**Shahjalal University of Science and Technology, Sylhet**

***Lab Report***

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***Experiment Name***: Determination of active surface area of Pt surface using reversible cyclic voltammetry and evaluation of diffusion coefficient of arsenite.

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**Experiment Title**

Determination of active surface area of Pt surface using reversible cyclic voltammetry and evaluation of diffusion coefficient of arsenite.

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| Abstract  Cyclic Voltammetry has a multipurpose electroanalytical technique for the study of electroactive species, the method displays redox behavior 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 experiment was to determine the diffusion coefficient (*D*) of the *K4[Fe(CN)6]* and *NaAsO2*, electrochemical nature of *K4[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, and active surface area of Pt electrode. All the reagents used for this experiment were analytical grade. *K4[Fe(CN)6]* and *NaAsO2*solutions were prepared. The experiment has been implemented with the principles of cyclic voltammetry. The relationship between the scan rate and the peak current was investigated and the result shows that there is a direct relationship between scan rate and peak current that is *Ip α V1/2*. As articulated on the above voltammograms, the peak current increases with the augmentation of the concentrations of *K4[Fe(CN)6]*, So that, we conclude the manifestation of direct relationship between peak current and concentration of analytes. The experiment 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 *K4[Fe(CN)6]* and *NaAsO2* were determined; reversible and irreversible respectively. |
| Keywords  Ferricyanide, Cyclic Voltammetry (CV), Sodium arsenite, platinum (Pt) electrode, active surface area, diffusion coefficient *(D)*. |
| Introduction  Cyclic voltammetry is a method used for investigating of the electrochemical behavior of a system. It was first described in 1938 and pronounced theoretically by Randies. Cyclic voltammetry is the most broadly used technique for obtaining qualitative information about electrochemical reactions. 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. 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. 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. 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. CV has become a very popular technique for electrochemical studies of new systems and has proved as a sensitive tool for obtaining information about complicated electrode reactions. 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 diffusion coefficient (Do) etc., of a number of redox reactions and associated chemical reactions. These methods are especially useful in both oxidation and reduction process and to study the multiple electron transfer in an electrochemical reaction.  Potassium ferrocyanide is a bright red salt with a chemical formula *K4[Fe(CN)6]*. The salt contains the octahedral coordinated *[Fe(CN)6]4*- ion. It is soluble in acetonitrile-water media (1:1) and its solution shows some green-yellow fluorescence. Like other metal cyanides, solid potassium ferrocyanide has a complicated polymeric structure. The polymer consists of octahedral *[Fe(CN)6]4*- centers cross linked with *K+* ions that are bound to the *CN* ligands. The *K+---NCFe* linkages break when the solid is dissolved in water-acetonitrile media. 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. *[Fe(CN)6]4*- consists of a *Fe4+* center bound in octahedral geometry to six cyanide ligands . The complex has Ohsymmetry. The iron is low spin and easily reduced to the related ferrocyanide ion *[Fe(CN)6]4*-, which is a ferrous (*Fe2+*) derivative. This redox couple is reversible and entails no making or breaking of Fe-C bonds:  *[Fe(CN)6]3*-+ e− → *[Fe(CN)6]4*-  The Randles-Sevcik equation describes the relationship between peak current (Ip), scan rate (ν), and diffusion coefficient (D):    where:  Ip is the peak current (A).  n is the number of electrons transferred.  A is the active surface area ().  D is the diffusion coefficient ().  C is the concentration of the electroactive species ().  v is the scan rate (V/s).   |  |  | | --- | --- | |  | **Cyclic Voltammogram** | | Fig 01. Potentiostat used for CV | Fig02. Cyclic Voltammogram |   When the peak current is plotted against the square root of the scan rate , the result is a straight line passing through the origin for a diffusion-controlled reversible process.  The slope of the ​ vs. plot is proportional to , providing valuable information about the redox system.  Fig03. Typical peak current vs square root of scan rate plot. |
| Experimental  Materials Required   1. Beaker 2. 0.1 M solution 3. 0.01 M arsenite solution () 4. Potassium ferrocyanide solution 5. Deionized water 6. Potentiostat (CHI660-Worksation) 7. Platinum working electrode (Pt) 8. Ag/AgCl reference electrode 9. Platinum wire counter electrode   Procedure   1. The Pt electrode was cleaned thoroughly using a standard procedure. 2. 0.1 M H2SO4 solution as supporting electrolyte and 0.01 M arsenite solution (NaAsO2) was prepared. 3. The electrochemical cell with the Pt electrode as the working electrode, a reference electrode (e.g., Ag/AgCl), and a counter electrode (e.g., platinum wire) was assembled. 4. Cyclic voltammetry measurements at different scan rates (e.g., 10, 20, 30, 40, 50, 75, 100 mV/s) were performed. The current-voltage curves for each scan rate were recorded. 5. The peak current (Ip) for the oxidation and reduction peaks at each scan rate were determined. 6. Peak current (Ip) vs square root of the scan rate () was plotted. The slope of the linear regression line was calculated. 7. The active surface area of the Pt electrode was determined using the Randles-Sevcik equation. |
| Calculation and Graph  Fig04. CV plot for various scan rates of potassium ferrocyanide    Fig05. Ip vs plot of potassium ferrocyanide    Fig 06. CV plot for various scan rate of arsenite solution    Fig 07. vs plot of arsenite solution  Calculation of active surface area of Pt electrode:  According to the Fig 05. we get the slope of vs ,  .  So, the active surface area of Pt electrode is  Calculation of Diffusion coefficient of arsenite:  According to the Fig 07. we get the slope of vs ,  So, the diffusion coefficient of arsenite solution is  Or  Suppose Electrode Area = (A) = πr2= 3.14 x (0.15cm)2 = 0.07065 cm2  According to the Fig07. we get the slope of vs ,  So, the diffusion coefficient of arsenite solution is  Results and Discussion  Active Surface Area of Pt Electrode: The active surface area of the Pt electrode was determined to be .  Diffusion Coefficient of Arsenite: The diffusion coefficient of arsenite was found to be or,  Electrochemical behaviors of *K4[Fe(CN)6]* and *NaAsO2* were examined, as a result *K4[Fe(CN)6]* under goes redox reaction( forward and back ward scan of electron) while *NaAsO2* under goes only forward scan so that both gives voltammograms which have different shapes which are shown in fig. 04, and 06. 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 Ip α V1/2. As articulated on the above voltammograms, the peak current increases with the augmentation of the concentrations of *K4[Fe(CN)6]*, So that, we 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.  Conclution  The cyclic voltammetry method was successfully applied to check the electro chemical behaviors’ of *K4[Fe(CN)6]* and *NaAsO2*. The dependence of peak current on scan rate of CV and concentration of electrolyte 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 *K4[Fe(CN)6]* and *NaAsO2* were determined; reversible and irreversible respectively.  Software Used   1. Electrochemical Workstation- CHI660 2. Sigmaplot 14   References   1. Cyclic Voltammetric (CV) evaluation of electro chemical behaviors of K3[Fe (CN) 6] and Uric Acid.   <https://www.eajournals.org/wp-content/uploads/Cyclic-Voltammetric-CV-evaluation-of-electro-chemical-behaviors-of-K3-Fe-CN-6-and-Uric-Acid.pdf>   1. Elgrishi, N., Rountree, K. J., McCarthy, B. D., Rountree, E. S, & Dempsey, J. L. (2018). A Practical Beginner’s Guide to Cyclic Voltammetry. Journal of Chemical Education, 95(2), 197–206. Retrieved from. <https://pubs.acs.org/doi/10.1021/acs.jchemed.7b00361> 2. Kissinger, P. T., & Heineman, W. R. (1983). Cyclic Voltammetry. Journal of Chemical Education, 60(9), 702–706. Retrieved from <https://pubs.acs.org/doi/10.1021/ed060p702> |