/s scan rate: $I_p = (2.69 \text{ x } 10^5)\, n^{3/2}\, v^{1/2}\, D^{1/2}$ A C [1], $D^{1/2} = I_p/((2.69x10^5)n^{3/2}v^{1/2}AC)$, $D^{1/2} = 126.76/2.69x10^5\ (1)^{3/2}\ x\ (100x10^{-3})^{1/2}\ x0.07065x5$, $D^{1/2}$=126.76 /0.300493x10^5= 421.9707x10^{-11} , D=178059.2716 x$10^{-10}$$cm^2$/se=1.78x$10^{-5}$$cm^2$/se.

For Uric Acid at different 5mM, I_p=2.99x105n $(\alpha n_\alpha)^{1/2}$ $ACD^{1/2}$ $V^{1/2}$ [1], $D^{1/2}$ =I_p/2.99x105n $(\alpha n_\alpha)^{1/2}$ $ACV^{1/2}$, D= (13.5′2.99x10^5 $(\alpha n_\alpha)^{1/2}$ $(1)^{3/2}$ x $(100x10^{-3})^{1/2}$ x0.07065x5$)^2$=1.595/αn_αx$10^{-7}$$cm^2$/se.

DISCUSSION

Electrochemical behaviors of $K_3[Fe(CN)_6]$ and uric acid were examined, as a result $K_3[Fe(CN)_6]$ under goes redox reaction(forward and back ward scan of electron) while uric acid under goes only for ward scan so that both gives voltammograms which have different shapes which are shown in fig. 1, 2 and3. The relationship between the scan rate and the peak current were investigated and the result shows that there is a direct relationship between scan rate and peak current that is $I_p \alpha\ V^{1/2}$. As articulated on the above voltammograms, the peak current increases with the augmentation of the concentrations of $K_3[Fe(CN)_6]$, So that, the researcher conclude the manifestation of direct relationship between peak current and concentration of analytes. The experiment of this research shows that the increasing of diffusion coefficient (D) with increasing of concentrations /and scan rate.The peak currents and peak splitting fluctuate with variation of scan rate of CV. Similarly, the peak currents and peak splitting vacillate with variation of concentration of the analytes.

CONCLUSIONS

The cyclic voltammetry method was successfully applied to check the electro chemical behaviours' of $K_3[Fe(CN)_6]$ and uric acid. The dependence of peak current on scan rate of CV and concentration of electraolyte analyte were examined under optimal conditions. CV therefore can be used as an indication of major analytical tool for the determination of the trace elements which are electro active in nature. The electrochemical nature of $K_3[Fe(CN)_6]$ and uric acid were determined; reversible and irreversible respectively.

REFERENCES

1. Nkunu Z. N., Kamau G. N., Kithure J. G., Muya C.N. Electrochemical Studies of Potassium Ferricyanide in Acetonitrile-Water Media (1:1) using Cyclic Voltammetry Method. International Journal of Scientific Research and Innovative Technology, **2017**, 4, 5, 52-58.
2. J.Randles, Trans. A cathode ray polarograph. Faraday Society, **1948**, 44, 32- 327.
3. D.B.Hibbert, "Introduction to Electrochemistry" (Macmillan, London Eds), **1993**.
4. A.E.Kaifer, M.G.Kaifer, "Supramolecular Electrochemistry" (Willey, VCH, New York Eds), **1999**.
5. A.J.Bard, L.R.Faulkner, "Electrochemical Methods: Fundamentals and Applications" (John Willey & Sons Eds), **1996**.
6. D.G.Davis, in D. Dolphin, Ed., "Physical Chemistry the porphyrins", (Academic Press, NY Eds), **1978**.
7. R.S.Nicholson, I.Shain, Anal. Chem. **1964**, 36, 706.
8. 33. A.W.Bott, Current Separations. **1997**, 16, 61.
9. Sharpe, A. G. The Chemistry of Cyano Complexes of the Transition Metals. London: Academic Press, **1976**.
10. Figgis, B.N.; Gerloch, M.; Mason, R. "The crystallography and paramagnetic anisotropy of potassium ferricyanide" Proceedings of the Royal Society of London, Series A: Mathematical and Physical Sciences, **1969**, vol. 309, 91-118.
11. Zanello P, "Inorganic Electrochemistry: Theory, Practice and Application" The Royal Society of Chemistry, **2003**, ISBN 0-85404-661-5.
12. Stroebel, L.; Zakia, R. D. "Farmer's Reducer". The Focal Encyclopedia of Photography. Focal Press. p. 297. **1993**, ISBN 978-0-240-51417-8.
13. Carson, F. L. Histotechnology: A Self-Instructional Text (2nd ed.). Chicago: American Society of Clinical Pathologists. **1997**, 209–211. ISBN 0-89189-411-X.
14. Muya, C. N., Guto, P. M., Wangui, T. W., &Kamau, G. N. Electrocatalytic Decompsition of (3ar, 7as) 2-[(trichloromethyl) sulfanyl]-3a, 4, 7, 7a-tetrahydro-1h-isoindole-1, 3 (2h)-Dione (Captan) Pesticide Residue using Cyanocobalamin. International Journal of BioChemiPhysics, **2015**, 23.
15. Wanjau Tabitha Wangui, Geoffrey NjugunaKamau, Mwaniki Silas Ngari, Muya Catherine Njambi. Electrocatalytic Reduction of 2,2,2–Trichloro-1, 1-Bis (4-Chlorophenyl) Ethanol (Dicofol) in Acetonitrile Aqueous Solution Using Cyanocobalamin as a Catalyst, Science Journal of Chemistry, **2015**, 3, 1, 1-10.
16. Tanuja SB, Kumara Swamy BE and Vasantakumar Pai K. Electrochemical Response of Dopamine in Presence of Uric Acid at Pregabalin Modified Carbon Paste Electrode: A Cyclic Voltammetric Study. J. Anal. and Bioanal Tech, **2016**, 7, 1, 1-6.
17. Grabowska I, Chudy M, Dybko A, Brzoz Z. Simultaneous determination of ascorbic acid, adrenaline and uric acid at a hematoxylin multi-wall carbon nanotube modified glassy carbon electrode. Sensors Actuators B: **2010**, 666-672.

18. Heinig M, Johnson RJ. Role of uric acid in hypertension, renal disease, and metabolic syndrome. Cleve Clin J Med, **2006**, 73: 1059-1064.
19. Manjunatha JE, Swamy BEK, Mamatha GP, Gilbert O, Sherigara BS. Poly (maleic acid) Modified Carbon Paste Electrode for Simultaneous Detection of Dopamine in the Presence of Uric Acid: A Cyclic Voltammetric Study. Anal Bioanal Electrochem, **2011**, 3: 146-159.