

Investigation of the Effect of Water Structure Modifiers in Aqueous Solution for the Electroanalysis of Metal Ions

by

Most. Jaheda Akhtar

Student ID: 0417032710

In the partial fulfillment of the requirement for the degree
of

MASTER OF SCIENCE IN CHEMISTRY



Department of Chemistry

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY

February 2020

রসায়ন বিভাগ

বাংলাদেশ প্রকৌশল বিশ্ববিদ্যালয়
ঢাকা-১০০০



Department of Chemistry

Bangladesh University of Engineering
and Technology (BUET),
Dhaka-1000, Bangladesh

The thesis work entitled “*Investigation of the Effect of Water Structure Modifiers in Aqueous Solution for the Electroanalysis of Metal Ions*” submitted by Most. Jaheda Akhtar, Student ID: 0417032710 of Session: April 2017, has been found **satisfactory** for the partial fulfillment of the requirement for the degree of Master of Science in Chemistry on 02 February 2020.

BOARD OF EXAMINERS

1. Dr. Chanchal Kumar Roy
Assistant Professor
Department of Chemistry
BUET, Dhaka

Chairman

2. Dr. Md. Shakhawat Hossain Firoz
Professor and Head
Department of Chemistry
BUET, Dhaka

Member
(Ex-officio)

3. Dr. Md. Nazrul Islam
Professor
Department of Chemistry
BUET, Dhaka

Member

4. Dr. Md. Mominul Islam
Associate Professor
Department of Chemistry
DU, Dhaka

Member
(External)

CANDIDATE'S DECLARATION

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

.....

(Most. Jaheda Akhtar)

Signature of the candidate

DEDICATION

I dedicate this thesis to

My Beloved Parents
&
Honorable Supervisor

Table of Contents

| | |
|--|------|
| List of Tables and Figures..... | ix |
| List of Abbreviations of Technical Symbols and Terms | xiii |
| Acknowledgement | xiv |
| Abstract..... | xvi |

| | |
|--|----|
| CHAPTER 1 Introduction..... | 2 |
| 1.1 General Introduction | 2 |
| 1.2 The Scope of Electrochemistry | 3 |
| 1.2.1 Importance of electroanalysis | 4 |
| 1.3 The Nature of Electrode Reactions | 5 |
| 1.4 Faradaic Processes..... | 6 |
| 1.4.1 Mass transport controlled reactions | 7 |
| 1.5 Cyclic Voltammetry | 8 |
| 1.5.1 Reversible system | 10 |
| 1.5.2 Study of a reaction mechanism | 11 |
| 1.6 Supporting Electrolyte..... | 12 |
| 1.6.1 Effect of supporting electrolyte..... | 13 |
| 1.7 Water Structure | 13 |
| 1.7.1 Proton transport in water..... | 14 |
| 1.7.2 Effect of urea on water structure..... | 15 |
| 1.7.3 Effect of fructose on water structure..... | 17 |
| 1.8 Aims of Current Research | 19 |
| CHAPTER 2 Experimental..... | 27 |
| 2.1 Materials and Instrument..... | 27 |
| 2.1.1 Chemicals and reagents..... | 27 |
| 2.1.2 Cells and electrodes | 27 |
| 2.1.3 Instruments..... | 28 |
| 2.2 Method of Preparation..... | 28 |
| 2.2.1 Preparation of stock solution KCl..... | 28 |

| | | |
|--|--|----|
| 2.2.2 | A stock solution of potassium ferricyanide | 28 |
| 2.2.3 | Preparation of stock solution urea..... | 28 |
| 2.2.4 | Preparation of stock solution fructose..... | 29 |
| 2.2.5 | Preparation of stock solution cadmium sulfate | 29 |
| 2.2.6 | A stock solution of lead nitrate | 29 |
| 2.2.7 | Preparation of stock solution thiourea | 29 |
| 2.3 | Measurements..... | 29 |
| 2.3.1 | Electrochemical measurements..... | 29 |
| 2.3.2 | Conductivity measurements..... | 30 |
| CHAPTER 3 Results and Discussion | | 33 |
| 3.1 | Effect of Conventional Supporting Electrolyte for the Electroanalysis of Ferric Ion..... | 33 |
| 3.1.1 | Effect of conventional supporting electrolyte for the electroanalysis of lead ion | 35 |
| 3.1.2 | Effect of conventional supporting electrolyte for the electroanalysis of cadmium ion | 37 |
| 3.2 | Effect of Urea with Conventional Supporting Electrolyte for the Electroanalysis of Ferric Ion..... | 38 |
| 3.2.1 | Effect of urea with conventional supporting electrolyte for the electroanalysis of lead ion..... | 40 |
| 3.2.2 | Comparison of urea with conventional supporting electrolyte for the electroanalysis of lead ion..... | 42 |
| 3.2.3 | Effect of urea with conventional supporting electrolyte for the electroanalysis of cadmium ion | 42 |
| 3.2.4 | Comparison of urea with conventional supporting electrolyte for the electroanalysis of cadmium ion | 44 |

| | | |
|-------|---|----|
| 3.3 | Electrochemical Behavior of Ferric Ion with Conventional Supporting Electrolyte in Presence of Urea..... | 44 |
| 3.4 | Effect of Fructose with Conventional Supporting Electrolyte for the Electroanalysis of Ferric Ion | 46 |
| 3.4.1 | Effect of fructose with conventional supporting electrolyte for the electroanalysis of lead ion..... | 49 |
| 3.4.2 | Comparison of fructose with conventional supporting electrolyte for the electroanalysis of lead ion..... | 50 |
| 3.4.3 | Effect of fructose with conventional supporting electrolyte for the electroanalysis of cadmium ion | 51 |
| 3.4.4 | Comparison of fructose with conventional supporting electrolyte for the electroanalysis of cadmium ion | 52 |
| 3.5 | Effect of Conventional Supporting Electrolyte in the Presence of Thiourea for the Electroanalysis of Ferric Ion | 53 |
| 3.6 | pH Measurement of Urea and Fructose in Aqueous Solution..... | 53 |
| 3.7 | Conductometric Measurement of Urea and Fructose in Aqueous Solution | 55 |
| 3.7.1 | Proposed mechanism of interaction for urea and fructose..... | 56 |
| 3.8 | Conclusion..... | 58 |

List of Tables and Figures

List of Tables

| | |
|---|----|
| Table 3.1.1.1 The values of peak currents of 1 mM Pb ²⁺ for different concentration of KCl in aqueous solution..... | 36 |
| Table 3.1.2.1 The values of peak currents of 1 mM Cd ²⁺ with different concentration of KCl in aqueous solution | 37 |
| Table 3.2.3.1 The values of peak currents of 1 mM Cd ²⁺ with 45 mM KCl for different concentration of urea in aqueous solution | 43 |
| Table 3.4.3.1 The values of peak currents for 1 mM Cd ²⁺ with 45 mM KCl for different concentration of fructose in aqueous solution | 51 |

List of Figures

| | |
|---|----|
| Figure 1.4.1.1 The three modes of mass transport | 8 |
| Figure 1.5.1 Potential time excitation signal in the cyclic voltammetric experiment. 8 | |
| Figure 1.5.2 Typical cyclic voltammogram | 9 |
| Figure 1.7.1 Water structure..... | 14 |
| Figure 1.7.1.1 a. Eigen (H_9O_4^+) and b. Zundel (H_5O_2^+) cationic complexes | 14 |
| Figure 1.7.1.2 Grotthus mechanism or structural diffusion (a) Hydronium cation (b) Zundel complex and (c) again a hydronium cation..... | 15 |
| Figure 1.7.2.1 Solvation structure of the urea molecule. One of the water molecules in the solvation shell shares two hydrogen bonds with urea..... | 16 |
| Figure 1.7.3.1 Fructose structure | 17 |
| Figure 1.7.3.2 In water solution, fructose exists as an equilibrium mixture of 70% fructopyranose and 22% fructofuranose | 18 |
| Figure 3.1.1.1 Cyclic voltammograms of 1 mM Pb^{2+} with different concentration of KCl at a scan rate 10 mVs^{-1} | 36 |
| Figure 3.1.2.1 Cyclic voltammograms of 1 mM Cd^{2+} with different concentration of KCl at a scan rate 10 mVs^{-1} | 37 |
| Figure 3.2.1 Cyclic voltammograms of 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$, 45 mM KCl and different concentration of urea at a scan rate 50 mVs^{-1} | 38 |
| Figure 3.2.2 Peak current vs concentration of urea containing 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ and 45 mM KCl solution at a scan rate 50 mVs^{-1} | 39 |
| Figure 3.2.3 Peak potential vs concentration of urea containing 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ and 45 mM KCl solution at a scan rate 50 mVs^{-1} | 39 |
| Figure 3.2.4 Comparison among 45 mM KCl, 5 mM urea with 45 mM KCl and 100 mM KCl for 1 mM Fe^{3+} at a scan rate 50 mVs^{-1} | 40 |

| | |
|---|----|
| Figure 3.2.1.1 Cyclic voltammograms of 1 mM Pb ²⁺ containing 45 mM KCl and different concentration of urea aqueous solution at a scan rate 10 mVs ⁻¹ | 41 |
| Figure 3.2.1.2 Peak current vs concentration of urea at a scan rate of 10 mVs ⁻¹ | 41 |
| Figure 3.2.2.1 Comparison among 45 mM KCl, 5 mM urea with 45 mM KCl and 100 mM KCl for 1 mM Pb ²⁺ at a scan rate 10 mVs ⁻¹ | 42 |
| Figure 3.2.3.1 Cyclic voltammograms of 1 mM Cd ²⁺ with 45 mM KCl for different concentration of urea at a scan rate 10 mVs ⁻¹ | 43 |
| Figure 3.2.4.1 Comparison among 45 mM KCl, 5 mM urea with 45 mM KCl and 100 mM KCl for 1 mM Cd ²⁺ at a scan rate 10 mVs ⁻¹ | 44 |
| Figure 3.3.1 Cyclic voltammograms for different concentration of [Fe(CN) ₆] ³⁻ with 45 mM KCl in presence of 5 mM urea at a scan rate 10 mVs ⁻¹ | 45 |
| Figure 3.3.2 Peak currents vs concentration of [Fe(CN) ₆] ³⁻ with 45 mM KCl in presence of 5 mM urea at a scan rate 10 mVs ⁻¹ | 45 |
| Figure 3.4.1 Cyclic voltammograms of 1 mM [Fe(CN) ₆] ³⁻ with 45 mM KCl and adding the different concentration of fructose at a scan rate 50 mVs ⁻¹ | 46 |
| Figure 3.4.2 Peak current vs concentration of fructose-containing 1 mM [Fe(CN) ₆] ³⁻ solution and 45 mM KCl at scan rate 50 mVs ⁻¹ | 47 |
| Figure 3.4.3 Peak potential vs concentration of fructose-containing 1 mM [Fe(CN) ₆] ³⁻ solution and 45 mM KCl at a scan rate 50 mVs ⁻¹ | 47 |
| Figure 3.4.4 Comparison among 45 mM KCl, 10 mM fructose with 45 mM KCl and 100 mM KCl for 1 mM [Fe(CN) ₆] ³⁻ at a scan rate 10 mVs ⁻¹ | 48 |
| Figure 3.4.1.1 Cyclic voltammograms of 1 mM Pb ²⁺ containing 45 mM KCl and different concentration of fructose at a scan rate 10 mVs ⁻¹ | 49 |
| Figure 3.4.1.2 Peak current vs concentration of fructose-containing 45 mM KCl at a scan rate 10 mVs ⁻¹ | 50 |

| | |
|--|----|
| Figure 3.4.2.1 Comparison among 45 mM KCl, 10 mM fructose with 45 mM and 100 mM KCl for 1 mM Pb ²⁺ at a scan rate 10 mVs ⁻¹ | 50 |
| Figure 3.4.3.1 Cyclic voltammograms of 1 mM Cd ²⁺ with 45 mM KCl for different concentration of fructose at a scan rate 10 mVs ⁻¹ | 51 |
| Figure 3.4.4.1 Comparison among 45 mM KCl, 10 mM fructose with 45 mM KCl and 100 mM KCl for 1 mM Cd ²⁺ at a scan rate 10 mVs ⁻¹ | 52 |
| Figure 3.5.1 Cyclic voltammograms of 1 mM [Fe(CN) ₆] ³⁻ in presence of 50 mM thiourea for different concentration of KCl at a scan rate 50 mVs ⁻¹ | 53 |
| Figure 3.6.1 pH vs different concentration of urea aqueous solution | 54 |
| Figure 3.6.2 pH vs concentration of fructose aqueous solution | 54 |
| Figure 3.7.1 Specific conductance vs different concentration of urea aqueous solution | 55 |
| Figure 3.7.2 Specific conductance vs different concentration of fructose aqueous solution..... | 56 |
| Figure 3.7.1.1 Mechanism of interaction of urea with the water molecule | 57 |
| Figure 3.7.1.2 Structural diffusion of the Zundel complex..... | 57 |
| Figure 3.7.1.3 Mechanism of interaction of fructose with the water molecule | 58 |

List of Abbreviations of Technical Symbols and Terms

1. Standard potential (E°)
2. Potential (E)
3. Universal gas constant (R)
4. Kelvin temperature (T)
5. Faraday constant (F)
6. Number of electrons (n)
7. Concentration (C)
8. Cyclic voltammogram (CV)
9. Anodic peak potential (E_{pa})
10. Cathodic peak potential (E_{pc})
11. Anodic peak current (i_{pa})
12. Cathodic peak current (i_{pc})
13. Platinum electrode (PtE)
14. Platinum wire (Pt)
15. The silver-silver chloride reference electrode (Ag/AgCl RE)
16. The counter electrode (CE)
17. The working electrode (WE)
18. Potassium chloride (KCl)
19. Peak potential separation (ΔE_p)
20. Half peak potential ($E_{P/2}$)

Acknowledgement

At the very beginning, I humbly acknowledge my deepest gratitude to the almighty, the most gracious, benevolent and merciful creator for his infinite mercy bestowed on me in carrying out the research work presented in the dissertation. It is a great pleasure for me to acknowledge my deepest sense of gratitude, sincere, appreciation, heartfelt indebtedness and solemn regards to my reverend teacher and supervisor Dr. Chanchal Kumar Roy, Assistant Professor, Department of Chemistry, Bangladesh University of Engineering and Technology (BUET), for his kind supervision, indispensable guidance, valuable and constructive suggestions, liberal help and continuous encouragement during the whole period. It is obvious that his attributive contribution and efforts have greatly shaped me into what I am today. In fact, I am quite lucky to be a part of his ambitious research team.

It is my great honor to convey my sincere gratitude to my respected teacher Professor Dr. Md. Shakhawat Hossain Firoz, honorable Head of the Department of Chemistry, BUET for giving me his wonderful support to move through the academic processes during this M.Sc. program. I am thankful to all other respected teachers of the Department of Chemistry, BUET, for their time to time support. I would also like to thank all the officers and staff of the Department of Chemistry, BUET for their continuous help during my study period. I thank CASR, BUET for funding this project, Department of Chemistry, BUET for all the supports it provided in the project.

I am highly grateful to all members of the board of examiners for their valuable suggestions and resourceful comments.

I would like to express my sincere appreciation to my dear fellow members of the Advanced Research Laboratory for their friendly cooperation and lovely encouragement throughout my research period. Also, thanks go to Mohammad Mozammel Hosen, Md. Mazharul Islam and Md. Akter Hossain Reaz for their helping hand in case of electrochemical measurements. I am very proud to be a first member of the Advanced Research Laboratory (ARL).

Finally, I would like to express my heartfelt indebtedness and profound gratitude to my beloved mother, father and all of my family members for their continuous inspiration and immeasurable sacrifices throughout the period of my study.

February 02, 2020

Most. Jaheda Akhtar

Abstract

Supporting electrolytes are used in excess amount for making the electrochemical process purely diffusional for the electroanalysis. The addition of supporting electrolytes is essential for the successful performance of electrochemical experiments. It decreases the solution resistance and suppresses the electrostatic migration of ionic species towards the electrodes to achieve a diffusion-controlled process. Although supporting electrolytes have advantages, but still, it has some problems. The problems are; it mostly increases the ionic strength of the solution and greatly affects the activities of ions present in the solution. Water structure modifier can be an alternative option to replace supporting electrolytes for electroanalysis. In this work, we added a water structure breaker, urea, non-electrolyte in aqueous solution to achieve the diffusion-controlled process. It has been observed that urea can increase the conductivity of the solution by the alteration of the water-structure. Different concentrations of urea have been added to the solution of various salts, such as iron, lead, cadmium in absence and presence of an insufficient amount of supporting electrolyte and their electrochemical behavior has been observed by cyclic voltammetry (CV). Shift in electrochemical peak potential and peak current support the influence of urea on electroanalysis. It has been also observed that a diffusion-controlled calibration is possible in the presence of urea. On the other hand, the addition of fructose, water-structure maker increases aqueous solution resistance and resulted in difficulties in achieving the diffusion-controlled process without supporting electrolytes. Therefore, we think and hope that this process will be very helpful for establishing a conceptual basis for proposing an alternate procedure in developing a low-cost electrochemical protocol for the electroanalysis of metal ions.

Keywords: supporting electrolyte (KCl); urea; fructose; cyclic voltammetry (CV); metal ions (Fe^{3+} , Pb^{2+} and Cd^{2+})

CHAPTER 1

Introduction

CHAPTER 1

Introduction

1.1 General Introduction

Voltammetric and amperometric measurements have been broadly used in the laboratory for the electroanalysis of metal ions in aqueous medium [1, 2]. The excess supporting electrolyte is usually added to the analyte solution for making the process purely diffusional [3]. Added supporting electrolyte significantly increases solution conductivity [4] and decreases the ohmic potential drop [5], which greatly reduces the influence of the electric field produced by the electrode in the electrochemical measurements [6]. However, the addition of supporting electrolyte can introduce many complications. It mostly increases the ionic strength of the solution [7] and greatly affects the activities of ions present in the solution [8]. It also affects the mobility of analytes. Moreover, the interactions between the supporting electrolyte and the analyte can be significant and should not be completely ignored. There have been many approaches to avoid the use of supporting electrolytes in electrochemical measurements, such as the use of microelectrodes, rotating disk electrodes, etc [9]. But these techniques are associated with the expensive price of materials and complicity in measurements for practical applications.

The water structure modification would be a new way of finding an alternative way of supporting electrolytes [10, 11]. In this research, we use different water structure modifiers such as urea and fructose to alter the normal structure of water. Variation of water structure paves the way of releasing bound protons (H^+) in aqueous solution. The high mobility of protons (five times faster than K^+ and Cl^-) will increase the solution conductivity and decrease the solution resistance. Hence the electrochemical process will be diffusion controlled. Therefore the concentration of metal ions can be determined in the absence of supporting electrolytes through electroanalysis.

In this work, we performed cyclic voltammetry and recorded the electrochemical signals; cathodic peak current, anodic peak current, cathodic peak potential, and anodic peak potential with the gradual addition of water structure modifiers. The electrochemical behavior of different metal ions has also been studied in the absence of supporting electrolytes and in the presence of water structure modifiers. Initially, the effect of supporting electrolytes and water structure modifiers has been compared for the determination of metal ions by electroanalysis. Afterwards, a relationship between the electrochemical signals of metal ions and their corresponding concentration has been established in the presence of a small amount of supporting electrolyte and in the presence of water structure modifiers such as urea and fructose. Additionally, the determination of metal ions by electroanalysis has been investigated in the presence of a small amount of supporting electrolytes. Here the conceptual scope of the electrochemical analysis in absence of supporting electrolytes has been discussed.

1.2 The Scope of Electrochemistry

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction reaction [12]. It involves chemical phenomena associated with charge separation. Sometimes this charge separation leads to charge transfer, which can occur homogeneously in solution, or heterogeneously on electrode surfaces [13]. In reality, to assure electro-neutrality, two or more charge transfer half-reactions take place, in opposing directions.

The importance of electrochemistry is undeniable we literally cannot live without electrochemistry for proper cell function and transmission of signals through the nervous system. It is also vital in a wide range of important technological applications. For example, batteries are important not only in storing energy for mobile devices and vehicles but also for load leveling to enable the use of renewable energy conversion technologies [14]. It is used for the treatment of water [15]. It is involved in the

production of materials by electro-refining or electrodeposition as well as the destruction of materials by corrosion [16].

1.2.1 Importance of electroanalysis

Electroanalytical techniques are concerned with the interplay between electricity and chemistry, namely the measurements of electrical quantities, such as potential, current, or charge, and their relationship to chemical parameters [17]. Such a case of electrical measurements for analytical purposes has found a vast range of applications, including environmental monitoring, industrial quality control, and biomedical analysis. Indeed, electrochemical probes are receiving a major share of the attention in the development of chemical sensors.

In contrast, many chemical measurements that involve homogeneous bulk solutions [18], electrochemical processes that take place at the electrode solution interface [19]. The distinction between various electroanalytical techniques reflects the type of electrical signal used for the quantitation. The two principal types of electroanalytical measurements are potentiometric and potentiostatic [20]. Both types require at least two electrodes (conductors) and a conducting sample (electrolyte) solution, which constitutes the electrochemical cell. The electrode surface is thus a junction between an ionic conductor and an electronic conductor.

One of the two electrodes responds to the target analyte and is thus termed the working electrode. The second one is the reference electrode whose potential is constant and it is independent of the sample composition [21]. Electrochemical cells can be classified as electrolytic when they consume electricity from an external source or galvanic if they are used to produce electrical energy. Potentiometry is of great practical importance, is a static (zero current) technique in which the information about the sample composition is obtained from the measurement of the potential established across a membrane [22]. Controlled potential (potentiostatic) techniques deal with the study of charge- transfer processes at the electrode-solution interface and are based on

dynamic (no zero current) situations [23]. Here, the electrode-potential is being used to derive an electron-transfer reaction and the resultant current is measured.

1.3 The Nature of Electrode Reactions

Electrode reactions are heterogeneous and take place in the interfacial region between electrode and solution [24], the region where charge distribution differs from that of the bulk phases. The electrode process is affected by the structure of this region.

However, we first assume that there is no effect apart from charge separation. At each electrode, charge separation can be represented by capacitance and the difficulty of charge transfer by a resistance [25]. For the rest of this and the ensuing sections, we consider only one of the electrodes. The electrode can act as only a source for reduction or a sink for the oxidation of electrons transferred to or from species in solution [19], as in



Where O and R are the oxidized and reduced species respectively.

Alternatively, it can take part in the electrode reaction, as in dissolution of a metal M:



In order for electron transfer to occur, there must be a correspondence between the energies of the electron orbitals where transfer takes place in the donor and acceptor. In the electrode, this level is the highest filled orbital, which is metal is the Fermi energy level, EF [26]. Insoluble species, it is simply the orbital of the valence electron to be given or received.

Thus for a reduction, there is a minimum energy that the transferable electrons from the electrode must have before transfer can occur [27] which corresponds to a sufficiently negative potential for an oxidation, there is a maximum energy that the lowest unoccupied level in the electrode can have in order to receive electrons from species in solution, corresponding to a sufficiently positive potential [28]. The values of the potentials can be controlled externally. In this way, we can control which way an electrode reaction occurs and to what extent. However, before this, we return to the

structure of the interfacial region. The change in charge distribution from the bulk in this region means that the relevant energy levels in reacting species and in the electrode are not the same as in the bulk phases, and soluble species need to adjust their conformation for electron transfer to occur. These effects should be corrected for in the treatment of kinetics of electrode processes [29] the thinner the interfacial region the better and this can be achieved by the addition of a large concentration of inert electrolyte.

1.4 Faradaic Processes

The objective of controlled-potential electroanalytical experiments is to obtain a current response that is related to the concentration of the target analyte [30]. This objective is accomplished by monitoring the transfer of electrons during the redox process of the analyte:



Where, O and R are the oxidized and reduced forms respectively, of the redox couple. Such a reaction will occur in a potential region that makes the electron transfer thermodynamically or kinetically favorable [31]. For systems controlled by the laws of thermodynamics, the potential of the electrode can be used to establish the concentration of the electroactive species [$C_O(0, t)$ and $C_R(0, t)$] at the surface according to the Nernst equation [32, 33]:

$$E = E^0 + \frac{2.3RT}{nF} \log \frac{C_O(0, t)}{C_R(0, t)} \quad \dots\dots\dots(4)$$

Where E^0 is the standard potential for the redox reaction, R is the universal gas constant (8.314 JK⁻¹mol⁻¹), T is the kelvin temperature, n is the number of electrons transferred in the reaction, and F is the Faraday constant (96,487 coulombs).

On the negative side of E^0 , the oxidized form tends to be reduced, and the forward reaction (i.e. reduction) is more favorable. The current resulting from a change in the oxidation state of the electroactive species is termed the faradaic current because it obeys Faraday's law (i.e. the reaction of 1 mole of substance involves a change of $n \times 96,487$ coulombs).

The faradaic current is a direct measure of the rate of the redox reaction. The resulting current-potential plot, known as the voltammogram, is a display of the current signal (vertical axis) versus the excitation potential (horizontal axis). The exact shape and magnitude of the voltammetric response are governed by the processes involved in the electrode reaction.

The total current is the summation of the faradaic currents for the sample and blank solutions, as well as the nonfaradaic charging background current.

Simple reactions involve only mass transport of the electroactive species to the electrode surface, the electron transfer across the interface and the transport of the product back to the bulk solution [34].

1.4.1 Mass transport controlled reactions

Mass transport occurs in three different modes:

❖ Diffusion:

The spontaneous movement under the influence of concentration gradient [35] (i.e. from regions of high concentration to regions of lower concentration), aimed at minimizing concentration differences.

❖ Migration:

Movement of charged particles along an electrical field [36] (i.e. the charge is carried through the solution by ions according to their transference number).

❖ Convection:

Transport to the electrode by a gross physical movement [37], such fluid flow occurs with stirring or flow of the solution and with rotation or vibration of the electrode (i.e. forced convection) or due to density gradients (i.e. natural convection).

These modes of mass transport are illustrated in fig. 1.4.1.1.

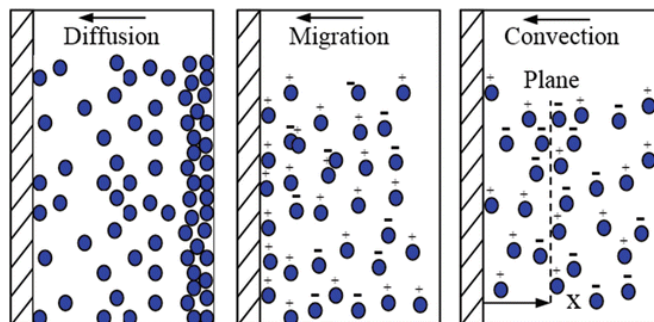


Figure 1.4.1.1 The three modes of mass transport

1.5 Cyclic Voltammetry

It is the most widely used technique for acquiring qualitative information about electrochemical reactions [38]. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes, on the kinetics of homogeneous electron transfer reactions and on coupled chemical reactions or adsorption processes [39, 40].

It is often the first experiment performed in an electroanalytical study. It offers a rapid location of redox potentials of the electroactive species and convenient equation of the effect of media upon the redox process [41]. A CV consists of scanning linearly the potential of a stationary working electrode using a triangular potential waveform [42, 43] in fig. 1.5.1.

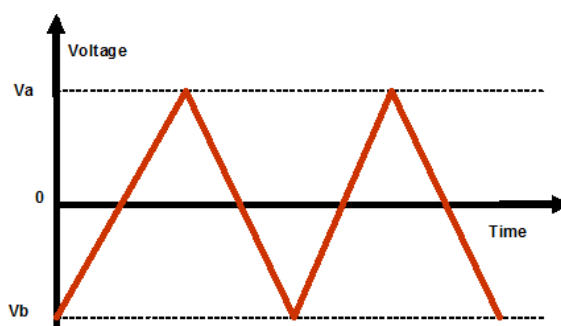


Figure 1.5.1 Potential time excitation signal in the cyclic voltammetric experiment

The CV is based on a linear potential waveform; that is, the potential is changed as a linear function of time [44] (fig. 1.5.1). Thus, a voltammogram is a display of current versus potential. The rate of change of potential with time is referred to as the scan rate. The potential is measured between the reference electrode [45] and the working electrode [46] and the current is measured between the working electrode and the counter electrode. This data is then plotted as current (i) vs. potential (E) (Figure 1.3). As the waveform shows, the forward scan produces a current peak for any analyte that can be reduced through the range of the potential scan. The current will increase as the potential reaches the reduction potential of the analyte, but then falls off as the concentration of the analyte is depleted close to the electrode surface [47]. As the applied potential is reversed, it will reach a potential that will re-oxidize the product formed in the first reduction reaction, and produce a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape to the reduction peak [48].

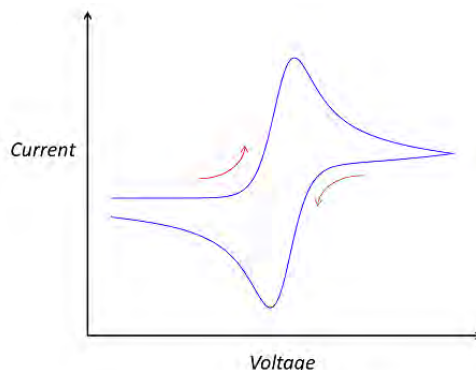


Figure 1.5.2 Typical cyclic voltammogram

As a result, information about the redox potential and electrochemical reaction rates of the compounds is obtained. The important parameters for a CV are the peak potentials; anodic peak potential (E_{pa}), cathodic peak potential (E_{pc}) and peak currents; anodic peak current (i_{pa}), cathodic peak current (i_{pc}) and half-wave potential ($E_{1/2}$), which are measured using the Peak Parameters operation. If a redox system remains in equilibrium throughout the potential scan, the redox process is said to be reversible

[49] (equilibrium) requires that the surface concentrations of oxidant (O) and reductant (R) are maintained at the values required by the Nernst equation.

The following parameter values are used to characterize the CV of a reversible process [50]:

- The separation of peak potential between the current peaks for all scan rates:

$$\Delta E_p = E_{pa} - E_{pc} = \frac{59}{n} \text{ mV} \dots\dots\dots(5)$$

Where n is the number of electrons

ΔE_p is the peak potential separation

- The positions of peak potential do not alter as a function of the potential scan rate.
- The ratio of the anodic to the cathodic peak current is equal to one.
- The cathodic and anodic peak currents are proportional to the square root of the scan rate.
- The peak width is equal to 28.5/n mV for all scan rates.

1.5.1 Reversible system

The peak current for a reversible couple (at 25⁰ C), is given by the Randles-Sevcik equation [51]:

$$i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}Cv^{1/2} \dots\dots\dots(6)$$

Where,

i_p is the peak current

n is the number of electrons

A is the electrode area (cm², the Pt distance has a diameter of 2 mm)

D is the diffusion coefficient (cm³mol⁻¹s⁻¹)

C is the concentration (mol cm⁻³)

v is the scan rate (Vs⁻¹)

Accordingly, the current is directly proportional to concentration and increases with the square root of the scan rate. The ratio of the reverse to forward peak currents, i_{pa}/i_{pc} ,

is unity for a simple reversible couple. This peak ratio can be strongly affected by chemical reactions coupled to the redox process. The current peaks are commonly measured by extrapolating the preceding baseline current. The position of the peaks on the potential axis (E_p) is related to the formal potential of the redox process.

The formal potential for a reversible couple is centered between E_{pa} and E_{pc} :

$$E^0 = \frac{E_{pa} + E_{pc}}{2} \dots\dots\dots(7)$$

The separation between the peak potential (for a reversible couple) is given by

$$\Delta E_p = E_{pa} - E_{pc} = \frac{0.059}{n} V = \frac{59}{n} mV \dots\dots\dots (8)$$

The peak separation can be used to determine the number of electrons transferred, and as a criterion for a Nerstian behavior. Both the cathodic and anodic peak potentials are independent of the scan rate. It is possible to relate the half-peak potential ($E_{P/2}$) to the polarographic half-wave potential ($E_{1/2}$).

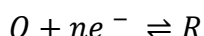
$$E_{P/2} = E_{1/2} \pm \frac{0.028}{n} V \dots\dots\dots(9)$$

Here, the sign is positive for a reduction process.

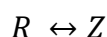
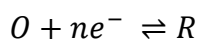
1.5.2 Study of a reaction mechanism

Electrochemical Mechanisms Involving Coupled Chemical Reactions [52]

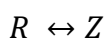
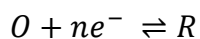
- Reversible electron transfer, no chemical complications :



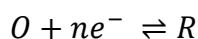
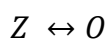
- Reversible electron transfer followed by a reversible chemical reaction, EC mechanism



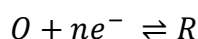
- Reversible electron transfer followed by an irreversible chemical reaction, EC mechanism:



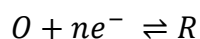
- Reversible chemical reaction preceding an irreversible electron transfer, EC mechanism:



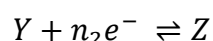
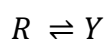
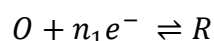
- Reversible electron transfer followed by an irreversible degeneration of starting materials, catalytic mechanism:



- Irreversible electron transfer followed by an irreversible degeneration of starting materials, catalytic mechanism:



- Multiple electron transfer with intervening chemical reaction, ECE mechanism:



1.6 Supporting Electrolyte

A supporting electrolyte is an electrolyte containing chemical species that are not electroactive which has an ionic strength and conductivity much larger than those due to the electroactive species added to the electrolyte. Supporting electrolytes is also sometimes referred to as inert electrolyte or inactive electrolyte.

Supporting electrolytes are widely used in electrochemical measurements when control of electrode potentials is required [53]. This is done to increase the conductivity of the solution, to practically eliminate the so-called IR drop, to eliminate the transport

of electroactive species by ion migration in the electric field, to maintain constant ionic strength, to maintain constant pH, etc.

1.6.1 Effect of supporting electrolyte

An electrolyte solution, whose constituents are not electroactive in the range of applied potentials being studied, and whose ionic strength is usually larger than the concentration of an electroactive substance to be dissolved in it. Supporting electrolytes are required in controlled-potential experiments to decrease the resistance of the solution, eliminate electromigration effects, and maintain a constant ionic strength while KCl, KNO₃, ammonium chloride, NaOH or HCl are widely used when water is employed as a solvent [54]. The composition of the electrolyte may affect the selectivity of voltammetric measurements.

For example, the tendency of most electrolytes to complex metal ions can benefit the analysis of mixtures of metals.

The supporting electrolyte should be prepared from highly purified reagents, and should not be easily oxidized or reduced. The usual electrolyte concentration ranges excess of 0.1 to 1.0 M i.e. in a large excess of the concentration of all electroactive species.

1.7 Water Structure

Water molecules consist of two hydrogen atoms and one oxygen atom that is held together by a covalent bond. Covalent bonds are formed between atoms that are sharing electrons. Neighboring water molecules are held together by uneven charge; this is hydrogen bonding. A dipole character of water causes hydrogen bonding. Because of the tetrahedral structure, water molecules have uneven charge distribution. Water is a compound made up of polar molecules. A polar molecule is a molecule in which opposite ends have opposite electric charges [55].

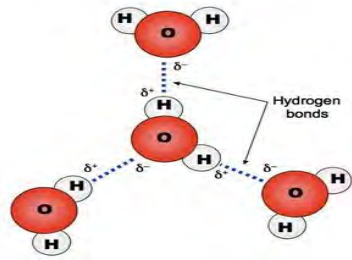
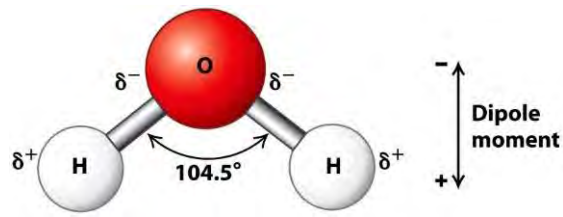


Figure 1.7.1 Water structure

1.7.1 Proton transport in water

Protons in water are inherently part of the water network. It is generally accepted that a free proton in water does not exist, rather it will always be forming a hydronium ion (H₃O⁺). Generally in chemistry, it is accepted that, when talking about a proton in water, the hydronium cation is meant.

Protons in water have been found to form several complexes or cations that give a more accurate description of their dynamics, these are the Eigen (H₉O₄⁺) and Zundel (H₅O₂⁺) cationic complexes [56] as shown in fig. 1.7.1.1.

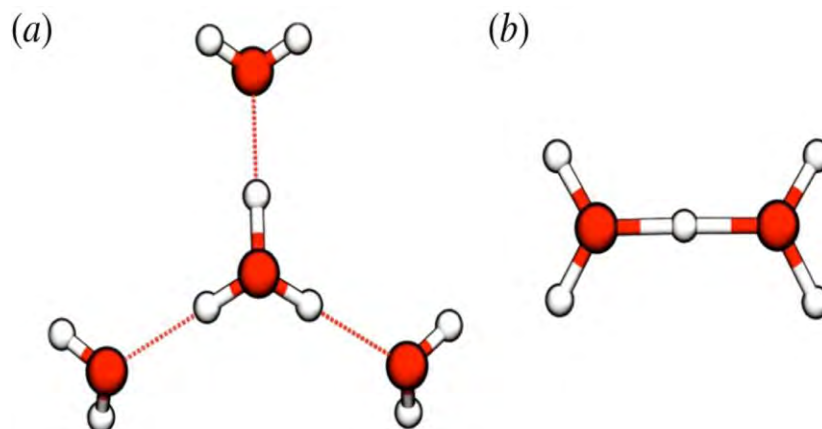


Figure 1.7.1.1 a. Eigen (H₉O₄⁺) and b. Zundel (H₅O₂⁺) cationic complexes

The Eigen complex consists of a hydronium cation surrounded by three water molecules that are hydrogen-bonded to the three hydrogen atoms of the hydronium. The Zundel complex consists of two water molecules both hydrogen-bonded to one proton.

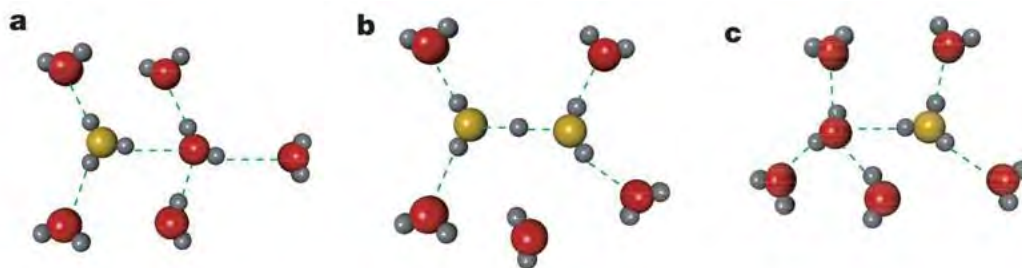


Figure 1.7.1.2 Grotthuss mechanism or structural diffusion (a) Hydronium cation (b) Zundel complex and (c) again a hydronium cation

A hydronium ion in water is surrounded by molecules that are almost the same, with the only difference is one excess proton. The proton hopping mechanism or Grotthuss mechanism [57, 58] is the process where this excess proton hops over to a neighboring water molecule as shown in fig.1.7.1.2. It involves the formation of the Eigen and Zundel complex in order to pass on the excess proton from molecule to molecule. Structural diffusion of protons [59] in water is a much faster process than vehicle diffusion. That is because for structural diffusion the major entity that is transferred is the charge which can easily be passed on from molecule to molecule.

1.7.2 Effect of urea on water structure

It is an organic compound with chemical formula $\text{CO}(\text{NH}_2)_2$. This amide has two NH_2 groups joined by a carbonyl functional group. It is colorless, odorless solid, highly soluble in water. Dissolved in water, it is neither acidic nor alkaline. Urea can serve as a hydrogen source for subsequent power generation in fuel cells [60].

Urea dissolves in water forming hydrogen bonds with water at both the amine and carbonyl headgroups. The following phenomena are observed:

- The addition of urea to water increases the solubility of hydrocarbon gases while making them dissolve with a smaller evolution of heat is interpreted as a primarily statistical phenomenon.
- For this purpose, it is treated in terms of a skeleton model in which not only is water presented as a two-species mixture of dense but also bulky constituents.
- Urea incorporates readily into the water, forming pronounced hydrogen bonds with water at both the amine and carbonyl headgroups.
- In addition to urea also hydrogen bonds to itself, forming chains or clusters consisting of up to approximately 60 urea molecules in a cluster [61].
- Urea has described as a structure breaker, structure maker [62, 63] or a remarkably neutral towards the water.

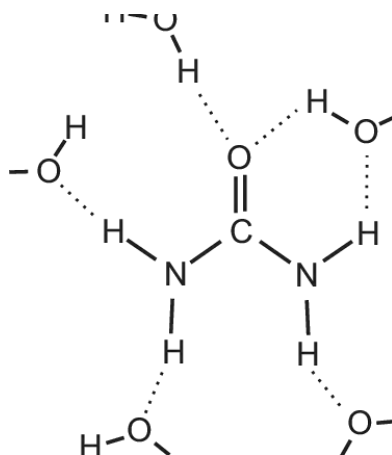


Figure 1.7.2.1 Solvation structure of the urea molecule. One of the water molecules in the solvation shell shares two hydrogen bonds with urea

The required potential for the electrolysis of pure water is 1.23 V at 25 °C. The operating potential is actually 1.48 V or higher in practical electrolysis.

Urea has better hydrogen bonding capability with good hydrogen bond donor group N-H and an acceptor group C=O. Urea tends to break the water cluster by their increased capability of hydrogen bonding. So urea can be referred to as a structure breaker modifier [64].

1.7.3 Effect of fructose on water structure

Fructose is a six-carbon polyhydroxy ketone. Crystalline fructose adopts a cyclic six-membered structure owing to the stability of its hemiketal and internal hydrogen bonding. This form is formally called D-fructopyranose. In water solution, fructose exists as an equilibrium mixture of 70% fructopyranose and 22% fructofuranose, as well as small amounts of three other forms including the acyclic structure. At lower concentration D-fructose has the water cluster structure breaking capability [65], water fructose interaction occurs and it acts as a water structure breaker [66] on the temperature dependence of water structure.

On the other hand, at higher concentrations, the fructose-fructose interaction becomes stronger as they aggregate surrounding water clusters which have a weak influence on disrupting water clusters and acts as a water structure maker.

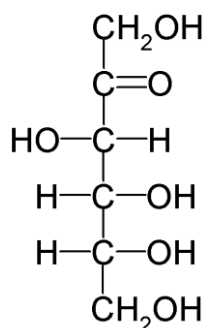


Figure 1.7.3.1 Fructose structure

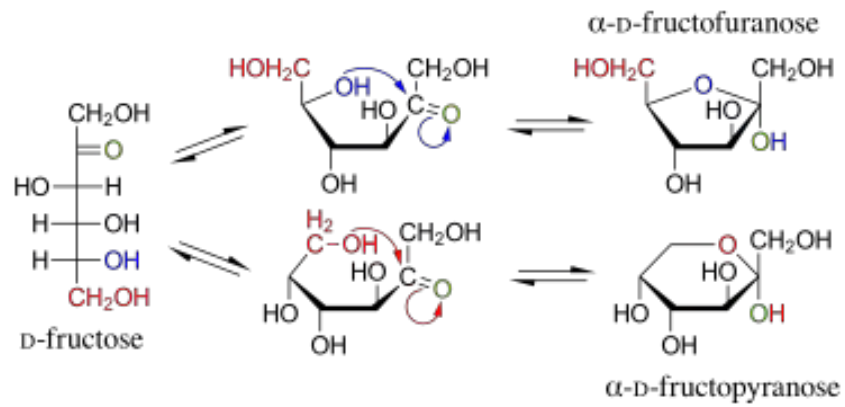


Figure 1.7.3.2 In water solution, fructose exists as an equilibrium mixture of 70% fructopyranose and 22% fructofuranose

1.8 Aims of Current Research

The major objectives of this research work are as follows:

- i. Investigation of the effect of water structure modifiers in aqueous solutions
- ii. Study of the electrochemical behavior of different metal ions by different electrochemical techniques in the absence of supporting electrolytes and in the presence of water structure modifiers.
- iii. Comparison of the effect of supporting electrolytes and water structure modifiers for the determination of metal ions by electroanalysis
- iv. Addition of information to the current state of understanding of water structure modifications
- v. Establishment of the comprehensive relationships between the amount of water structure modifiers and concentration of analyte for determination by electroanalysis
- vi. Developing the low-cost electrochemical protocols for electroanalysis of metal ions

References

- [1] N. Elgrishi, K.J. Rountree, B.D. McCarthy, E.S. Rountree, T.T. Eisenhart, J.L. Dempsey, “A practical beginner’s guide to cyclic voltammetry”, *J. Chem. Educ.*, vol. 95, pp. 197–206, 2018.
- [2] P. T. Kissinger and W. R. Heineman, “Cyclic voltammetry”, *J. Chem. Educ.*, vol. 60, pp. 702, 1983.
- [3] S. R. Belding, J. G. Limon-Petersen, E. J. F. Dickinson, and R. G. Compton, “Cyclic Voltammetry in the Absence of Excess Supporting Electrolyte Offers Extra Kinetic and Mechanistic Insights: Comproportionation of Anthraquinone and the Anthraquinone Dianion in Acetonitrile”, *Angew. Chem. Int. Ed.*, vol. 49, pp. 9242–9245, 2010.
- [4] K. Ngamchuea, C. Batchelor-McAuley, and R. G. Compton, “Anodic stripping voltammetry of silver in the absence of electrolytes: Theory and experiment”, *J. Electroanal. Chem.*, vol. 830-831, pp. 122-130, 2018.
- [5] K. Ngamchuea, C. Batchelor-McAuley, and R. G. Compton, “Understanding electroanalytical measurements in authentic human saliva leading to the detection of salivary uric acid”, *Sens. Actuator B-Chem.*, vol. 262, pp. 404-410, 2018.
- [6] B. Shruthi, B. J. Madhu, and V. B. Raju, “Influence of TiO₂ on the electrochemical performance of pasted type β -nickel hydroxide electrode in alkaline electrolyte”, *J. Energy Chem.*, vol. 25, pp. 41-48, 2016.
- [7] R. Pauliukaite and E. Norkus, “Influence of the ionic strength and the nature of supporting electrolyte on electrooxidation of formaldehyde at Pt and Cu”, *Acta Chim. Slov.*, vol. 54, pp. 617-622, 2007.
- [8] S. R. Belding and R. G. Compton, “Cyclic voltammetry in the absence of excess supporting electrolyte: The effect of analyte charge”, *J. Electroanal. Chem.*, vol. 683, pp. 1–13, 2012.
- [9] S. L. Wu, M. E. Orazem, B. Tribollet, and V. Vivier, “The impedance response of rotating disk electrodes”, *J. Electroanal. Chem.*, vol. 737, pp. 11-12, 2015.

- [10] R. Horcajada, M. Okajima, S. Suga, and J. I. Yoshida, "Microflow electroorganic synthesis without supporting electrolyte", *Chem. Commun.*, pp. 1303-1305, 2005.
- [11] E. Meyer, "Internal water molecules and H-bonding in biological macromolecules: A review of structural features with functional implications", *Protein Sci.*, pp. 1543-1562, 1992.
- [12] J. T. Warner, "Electrochemistry basics", in *Li-Ion Battery Chemistries*, pp. 17-41, 2019.
- [13] C. Brett, "Fundamentals of electrochemistry", in *Piezoelectric Transducers and Applications*, pp. 223-239, 2008.
- [14] V. Etacheri, R. Marom, R. Elazari, G. Salitra, and D. Aurbach, "Challenges in the development of advanced Li-ion batteries: A review", *Energy Environ. Sci.*, vol. 4, pp. 3243-3262, 2011.
- [15] Y. Shao, "Electrochemistry at liquid/liquid interfaces", in *Handbook of Electrochemistry*, pp. 785-809, 2007.
- [16] Y. D. Gamburg, G. Zangari, Y. D. Gamburg, and G. Zangari, "Technologies for the Electrodeposition of Metals and Alloys: Materials and Electrolyte Selection, Substrate substrate Preparation", in *Theory and Practice of Metal Electrodeposition*, pp. 253-263, 2011.
- [17] K. H. Lubert and K. Kalcher, "History of electroanalytical methods," *Electroanalysis*, vol. 22, pp. 1937-1946, 2010.
- [18] S. Q. Wang, S. Ravindranath, and P. E. Boukany, "Homogeneous shear, wall slip, and shear banding of entangled polymeric liquids in simple-shear rheometry: A roadmap of nonlinear rheology", *Macromolecules*, vol. 44, pp. 183-190, 2011.
- [19] E. J. Calvo, "Fundamentals. The Basics of Electrode Reactions", *Comprehensive Chemical Kinetics*, vol. 26, pp. 1-78, 1986.
- [20] P. Grunow, J. Rappich, and J. K. Dohrmann, "Photoelectrochemical processes at an n-type CdS: I single-crystal electrode as studied by photothermal laser beam deflection: Energy conversion efficiencies and Peltier heats", *J. Electroanal. Chem.*, vol. 337, pp. 181-186, 1992.

- [21] H. Kahlert, "Micro-reference electrodes", in *Handbook of Reference Electrodes*, pp. 289-303, 2013.
- [22] A. Malon, E. Bakker, and E. Pretsch, "Backside calibration potentiometry: Ion activity measurements with selective supported liquid membranes by calibrating from the inner side of the membrane", *Anal. Chem.*, vol. 79, pp. 632-638, 2007.
- [23] S. Y. Chen *et al.*, "Effects of Salinity on Oil Recovery (the 'dilution Effect'): Experimental and Theoretical Studies of Crude Oil/Brine/Carbonate Surface Restructuring and Associated Physicochemical Interactions", *Energy and Fuels*, vol. 31, pp. 8925-8941, 2017.
- [24] T. Zawodzinski, S. Minteer, and G. Brisard, "Physical and analytical electrochemistry: The fundamental core of electrochemistry", *Electrochem. Soc. Interface.*, 2006.
- [25] H. Ueno and M. Kaneko, "Investigation of a nanostructured polysaccharide solid medium for electrochemistry", *J. Electroanal. Chem.*, vol. 568, pp. 87-92, 2004.
- [26] T. Sakurai, S. Toyoshima, H. Kitazume, S. Masuda, H. Kato, and K. Akimoto, "Influence of gap states on electrical properties at interface between bathocuproine and various types of metals", *J. Appl. Phys.*, vol. 107, 2010.
- [27] T. J. Meyer, "Physical Mechanisms and Chemical Patterns", *Acc. Chem. Res.*, vol. 22, pp. 163-170, 1989.
- [28] R. K. Vijayaraghavan, F. Gholamrezaie, and S. C. J. Meskers, "Photovoltaic effect in self-assembled molecular monolayers on gold: Influence of orbital energy level alignment on short-circuit current generation", *J. Phys. Chem. C*, vol. 117, pp. 1682016829, 2013.
- [29] L. M. Da Silva, L. A. De Faria, and J. F. C. Boodts, "Electrochemical ozone production: Influence of the supporting electrolyte on kinetics and current efficiency", *Electrochim. Acta*, vol. 48, pp. 699-709, 2003.
- [30] C. E. M. Berger, H. K. Datta, and B. R. Horrocks, "Simulation of generation-collection experiments with homogeneous kinetics: Application to electrochemical investigation of superoxide radical anion generation by

- osteoclasts on bone”, *Phys. Chem. Chem. Phys.*, vol. 13, pp. 5288-5297, 2011.
- [31] G. M. Soriano, W. A. Cramer, and L. I. Krishtalik, “Electrostatic effects on electron-transfer kinetics in the cytochrome f- plastocyanin complex”, *Biophys. J.*, vol. 73, pp. 3265-3276, 1997.
- [32] M. M. Walczak, D. a. Dryer, D. D. Jacobson, M. G. Foss, and N. T. Flynn, “pH-Dependent redox couple: illustrating the nernst equation”, *J. Chem. Educ.*, vol. 74, pp. 1195-1197, 1997.
- [33] B. Timmer, M. Sluyters-Rehbach, and J. H. Sluyters, “Electrode kinetics and double layer structure”, *Surf. Sci.*, vol. 18, pp. 44-61, 1969.
- [34] Y. Castrillejo, M. R. Bermejo, P. Díaz Arocas, A. M. Martínez, and E. Barrado, “Electrochemical behaviour of praseodymium (III) in molten chlorides”, *J. Electroanal. Chem.*, vol. 575, pp. 61-74, 2005.
- [35] N. G. Ermakova, “Khemitaksis v norme i patologii.”, *Arkh. Patol.*, 1983.
- [36] A. N. Stepanenko, V. V. Papko, and V. M. Vinogradov, “On the mechanism of magnetic field appearance in the electrical treatment of oil emulsions”, *Soviet Surf. Eng. Appl. Electrochem.*, pp. 79-81, 1985.
- [37] T. H. Yang, S. Il Pyun, and Y. G. Yoon, “Hydrogen transport through Pd electrode: Current transient analysis”, *Electrochim. Acta*, vol. 42, pp. 1701-1708, 1997.
- [38] J. Wu, X. Z. Yuan, and H. Wang, “Cyclic voltammetry”, in *PEM Fuel Cell Diagnostic Tools*, pp. 71-85, 2011.
- [39] M. V. Mirkin, “Determination of electrode kinetics”, in *Handbook of Electrochem.*, pp. 639-660, 2007.
- [40] D. H. Evans, “One-electron and two-electron transfers in electrochemistry and homogeneous solution reactions”, *Chem. Rev.*, vol. 108, pp. 2113-2144, 2008.
- [41] V. S. Bryantsev, D. Addison, and G. V. Chase, “Comment on using cyclic voltammetry to determine a standard potential of a reversible redox couple involving oxidation or reduction of a gas”, *J. Electrochem. Soc.*, vol. 160, 2013.
- [42] B. Speiser, “Linear Sweep and Cyclic Voltammetry”, in *Encyclopedia of Electrochemistry*, 2007.
- [43] Y. Uchida, E. Kätelhön, and R. G. Compton, “Cyclic voltammetry with non-

- triangular waveforms: Electrochemically irreversible and quasi-reversible systems”, *J. Electroanal. Chem.*, vol. 810, pp. 135-144, 2018.
- [44] BASi®, “BASi® | Linear Sweep Voltammetry/Cyclic Voltammetry”, *Setting Up a Linear Sweep/Cyclic Voltammetry Experiment*, 2018.
- [45] H. Kahlert, “Reference electrodes”, in *Electroanalytical Methods: Guide to Experiments and Applications*, pp. 291-308, 2010.
- [46] Š. Komorsky-Lovrić, “Working electrodes”, in *Electroanalytical Methods: Guide to Experiments and Applications*, pp. 273-290, 2010.
- [47] V. Mirčeski and Ž. Tomovski, “Voltammetry based on fractional diffusion”, *J. phys. Chem. B*, vol. 113, pp. 2794-2799, 2009.
- [48] E. Laviron, “The use of linear potential sweep voltammetry and of a.c. voltammetry for the study of the surface electrochemical reaction of strongly adsorbed systems and of redox modified electrodes”, *J. Electroanal. Chem.*, vol. 100, pp. 263-270, 1979.
- [49] M. Sathiya *et al.*, “Reversible anionic redox chemistry in high-capacity layered-oxide electrodes”, *Nat. Mater.*, vol. 12, pp. 827-835, 2013.
- [50] R. S. Nicholson, “Theory and Application of Cyclic Voltammetry for Measurement of Electrode Reaction Kinetics”, *Anal. Chem.*, vol. 37, pp. 1351-1355, 1965.
- [51] N. Neghmouche, A. Khelef, and T. Lanez, “Electrochemistry characterization of ferrocene/ferricenium redox couple at glassy carbon electrode”, *J. Fundament. Appl. Sci.*, vol. 1, pp. 23, 2015.
- [52] A. J. Bard and L. R. Faulkner, “*Fundamentals and Applications*”, *Annu. Rev. Mater. Sci.*, vol. 30, pp. 117-157, 1980.
- [53] S. Creager, “Solvents and supporting electrolytes”, in *Handbook of Electrochem.*, pp. 57-72, 2007.
- [54] P. S. Verma, R. C. Saxena, and A. Jayaraman, “Cyclic voltammetric studies of certain industrially potential iron chelate catalysts”, *Fresenius’ J. Anal. Chem.*, vol. 357, pp. 56-60, 1997.
- [55] N. Guggemos, P. Slavíček, and V. V. Kresin, “Electric dipole moments of nanosolvated acid molecules in water clusters”, *Phys. Rev. Lett.*, vol. 114, 2015.

- [56] A. A. Tulub, "DFT:B3LYP ab initio molecular dynamics study of the Zundel and Eigen proton complexes, H_5O_2^+ and H_9O_4^+ , in the triplet state in gas phase and solution", *J. Chem. Phys.*, vol. 120, pp. 1217-1222, 2004.
- [57] E. Gileadi and E. Kirowa-Eisner, "Electrolytic conductivity-the hopping mechanism of the proton and beyond", *Electrochim. Acta*, vol. 51, pp. 6003-6011, 2006.
- [58] J. Lobaugh and G. A. Voth, "The quantum dynamics of an excess proton in water", *J. Chem. Phys.*, vol. 104, pp. 2056-2069, 1996.
- [59] P. Choi, N. H. Jalani, and R. Datta, "Thermodynamics and Proton Transport in Nafion", *J. Electrochem. Soc.*, vol. 152, 2005.
- [60] S. Mekhilef, R. Saidur, and A. Safari, "Comparative study of different fuel cell technologies", *Renew. Sustain. Energy Rev.*, vol. 16, pp. 981-989, 2012.
- [61] A. K. Soper, E. W. Castner, and A. Luzar, "Impact of urea on water structure: A clue to its properties as a denaturant?", *Biophys. Chem.*, vol. 105, pp. 649-666, 2003.
- [62] D. Bandyopadhyay, S. Mohan, S. K. Ghosh, and N. Choudhury, "Molecular dynamics simulation of aqueous urea solution: Is urea a structure breaker?", *J. Phys. Chem. B*, vol. 118, pp. 11757-11768, 2014.
- [63] J. K. Carr, L. E. Buchanan, J. R. Schmidt, M. T. Zanni, and J. L. Skinner, "Structure and dynamics of urea/water mixtures investigated by vibrational spectroscopy and molecular dynamics simulation", *J. Phys. Chem. B*, vol. 117, pp. 13291-13300, 2013.
- [64] S. Funkner, M. Havenith, and G. Schwaab, "Urea, a structure breaker? Answers from THz absorption spectroscopy", *J. Phys. Chem. B*, vol. 116, pp. 13374-13380, 2012.
- [65] T. Afrin, N. N. Mafy, M. M. Rahman, M. Y. A. Mollah, and M. A. B. H. Susan, "Temperature perturbed water structure modification by d(-)-fructose at different concentrations", *RSC Adv.*, vol. 4, pp. 50906-50913, 2014.
- [66] M. T. I. Mredha, C. K. Roy, M. M. Rahman, M. Y. A. Mollah, and M. A. B. H. Susan, "An electrochemical approach to study water-d(-)fructose interactions", *Electrochim. Acta*, vol. 97, pp. 231-237, 2013.

CHAPTER 2
Experimental

CHAPTER 2

Experimental

2.1 Materials and Instrument

2.1.1 Chemicals and reagents

The chemicals and reagents used in this research were analytical grade and used without further purification. The chemicals and reagents which were used in this research are listed below:

- I. Potassium Chloride (KCl) (BDH)
- II. Urea ($\text{NH}_2\text{-CO-NH}_2$) (LOBA)
- III. Thiourea ($\text{NH}_2\text{-CS-NH}_2$) (Research Lab)
- IV. Fructose (BDH)
- V. Potassium Ferricyanide [$\text{K}_3\text{Fe}(\text{CN})_6$] (Merck)
- VI. Cadmium Sulfate (LOBA)
- VII. Lead Nitrate (E. Merck)

2.1.2 Cells and electrodes

Three electrodes were used for electrochemical measurements in this study are given below:

- I. Platinum Electrode (PtE)
- II. Platinum wire (Pt)
- III. Silver Silver Chloride Electrode (Ag/AgCl RE)

PtE has been used as a working electrode (WE), Pt wire as a counter electrode and Ag/AgCl as a reference electrode. WE where the reaction of interest occurs. RE provides a stable and reproducible potential which is independent of the sample composition. CE is a current-carrying electrode made of inert conducting metal. The WE surface was mirror polished and was cleaned by polishing with 0.05 μg alumina powder prior to each electrochemical measurement.

2.1.3 Instruments

Analysis of the samples was performed using the following instruments:

- 1) Digital balance (AB 265/S/SACT METTLER, Toletto, Switzerland)
- 2) pH meter (LAQUA, F-74, HORIBA)
- 3) Conductivity meter (LAQUA, F-74, HORIBA)
- 4) Cyclic voltammetry measurement (797 VA Computrace, Metrohm)

2.2 Method of Preparation

The stock solution of different chemicals with desired concentration was prepared by dissolving the required amount of chemicals in D.I. water in a 100 mL volumetric flask. These solutions were further used for the preparation of different chemical solutions of desired concentrations using the formulae $V_1S_1 = V_2S_2$. All of the aqueous solutions were prepared from deionized water. To ensure that contaminants were absent.

2.2.1 Preparation of stock solution KCl

A stock solution of KCl was prepared by weighing the required amount of KCl in a volumetric flask. Then deionized water was added up to the mark. For the electrochemical study, the different concentrations of KCl were used.

2.2.2 A stock solution of potassium ferricyanide

A stock solution of potassium ferricyanide was prepared by dissolving the solid reagent in deionized water to prepare the desired concentration.

2.2.3 Preparation of stock solution urea

The required amount of crystalline urea was dissolved to prepare a target concentration of urea solution in the volumetric flask using deionized water up to the mark. Urea solutions of various concentrations were prepared by means of dilution of this stock solution.

2.2.4 Preparation of stock solution fructose

A stock solution of fructose was prepared by dissolving the required amount of fructose in a volumetric flask and up to the mark using deionized distilled water. Fructose solutions of different concentrations were prepared by dilution of this stock solution.

2.2.5 Preparation of stock solution cadmium sulfate

A stock solution of cadmium sulfate was prepared by dissolving the solid reagent in deionized water to prepare the desired concentration in a volumetric flask.

2.2.6 A stock solution of lead nitrate

A stock solution of lead nitrate was prepared by dissolving the required amount of lead nitrate in a volumetric flask. The solution was made up to the mark using deionized distilled water. Lead nitrate solutions of various concentrations were prepared by means of dilution of this stock solution.

2.2.7 Preparation of stock solution thiourea

A stock solution of desired concentration was prepared by dissolving the required amount of thiourea in a volumetric flask. The solution was made up to the mark using deionized water. Thiourea solutions of various concentrations were prepared by means of dilution of this stock solution.

2.3 Measurements

2.3.1 Electrochemical measurements

The electrochemical measurement (Cyclic Voltammetry) of potassium ferricyanide and urea in aqueous solution were accomplished in the presence and absence of potassium chloride as supporting electrolyte [1]. Before to start the electrochemical experiments, the measuring solutions were purged with N₂ to maintain an inert atmosphere during the course of the experiments. The potential sweep rates, (ν) lies in

50 mVs⁻¹ and 10 mVs⁻¹. All the electrochemical measurements have been carried out at room temperature.

2.3.2 Conductivity measurements

An aqueous solution of urea was taken in a small beaker and placed in a thermostat and gradually adding the urea solution of different concentrations. Specific conductance [2] was measured by immersing the conductivity cell of the conductivity meter in the corresponding solutions.

References

- [1] R. J. Klingler and J. K. Kochi, "Electron-transfer kinetics from cyclic voltammetry. Quantitative description of electrochemical reversibility," *J. Phys. Chem.*, vol. 85, pp. 1731-1741, 1981.
- [2] N. P. Bansal and R. H. Doremus, "Chapter 13 - Electrical Conductivity," in *Handbook of Glass Properties*, pp. 381-449, 1986.

CHAPTER 3
Results and Discussion

CHAPTER 3

Results and Discussion

3.1 Effect of Conventional Supporting Electrolyte for the Electroanalysis of Ferric Ion

To investigate the electroanalysis of ferric ion, we have used potassium ferricyanide as an analyte which is soluble in aqueous solution [1]. The CV of 1 mM potassium ferricyanide in aqueous solution was studied as a scan rate of 50 mVs^{-1} at a Pt electrode with different concentrations of KCl as the supporting electrolyte and Ag/AgCl as the reference electrode. The potential was scanned from 600 to 0 mV followed by a reverse scan from 0 to 600 mV in fig. 3.1.1 for 1 mM potassium ferricyanide and gradually adding 10 to 400 mM aqueous KCl solution.

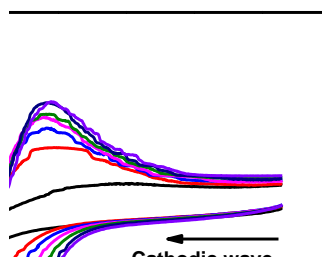


Figure 3.1.1 Cyclic voltammograms of 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in different concentration of KCl aqueous solution at a scan rate 50 mVs^{-1}

It can be easily observed from fig. 3.1.1 that the current increases with an increase in the concentration of KCl. This is because, when the control of electrode potentials is required, to eliminate the transport of electroactive species by ion migration in the electric field [2] and finally to increase the conductivity of the solution. This trend indicates that the redox equilibrium shifts in the right direction with the increase of electrolyte's concentration. This observation is attributed to the stronger attractions

between the reduced $[\text{Fe}(\text{CN})_6]^{4-}$ species and the cations of supporting electrolyte and can be clarified through the Nernst relation [3]. Specifically, the $[\text{Fe}(\text{CN})_6]^{4-}$ species is more sensitive to interactions with the cations of supporting electrolyte compared to the oxidized species $[\text{Fe}(\text{CN})_6]^{3-}$ species, since it is the most highly charged form of the redox couple. Thus, the activity of the reduced species $[\text{Fe}(\text{CN})_6]^{4-}$ decreases more of the oxidized species $[\text{Fe}(\text{CN})_6]^{3-}$ with increasing electrolyte concentration leading to an increase of the activity ratio $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ and consequently, to an increase of the equilibrium potential.

The cyclic voltammetric peak currents of $[\text{Fe}(\text{CN})_6]^{3-}$ in aqueous solution have been plotted with the concentration of KCl in fig. 3.1.2.

Figure 3.1.2 Variation of a cathodic peak, an anodic peak current of 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in different concentration of KCl aqueous solution at a scan rate of 50 mVs^{-1}

The cathodic peak current and anodic peak current increase with an increase in the concentration of KCl (as shown in fig. 3.1.2 above) due to the decrease of solution resistance.

It is interesting to mention that the ohmic drop effect tends to be reduced as the concentration of supporting electrolyte increases resulting in an increase of peak current density [4]. Supporting electrolyte needs one hundred times higher concentration than analyte for the diffusional controlled process [5].

It can be said that around 100 mM KCl is enough to get the stable current value and to achieve diffusion-controlled currents.

Figure 3.1.3 Variation of cathodic peak potential, anodic peak potential of 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in different concentration of KCl aqueous solution at a scan rate of 50 mVs^{-1}

From fig. 3.1.3 we can be observed that cathodic peak potential increases and anodic peak potential decreases slightly and their peak potential separation decreases. According to the theory [6], the smaller peak potential separation reflects faster kinetics of electron transfer reaction. Furthermore, the increase of electrolyte's concentration improves the kinetics of the redox reaction since it reduces the barrier of the interfacial electron transfer process. So it achieves a diffusion-controlled process by getting stable peak potential.

3.1.1 Effect of conventional supporting electrolyte for the electroanalysis of lead ion

The electrochemical behavior of lead nitrate was studied by CV measurements at PtE as a working electrode and Ag/AgCl as a reference electrode. Fig. 3.1.1.1 illustrates CV of 1 mM lead nitrate with 45 mM KCl and 100 mM KCl aqueous solution at the scan rate of 10 mVs^{-1} .

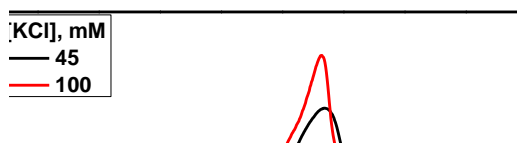


Figure 3.1.1.1 Cyclic voltammograms of 1 mM Pb²⁺ with different concentration of KCl at a scan rate 10 mVs⁻¹

It can be easily observed that the current increases with an increase in the concentration of KCl. This is because, when control of electrode potentials is required [2], to eliminate the transport of electroactive species by ion migration in the electric field and decrease the solution resistance.

Table 3.1.1.1 The values of peak currents of 1 mM Pb²⁺ for different concentration of KCl in aqueous solution

| Concentration of KCl, mM | i_{pc} | Concentration of KCl, mM | i_{pa} |
|-----------------------------|----------|-----------------------------|----------|
| 45 | 32.90 | 45 | 24.20 |
| 100 | 91.05 | 100 | 51.28 |

It can be noticed that one hundred times KCl is enough for getting stable current value and to attain a diffusion-controlled process in case of 1 mM lead nitrate solution. As electron transfers occur at the electrodes, the supporting electrolyte will migrate to balance the charge and complete the electrical circuit. Therefore it has been mentioned that large supporting electrolyte concentrations are necessary to increase solution conductivity.

3.1.2 Effect of conventional supporting electrolyte for the electroanalysis of cadmium ion

Fig. 3.1.2.1 describes CV of 1 mM cadmium sulfate for 45 mM KCl and 100 mM KCl aqueous solution at the scan rate of 10 mVs⁻¹.

It can be observed that the current increases with an increase in the concentration of KCl. This is because, when control of electrode potentials is required [6], to eliminate the transport of electroactive species by ion migration in the electric field.

Figure 3.1.2.1 Cyclic voltammograms of 1 mM Cd²⁺ with different concentration of KCl at a scan rate 10 mVs⁻¹

Table 3.1.2.1 The values of peak currents of 1 mM Cd²⁺ with different concentration of KCl in aqueous solution

| The concentration of KCl, mM | i_{pc} | The concentration of KCl, Mm | i_{pa} |
|---------------------------------|----------|---------------------------------|----------|
| 45 | 27.60 | 45 | 69.09 |
| 100 | 28.30 | 100 | 130.14 |

The cathodic peak current and anodic peak current increase with the increase of supporting electrolytes and to achieve a diffusion-controlled process due to a decrease of solution resistance. The conductivity of the solution is dependent on the concentrations of the dissolved salt. Without the electrolyte available to achieve charge

balance, the solution will be resistive to charge transfer. Therefore high absolute electrolyte concentrations are necessary.

3.2 Effect of Urea with Conventional Supporting

Electrolyte for the Electroanalysis of Ferric Ion

CV measurements were carried out in an aqueous solution of 1 mM potassium ferricyanide on a Pt electrode with 45 mM potassium chloride as the supporting electrolyte and Ag/AgCl as the reference electrode and gradually adding urea concentration from 0.1 to 5 mM at the scan rate 50 mVs^{-1} as shown below Fig. 3.2.1. An increase in current with an increase in the concentration of urea can observe due to the increasing proton transport rate. It is clear that potassium ferricyanide is electrochemically active [7] in the presence of urea. It may affect the water structure. One mechanism can be proposed to explain the action of urea in which urea acts as a “water structure breaker”.

Figure 3.2.1 Cyclic voltammograms of 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$, 45 mM KCl and different concentration of urea at a scan rate 50 mVs^{-1}

The variation of current with an increase in the concentration of urea has been plotted in fig. 3.2.2.

Figure 3.2.2 Peak current vs concentration of urea containing 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ and 45 mM KCl solution at a scan rate 50 mVs^{-1}

Fig. 3.2.2 shows that both the cathodic peak current and anodic peak current increase with an increase in the concentration of urea for increasing proton transport rate and decrease the solution resistance. The increase in current can be explained by the chaotropic effect of urea (denaturation of protein in the presence of additives). This indicates that potassium ferricyanide is free to move towards the electrode in the presence of urea solution and results in the decrease in the electrostatic attraction between urea and potassium ferricyanide species. So 5 mM urea is enough for getting stable peak current value and to establish a diffusion-controlled process.

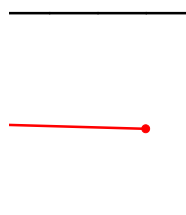


Figure 3.2.3 Peak potential vs concentration of urea containing 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ and 45 mM KCl solution at a scan rate 50 mVs^{-1}

The cathodic peak potential increases and anodic peak potential decreases and their peak potential separation decrease in presence of urea solution as shown in fig. 3.2.3. This indicates weak electrostatic interaction in the presence of urea between $[\text{Fe}(\text{CN})_6]^{3-}$ and KCl. Therefore we can say that it requires a diffusion-controlled process for getting stable peak potential and 5 mM urea is enough to attain a diffusion-controlled process.

The CV of 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ containing 45 mM KCl, 5 mM urea with 45 mM KCl and 100 mM KCl has been shown in fig. 3.2.4

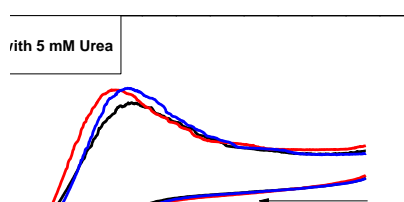


Figure 3.2.4 Comparison among 45 mM KCl, 5 mM urea with 45 mM KCl and 100 mM KCl for 1 mM Fe^{3+} at a scan rate 50 mVs^{-1}

It can be observed that from the curve addition of 5 mM urea with 45 mM KCl shows higher current compare with 45 mM and 100 mM KCl due to a decrease of solution resistance. Therefore, the addition of 5 mM urea with 45 mM KCl shows a higher current than 45 mM KCl and establishes a diffusion-controlled process because of the increasing proton transport rate.

3.2.1 Effect of urea with conventional supporting electrolyte for the electroanalysis of lead ion

Fig. 3.2.1.1 illustrates cyclic voltammograms of 1 mM lead nitrate with 45 mM KCl and gradually adding the concentration of urea from 0.5 to 5 mM aqueous solution at the scan rate 10 mVs^{-1} .

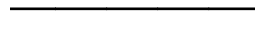


Figure 3.2.1.1 Cyclic voltammograms of 1 mM Pb^{2+} containing 45 mM KCl and different concentration of urea aqueous solution at a scan rate 10 mVs^{-1}

It can be easily observed that the current increases slightly with an increase in the concentration of urea due to a decrease in the solution resistance and significant change occur in 5 mM urea.

The cyclic voltammetric peak currents of lead nitrate in aqueous solution have been plotted with the concentration of urea in fig. 3.2.1.2.

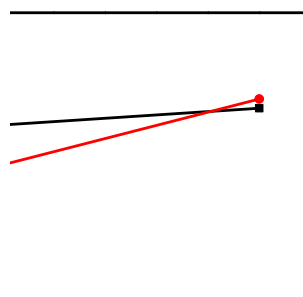


Figure 3.2.1.2 Peak current vs concentration of urea at a scan rate of 10 mVs^{-1}

It can be measured from fig. 3.2.1.2 that 5 mM urea may enough for obtaining a diffusion-controlled process because of decreasing solution resistance and this indicates the electrostatic interaction between the lead ion and KCl in the presence of urea.

3.2.2 Comparison of urea with conventional supporting electrolyte for the electroanalysis of lead ion

The CV of 1 mM lead nitrate-containing 45 mM KCl, 5 mM urea with 45 mM KCl and 100 mM KCl has been shown in fig. 3.2.2.1

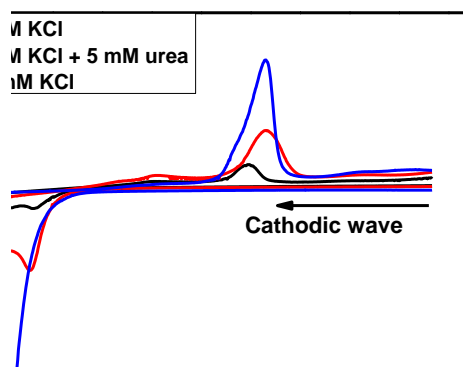


Figure 3.2.2.1 Comparison among 45 mM KCl, 5 mM urea with 45 mM KCl and 100 mM KCl for 1 mM Pb^{2+} at a scan rate 10 mVs^{-1}

From fig. 3.2.2.1 it is confirmed that in case of 5 mM urea containing 45 mM KCl the current is greater than 45 mM KCl but lower than 100 mM KCl and 5 mM urea containing 45 mM potassium chloride is enough to get stable peak current value and to achieve diffusion-controlled process because of decreasing solution resistance than 45 mM KCl. This establishes that lead nitrate-containing 5 mM urea with 45 mM KCl as supporting electrolyte is free to move towards the electrode than 45 mM KCl containing lead nitrate solution and results in the decrease in the electrostatic attraction between lead nitrate and KCl in presence of urea.

3.2.3 Effect of urea with conventional supporting electrolyte for the electroanalysis of cadmium ion

The cyclic voltammetric behavior of 1 mM cadmium sulfate with a 45 mM KCl aqueous solution has been shown in fig. 3.2.3.1 at the scan rate of 10 mVs^{-1} .

Figure 3.2.3.1 Cyclic voltammograms of 1 mM Cd²⁺ with 45 mM KCl for different concentration of urea at a scan rate 10 mVs⁻¹

Here the current increases with an increase in the concentration of urea due to an increase in proton transport rate.

Table 3.2.3.1 The values of peak currents of 1 mM Cd²⁺ with 45 mM KCl for different concentration of urea in aqueous solution

| Concentration of Urea, mM | i_{pc} | Concentration of Urea, mM | i_{pa} |
|------------------------------|----------|------------------------------|----------|
| 0.5 | 22.35 | 0.5 | 60.84 |
| 10 | 26.40 | 10 | 76.08 |

From table 3.2.3.1 it can be noted that the peak current increases with an increase in the concentration of urea solution and 10 mM urea shows stable peak current value and to achieve diffusion-controlled process because of decreasing solution resistance and increases the solution conductivity.

3.2.4 Comparison of urea with conventional supporting electrolyte for the electroanalysis of cadmium ion

The cyclic voltammetric measurements of 1 mM cadmium sulfate have been plotted with 5 mM urea containing 45 mM KCl, 45 mM KCl and 100 mM KCl in fig. 3.2.4.1.



Figure 3.2.4.1 Comparison among 45 mM KCl, 5 mM urea with 45 mM KCl and 100 mM KCl for 1 mM Cd²⁺ at a scan rate 10 mVs⁻¹

Here 5 mM urea containing 45 mM KCl shows the higher current than 45 mM KCl but lower than 100 mM KCl and it can be confirmed that 5 mM urea is enough for attaining stable current value and the process to be diffusional controlled because of decreasing solution resistance.

3.3 Electrochemical Behavior of Ferric Ion with Conventional Supporting Electrolyte in Presence of Urea

Electrochemical responses of potassium ferricyanide are sensitive to the concentration of 5 mM urea containing 45 mM KCl and gradually increasing the analyte concentration has been shown in fig. 3.3.1.

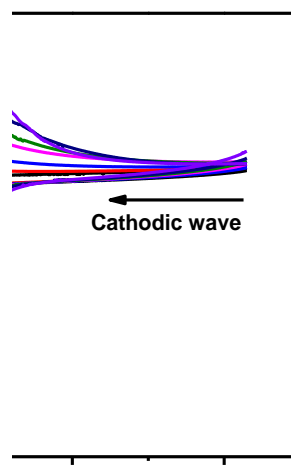


Figure 3.3.1 Cyclic voltammograms for different concentration of $[\text{Fe}(\text{CN})_6]^{3-}$ with 45 mM KCl in presence of 5 mM urea at a scan rate 10 mVs^{-1}

Figure 3.3.2 Peak currents vs concentration of $[\text{Fe}(\text{CN})_6]^{3-}$ with 45 mM KCl in presence of 5 mM urea at a scan rate 10 mVs^{-1}

Both the cathodic peak current and anodic peak current increase sharply with the increase in the concentration of potassium ferricyanide in fig. 3.3.2. As concentration is increased more electroactive potassium ferricyanide is diffused to the electrode surface [8], consequently current increases. Thus, the peak currents increase linearly with an increase in the concentration of potassium ferricyanide (as shown in fig. 3.3.2) and to attain a diffusion-controlled process due to a decrease of solution resistance.

3.4 Effect of Fructose with Conventional Supporting Electrolyte for the Electroanalysis of Ferric Ion

The cyclic voltammograms of 1 mM potassium ferricyanide with 45 mM KCl aqueous solution and gradually adding the different concentrations of fructose with the Ag/AgCl reference electrode at the scan rate 50 mVs^{-1} have been plotted in fig. 3.4.1.

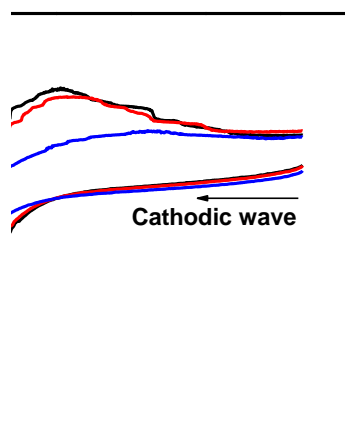


Figure 3.4.1 Cyclic voltammograms of 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ with 45 mM KCl and adding the different concentration of fructose at a scan rate 50 mVs^{-1}

In fig. 3.4.1 the cyclic voltammograms of 1 mM potassium ferricyanide in 10 mM fructose show a significant change in cathodic peak current and anodic peak current because of the decrease of proton transport rate and it may affect the water structure. Peak current vs concentration of fructose has been shown in fig. 3.4.2 at a scan rate of 50 mVs^{-1} .

Figure 3.4.2 Peak current vs concentration of fructose-containing 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ solution and 45 mM KCl at scan rate 50 mVs^{-1}

From fig. 3.4.2 it can be observed that the cathodic peak current and anodic peak current decrease with an increase in the concentration of fructose at a scan rate of 50 mVs^{-1} containing 45 mM KCl due to a decrease of proton transport rate and to indicate high solution resistance and the process does not diffusional.

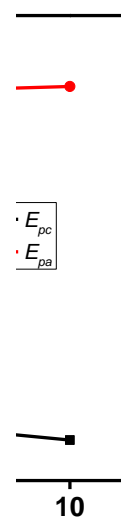


Figure 3.4.3 Peak potential vs concentration of fructose-containing 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ solution and 45 mM KCl at a scan rate 50 mVs^{-1}

From curve 3.4.3 it can be shown that the cathodic peak potential decreases and anodic peak potential increases slightly and their peak potential separation increases. This reveals strong electrostatic interaction between the $[\text{Fe}(\text{CN})_6]^{3-}$ and KCl in the presence of fructose. Therefore we can say that it attains a non-diffusional process.

The cyclic voltammetric behaviors of 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ with 10 mM fructose-containing 45 mM KCl, 45 mM KCl and 100 mM KCl have been shown in fig. 3.4.4.

Figure 3.4.4 Comparison among 45 mM KCl, 10 mM fructose with 45 mM KCl and 100 mM KCl for 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ at a scan rate 10 mVs^{-1}

From curve 3.4.4 it can be noticed that the addition of 10 mM fructose with 45 mM KCl shows lower current compare with 45 mM and 100 mM KCl. Peak potential separation increases with the addition of 10 mM fructose, the solution resistance increases and the process is not diffusion-controlled in case of 10 mM fructose due to a decrease of proton transport rate. Therefore, the decrease in peak current is observed indicating high solution resistance and the process does not diffusional.

3.4.1 Effect of fructose with conventional supporting electrolyte for the electroanalysis of lead ion

CV measurements of 1 mM lead nitrate with 45 mM KCl aqueous solution have been plotted at a scan rate of 10 mVs^{-1} in fig. 3.4.1.1.

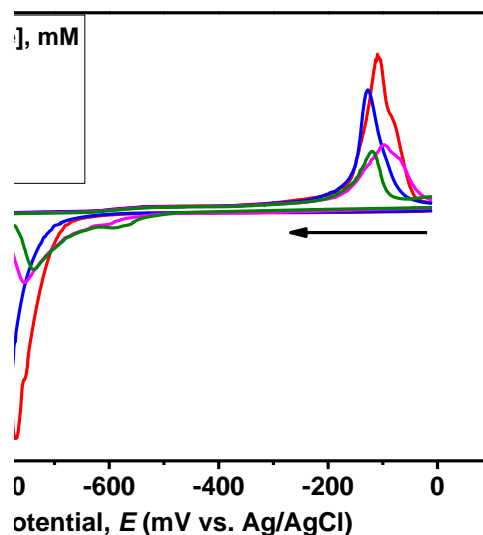


Figure 3.4.1.1 Cyclic voltammograms of 1 mM Pb^{2+} containing 45 mM KCl and different concentration of fructose at a scan rate 10 mVs^{-1}

Here the current decreases with an increase in the concentration of fructose. This is because when the proton transport rate decreases and significant change can observe in 10 mM fructose. This reveals that strong electrostatic interaction in the presence of fructose between lead nitrate and potassium chloride. It may affect the water structure. The cathodic peak current and anodic peak current have been shown with the concentration of fructose in fig. 3.4.1.2.



Figure 3.4.1.2 Peak current vs concentration of fructose-containing 45 mM KCl at a scan rate 10 mVs⁻¹

It is to be noted that the anodic peak current and cathodic peak current decrease with an increase in the concentration of fructose solution due to higher solution resistance and the process does not diffusional.

3.4.2 Comparison of fructose with conventional supporting electrolyte for the electroanalysis of lead ion

Cyclic voltammetric behavior of 1 mM lead nitrate with 10 mM fructose-containing 45 mM KCl and 100 mM KCl at scan rate 10 mVs⁻¹ have been plotted in fig. 3.4.2.1.

Figure 3.4.2.1 Comparison among 45 mM KCl, 10 mM fructose with 45 mM and 100 mM KCl for 1 mM Pb²⁺ at a scan rate 10 mVs⁻¹

Here in the case of 10 mM fructose-containing 45 mM KCl the peak current is lower than both 45 mM KCl and 100 mM KCl and does not achieve diffusion-controlled process due to increasing solution resistance and their proton transport rate decrease and their peak potential separation increase.

3.4.3 Effect of fructose with conventional supporting electrolyte for the electroanalysis of cadmium ion

Fig. 3.4.3.1 represents cyclic voltammograms of 1 mM cadmium sulfate for 45 mM KCl aqueous solution at the scan rate of 10 mVs⁻¹.

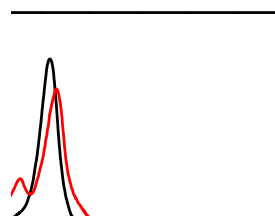


Figure 3.4.3.1 Cyclic voltammograms of 1 mM Cd²⁺ with 45 mM KCl for different concentration of fructose at a scan rate 10 mVs⁻¹

Here the current decreases slightly with an increase in the concentration of fructose. This is because when the proton transport rate decreases and current also decreases.

Table 3.4.3.1 The values of peak currents for 1 mM Cd²⁺ with 45 mM KCl for different concentration of fructose in aqueous solution

| Concentration of Fructose, mM | i_{pc} | Concentration of Fructose, mM | i_{pa} |
|----------------------------------|----------|----------------------------------|----------|
| 0.25 | 25.42 | 0.25 | 59.13 |
| 10 | 26.40 | 10 | 51.69 |

It can be noticed that the cathodic peak current increases slightly and the anodic peak current decreases with an increase in the concentration of fructose due to higher solution resistance.

3.4.4 Comparison of fructose with conventional supporting electrolyte for the electroanalysis of cadmium ion

The cyclic voltammetric quantifications of 1 mM cadmium sulfate with 10 mM fructose-containing 45 mM KCl, 45 mM KCl and 100 mM KCl have been shown in fig. 3.4.4.1.

Figure 3.4.4.1 Comparison among 45 mM KCl, 10 mM fructose with 45 mM KCl and 100 mM KCl for 1 mM Cd²⁺ at a scan rate 10 mVs⁻¹

From fig. 3.4.4.1 the current of 10 mM fructose-containing 45 mM KCl is lower than both 45 mM and 100 mM KCl for 1 mM cadmium sulfate. It can be noted that the process is not diffusional.

3.5 Effect of Conventional Supporting Electrolyte in the Presence of Thiourea for the Electroanalysis of Ferric Ion

Cyclic voltammograms of 1 mM potassium ferricyanide with 50 mM thiourea and gradually adding from 20 to 100 mM KCl aqueous solution at the scan rate 10 mVs⁻¹ in fig. 3.5.1

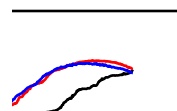


Figure 3.5.1 Cyclic voltammograms of 1 mM [Fe(CN)₆]³⁻ in presence of 50 mM thiourea for different concentration of KCl at a scan rate 50 mVs⁻¹

Here the current decreases significantly with an increase in the concentration of KCl because of higher solution resistance and finally peak current signal has been stopped.

3.6 pH Measurement of Urea and Fructose in Aqueous Solution

When the urea solution is added gradually, the pH value decreases slightly in fig. 3.6.1.

Figure 3.6.1 pH vs different concentration of urea aqueous solution

From fig. 3.6.1 for 0.1 to 5 mM urea concentration pH range is 6.09 to 6.2 and it stands for weakly acidic [9]. So it can be observed that there is no pH effect.

In contrast to when fructose is added gradually the pH value decreases in fig. 3.6.2.

Figure 3.6.2 pH vs concentration of fructose aqueous solution

From fig. 3.6.2 for 1 to 10 mM fructose concentration pH range is 5.75 to 5.98 and it stands for weakly acidic [10]. Therefore it can be noticed that there is no pH effect on fructose.

Finally, it can be said that there is no effect of pH for urea and fructose and it shows neutrality behavior.

3.7 Conductometric Measurement of Urea and Fructose in Aqueous Solution

The plot of conductivity vs the concentration of urea in aqueous solution has been shown in fig. 3.7.1.

Figure 3.7.1 Specific conductance vs different concentration of urea aqueous solution

From a conductivity curve, it can be said that when the urea solution is added gradually in aqueous solution, the conductivity has been increased due to the increase of more charge-carrying ions and their mobility has been increased. It can be observed that there was an effect of conductivity on urea and the proton transfer rate is increasing.

Conductivity vs concentration of fructose in aqueous solution has been plotted in fig. 3.7.2.

Figure 3.7.2 Specific conductance vs different concentration of fructose aqueous solution

In contrast to when fructose is added gradually the conductivity has been decreased. Therefore it can be said that more charge-carrying ions have been decreased and its mobility has been decreasing and finally the proton transfer rate is decreasing.

In the end, it can be said that urea and fructose have been used as water structure modifiers and urea acts as a water structure breaker and fructose acts as a water structure maker.

3.7.1 Proposed mechanism of interaction for urea and fructose

When urea is added to water, a small amount of water-urea cluster is formed by breaking of native water cluster. Urea increases the concentration of unbound water and helps in the proton exchange rate. The movement of protons in water is influenced by the ability to surround water molecules to reorient. So this increases the reorientation rate of the water molecules and finally, the proton transfer is increasing and to achieve a diffusion-controlled process. Therefore, they cause strong electrostatic ordering of nearby waters by breaking hydrogen bonds as shown in fig. 3.7.1.1.

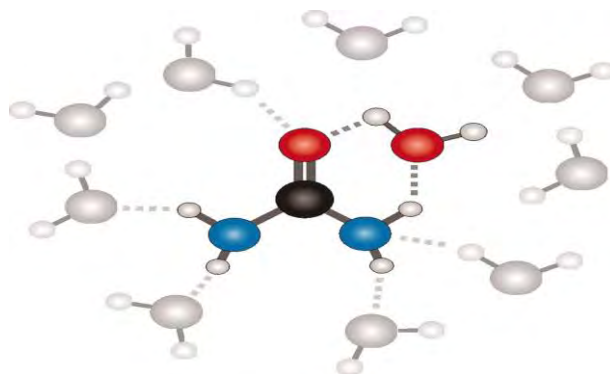


Figure 3.7.1.1 Mechanism of interaction of urea with the water molecule

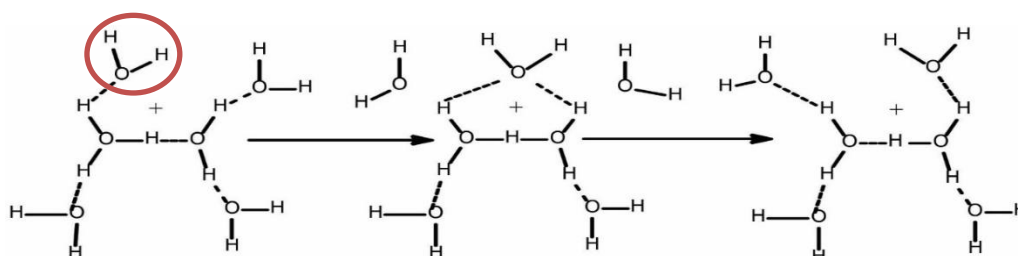


Figure 3.7.1.2 Structural diffusion of the Zundel complex

Structural diffusion of the Zundel complex has been shown in fig. 3.7.1.2. The excess proton is initially localized in the initial Zundel complex. The nearest neighbor water molecule which forms a hydrogen bond with oxygen as shown above. In the final state, this proton is bonded to oxygen, while another proton is now located inside the new Zundel complex. As the structural diffusion of the proton is being very fast, the solution resistance is decreasing and conductivity is increasing.

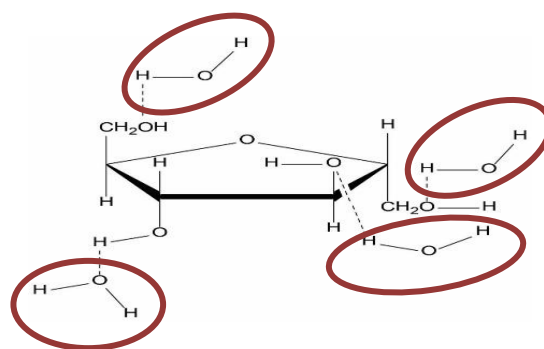


Figure 3.7.1.3 Mechanism of interaction of fructose with the water molecule

This is the mechanism of interaction of fructose. Here fructose decreases the concentration of unbound water because polar water molecules form multiple hydrogen bonds with each fructose molecule. So the proton hopping capacity is decreasing due to increasing solution resistance and decreasing conductivity.

3.8 Conclusion

In this research, the effect of water structure modifiers in aqueous solutions was successfully investigated by cyclic voltammetric technique. Water structure modifiers such as urea and fructose significantly change the electrochemical signal of metal ions for the electroanalysis of metal ions. The effect of supporting electrolytes and water structure modifiers has been compared for the determination of metal ions by electroanalysis. Water structure breakers have successfully improved peak currents. Water structure makers have decreased peak currents. The relationship between the amount of water structure modifiers and concentration of analyte has been established for the determination of metal ions by electroanalysis in the presence of a small amount of supporting electrolyte. The determination of metal ions by electroanalysis is possible in the presence of a small amount of supporting electrolytes such as potassium chloride and in the presence of water structure modifiers such as urea and fructose. The concentration of metal ions in aqueous solution has been determined from the peak currents. This study will help in developing a low-cost electrochemical protocol for electroanalysis of metal ions.

References

- [1] Z. O. Ameer and M. M. Husein, "Electrochemical Behavior of Potassium Ferricyanide in Aqueous and (w/o) Microemulsion Systems in the Presence of Dispersed Nickel Nanoparticles", *Sep. Sci. Technol.*, vol. 48, pp. 681-689, 2013.
- [2] G. Inzelt, "Electrode potentials", in *Handbook of Reference Electrodes*, pp. 1-14, 2013.
- [3] N. G. Tsierkezos and U. Ritter, "Influence of concentration of supporting electrolyte on electrochemistry of redox systems on multi-walled carbon nanotubes," *Phys. Chem. Liq.*, Vol. 50, no. 5, pp. 661-668, 2012
- [4] D. Y. Kim, J. Wang, J. Yang, H. W. Kim, and G. M. Swain, "Electrolyte and temperature effects on the electron transfer kinetics of $\text{Fe}(\text{CN})_6^{3-/4-}$ at boron-doped diamond thin-film electrodes," *J. Phys. Chem. C*, vol. 115, pp. 10026-10032, 2011.
- [5] E. J. F. Dickinson, J. G. Limon-Petersen, N. V. Rees, and R. G. Compton, "How much supporting electrolyte is required to make a cyclic voltammetry experiment quantitatively 'diffusional'? A theoretical and experimental investigation," *J. Phys. Chem. C*, vol. 113, no. 25, pp. 11157-11171, 2009.
- [6] R. S. Nicholson, "Theory and Application of Cyclic Voltammetry for Measurement of Electrode Reaction Kinetics", *Anal. Chem.*, vol. 37, no. 11, 1965.
- [7] S. Petrovic, "Cyclic Voltammetry of Hexachloroiridate(IV): An Alternative to the Electrochemical Study of the Ferricyanide Ion", *Chem. Educat.*, vol. 5, pp. 231-235, 2000.
- [8] a. W. Bott, "Practical Problems in Voltammetry: 4. Preparation of Working Electrodes", *Curr. Sep.*, vol. 16, pp. 79-84, 1997.
- [9] H. B. Bull, K. Breese, G. L. Ferguson, and C. A. Swenson, "The pH of urea solutions," *Arch. Biochem. Biophys.*, vol. 104, no. 2, pp. 297-304, 1964.
- [10] E. H. Ajandouz, L. S. Tchiakpe, F. Dalle Ore, A. Benajiba, and A. Puigserver, "Effects of pH on caramelization and Maillard reaction kinetics in fructose-lysine model systems", *J. Food Sci.*, vol. 66, pp. 926-931, 2001.