Surface Modified Electrode Used In the Electro-Analysis of N-Acetyl P-Aminophenol- A Pharmaceutical Drug

Duke Orata¹, Amir Yusuf¹* and Nineza Claire², Marina Mukabi¹, Damaris Mbuí¹
¹Department of Chemistry University of Nairobi Box 30197-00100, Nairobi
²University of Burundi Bujumbura, Burundi.

Abstract: In this paper we report on the electrochemical behavior of paracetamol or N-acetyl-p-aminophenol. In the electro-analysis bare carbon graphite and bentonite modified working electrode has been used in conjunction with cyclic voltammetry to study its redox properties. The results indicate that, the oxidation and reduction potentials of paracetamol occur at 0.600 V and 0.750 V. The paracetamol cyclic voltammogram is reversible. From the results obtained we observe that, paracetamol interacts with consumables such tea and milk; metal ions such as CO²⁺ and Fe²⁺. It is also shown to interact with vitamin, ferrous fumarate and hydrocortisone. The observed electrochemical behavior of paracetamol, if replicated at the cellular level, can give insight into its mechanism and interactive pathways.

Keywords: N-acetyl-p-aminophenol (paracetamol), surface modified electrode, working electrode

I. Introduction

Paracetamol or N-acetyl-p-aminophenol is an analgesic which is capable of relieving pain (headache reliever) and fever (1). The dose level is about 1000 mg per given time but not exceeding a daily dose of 4000 mg. An overdose taken for some time can be fatal since it slowly damages the liver (2,3 and 4). As compared to other analgesics, paracetamol has little anti-inflammatory activity. The mechanism of action is thought to be inhibition of cyclo-oxygenase (5). It acts through three pathways (6, 7, and 8). One of the methods used to synthesize paracetamol is by nitrating phenol to give a mixture of 2-nitrophenol and 4-nitrophenol. The latter is then reduced with sodium borohydride to give 4-aminophenol. This is then acetylated using acetic anhydride to give the product (9). In place of borohydride, hydrogenation is also a good alternative (10,11). The synthesis is shown in Scheme 1.

Scheme 1: Synthesis of paracetamol

In this paper we report on the redox behavior of paracetamol, using a bare carbon graphite working electrode and a clay montmorillonite (bentonite) modified electrode. The results suggest that paracetamol has redox active moieties/functional groups. This is exemplified by the reversible cyclic voltammograms obtained. In this paper we also report its interaction with consumables – Vitamin C, tea and milk, metal ions and prescription drugs such as ferrous fumarate and hydrocortisone.

II. Experimental section:

All the prescription drugs-paracetamol, ferrous fumarate, hydrocortisone and vitamin C were purchased from reputable pharmaceutical drug stores in Nairobi. They were used as received without further purification. All the acids H₂SO₄ were used as received without further purification. The CoSO₄ (Aldrich) and PbSO₄ (Aldrich) and FeSO₄ (BDH) were used as received. The electrolyte solutions were prepared using de-ionised water from a Millipore purification system. The carbon graphite working electrode was polished on a felt polishing cloth to obtain a glassy finish. The bentonite modified electrode was prepared as described by Orata and Segor (12).
Surface Modified Electrodes Used In Cyclic Voltammetric Profiling Of Quinine An Anti-Malarial Drug.

Duke Orata¹, Yusuf Amir¹, Claire Nineza², Damaris Mbuï, Marina Mukabi¹

¹. Department of Chemistry, University of Nairobi P.O. Box 30197-00100 Nairobi
². University of Burundi, Bujumbura *Author to whom all correspondence should be addressed

Abstract: In this paper electrochemical profiling of quinine, an effective anti-malarial drug administered to humans, was done using primarily the very versatile electrochemical technique- cyclic voltammetry. In the electro-analysis, the main supporting electrolyte used was sulphuric acid. The surface of the working electrode was modified using electronically conducting polymer- polyaniline and a clay montmorillonite- bentonite. Quinine and metal cation Cu²⁺, Co²⁺, Zn²⁺ and Sn²⁺ were also used to modify the electrode surface. The results obtained showed that quinine oxidation/reduction potential on bare carbon graphite electrode occurred at 0.495V/0.300V and 0.015V (0.25M H₂SO₄ supporting electrolyte). Bentonite modified electrode gave 0.434V/0.480V (1M H₂SO₄ supporting electrolyte) and 0.360V/0.345V (1M HCl supporting electrolyte). A mechanistic pathway for the oxidation of quinine has also been proposed. It was also observed from the results obtained from studies on the effect of consumables such as tea, glycine and milk on quinine, that milk totally suppressed the redox process in quinine. Amino acids which are the building blocks in proteins and which is an important macromolecule in humans, does not affect significantly the redox process in quinine.

Cyclic voltammetric profiling of quinine interaction with metal cations such as Cu²⁺, Co²⁺, Zn²⁺ and Sn²⁺ and drugs such as paracetamol, acetyl salicylic acid, hydrocortisone and ferrous fumarate revealed interactions between the redox centers.

Key Words: Surface modified electrodes, cyclic voltammetry, polyaniline, bentonite and quinine

I. Introduction:
Quinine has been a major asset in the fight against malaria, a disease caused by a one-celled parasite known as plasmodium thought to be transmitted to humans through the bite of a female Anopheles mosquito. The four distinct plasmodia that infect humans are: P. malarie, P. ovale, P. falciparum and P. vivax.

P. vivax and P. falciparum are the most common and P.falciparum the most deadly type of malaria infection. Extensive research has been conducted in an effort to contain malaria(1-17)

In this study we applied surface derivatised electrodes to study and assess the quality of anti-malarial drug quinine electrochemically.

In the analysis the oxidation-reduction profile of the quinine was analyzed using a versatile electrochemical tool- cyclic voltammetry. In addition, cyclic voltammetry was used to study redox interaction of quinine with consumables such as tea and milk, drugs such as acetylsalicylic acid, paracetamol, iso-nicotinic acid, hydrocortisone and ferrous fumarate. Quinine interaction with metal cations is also reported.

II. Experimental Section:
All chemical reagents were used as received without further purification, except the mononmer liquid Aniline (Aldrich 99%) which was triply distilled until colorless liquid was obtained. It was then stored under nitrogen.

All solutions were prepared using de-ionized water. The clay montmorillonite, bentonite (sourced from Athi River Mining Company Ltd., Kenya) was purified as described by Bard(18-19). It has a mesh size ranging from 150 to 200 μm, cation exchange capacity (CEC) 1.18-1.22 mM/g and a pH range of 8.4-9.6. The density of the bentonite is 1.25g/cm³ which are comparable to other clay minerals from different parts of the world (18). It has a solvent retention capacity of 22.5% and 4.8% for water and organic solvents respectively, while its moisture content is 8.5%. It swells by a factor of 1.7 and 1.4 in water and organic solvents respectively.

In generating the cyclic potential scans, two sets of instruments were used. These comprised of a Princeton Applied Research (PAR) model 173 pontentiostat/galvanostat, a logarithmic current converter model 369 that controlled the current, a PAR model 175 universal programmer and a PAR RE 0089 X-Y recorder.
Electrochemical Characterization of Amoxycillin, a Broad Spectrum Antibiotic on a Bentonite Host Matrix, Using Cyclic Voltammetry

Duke Oratı*, Yusuf Amir1, Claire Nineza2, Marina Mukabi1
1-Department Of Chemistry, University Of Nairobi, P. O. Box 30197-00100, Nairobi
2-University Of Burundi, Bujumbura

Abstract: In this paper we report on the redox properties of amoxycillin, a broad spectrum antibiotic, on a bentonite modified working electrode. The CV obtained with ethanol is well defined and quasi reversible suggesting fast electrode kinetics. The oxidation peak in the case of water exhibits a shoulder at 0.195v and a well defined peak at 0.465v with a broad reduction peak approximated at 0.450v. In the case of ethanol, there is a single well defined oxidation peak at 0.480v and a well defined reduction peak at 0.330v.

Interaction of amoxycillin with metal cations (co2+, pb2+, fe2+, cu2+), amino acids- methionine, leucine arginine and with hydrocortisone and paracetamol was assessed. The results obtained confirm the interactions of amoxil with these chemical substances. The amoxil redox potential is altered or inhibited in certain cases. This is informative given that these substances are commonly used together with amoxil as part of a prescription, notwithstanding the fact that the amino acids are important macromolecules in the human biochemical/physiological system.

The UV-vis spectrophotometric analysis showed that, the absorbance of amoxil is affected by electrolyte solution pH, probably an indication of the latter affecting the extent of conjugation in amoxil.

key words: amoxycillin (amoxil), antibiotic, bentonite, cyclic voltammetry

I. Introduction

Amoxil is a popular anti-biotic used globally as a broad spectrum antibiotic. The formulations of amoxil contain amoxycillin an analog of ampicillin. this broad spectrum antibiotic is effective against many gram-positive and gram negative micro-organisms. The chemical structure of amoxil is shown below in figure 1.

![Chemical Structure Of Amoxil](image)

Figure 1: Chemical Structure Of Amoxil.

Amoxil Chemical Structure In The IUPAC Notation Is (2S,5R,6R)-6-[(R)-(-)-2-Amino-2-(P-Hydroxyphenyl)Acetamido]-3,3-Dimethyl-7-Oxo-4-Thia-1-Azabicyclo[3.2.0]Heptane-2-Carboxylic Acid Trihydrate.

The molecular weight of amoxicillin is 419.45 and the molecular formula is C16H19N3O5S•3H2O. There has been significant electrochemical research in attempts to understand the redox properties of macromolecules. Surface modified electrodes have not featured prominently in these studies. references 1-14, and references therein.

In this paper, we report on the redox activity of amoxil on a bentonite modified carbon graphite working electrode.

Cyclic voltammetry has been used in the electro-analysis of amoxil and uv spectrophotometry used to assess its chromic properties.

II. Experimental section

Pharmaceutical grade amoxycillin powder and 500 mg amoxil tablets (Smithkline Beecham) were used as received. In the case of the prescription drugs purchased from local reputable chemists, the encapsulation was removed and the powder therein used in the electro-analysis without further purification.

All the acids and solvents were used as received without further purification. All solutions were prepared using triply distilled water or de-ionised water from a millipore purification system. The cyclic voltammograms were generated using PAR173 potentiostat/galvanostat used in conjunction with the PAR 175 universal programmer. The out-put signal was fed into a PAR 189 X-Y recorder.
Electro-Characterization of Polypyrolle Electrosynthesized on a Montmorillonite Host-Matrix, In Aqueous Media Containing Sulphuric Acid as Supporting Electrolyte.

Duke Orata*, Marina Mukabi, HellenNjenga, Amir Yusuf,
Department of Chemistry, University of Nairobi, P.O. Box 30197-00100, Nairobi, Kenya.

Abstract: In this paper polypyrolle has been electrosynthesised from an aqueous media containing the pyrolle monomer and sulphuric acid as the supporting electrolyte. The redox properties of polypyrolle on carbon graphite working electrode and on a clay montmorillonite host matrix has also been reported. The results obtained from plots of oxidative and reductive peak currents yield redox efficiencies above 95% for the polypyrolle redox process. The polypyrolle redox process is also shown to be diffusion limited. The reduction in the rate of electrodeposition of polypyrolle on a polyaniline loaded clay montmorillonite host matrix, is a veiled confirmation of intercalation of the polyaniline in montmorillonite matrix.

Key Words: Polypyrolle, Polyaniline, Electrosynthesised, Clay Montmorillonite (bentonite), Cyclic voltammogram, Host matrix

I. Introduction

Polymers have traditionally been considered exclusively as insulators, a property which has allowed their use in the fabrication of various electrical gadgets. During the 1970s, a new class of polymers referred to as electronically conducting polymers, possessing high electronic conductivity in the partially oxidized state was reported by several researchers. The emergence of these electronically conducting polymers resulted in a paradigmatic change in scientific thinking opening up new vistas/frontiers in chemistry, physics and materials science. Polyaniline the pioneer conducting polymer was prepared by Shirakawa and coworkers, while its 'doping 'by the group led by MacDiarmid and Heeger led to improved levels of conductivity. These splendid researches on electronically conducting polymers are found references (1-10) and references therein. Electronically conducting polymers- polyaniline, polythiophene, and polypyrrole have been the subject of intense research and this has been as a result of their unique properties such as low density, high anisotropy of electrical conduction, versatility in methods of production and non-metallic temperature dependence of conductivity.

Electrochemical and chemical methods have been used to synthesize these polymers. Electrochemical techniques enable controlled synthesis of these compounds in addition to allowing qualitative and quantitative assessment of their redox states.

Conducting polymers tend to be brittle, infusible, and intractable. The presence of conjugated double bonds and at times cross linked covalent bonds, result in strong inter- and intra-molecular interactions.

The application of these polymers in various fields require that, they be stable and easy to process, properties which are strongly dependent on on the processing conditions such as temperature, concentration, and stoichiometry as well as on the type of monomer, oxidant, dopant, and solvent used (1-10).

Electronically conducting polymers find application in the fields of energy storage, electrocatalysis, organic electrochemistry, bioelectrochemistry, photoelectrochemistry, electroanalysis, sensors, electrochromic displays, microsystem technologies, electronic devices, microwave screening and corrosion protection, etc (see references 11-13 and references therein).

In this paper the electrosynthesis and the redox features of polypyrolle electrogenerated from an aqueous media containing sulphuric acid as supporting electrolyte is reported. The working electrodes are bare carbon graphite and clay montmorillonite as a host matrix on carbon graphite electrode. Polypyrolle redox features on a polyaniline loaded montmorillonite host matrix is also reported.
Electroanalysis of Unconventional (Herbal) Drugs Using Surface Modified Electrodes in Conjunction with Cyclic Voltammetry

Duke Orata*, Yusuf Amir and Nineza Claire

1Department of Chemistry, University of Nairobi, P.O. Box 30197-00100, Nairobi
2Department of Chemistry, University of Burundi, Bujumbura.

Abstract: In this paper we report on the use of surface modified electrodes in conjunction with cyclic voltammetry to study the redox profiles of quinine in unconventional drugs-herbal medicine. The unconventional drugs used in the study include cinchona bark and malbet. The results show quinine in cinchona is redox active with the oxidation and reduction potentials on bare carbon graphite electrode occurring at 0.495 V and 0.345 V respectively. The oxidation/reduction potential on bentonite modified electrode occurred at 0.450 V (0.345 V and -0.030V). It was observed that, when in contact with the bentonite over along period, quinine in cinchona is physi-sorbed. The redox process of the quinine extract is diffusion limited. In the case of malbet the quinine in Alstonia scholaris was detected. The other natural products in malbet appear not to be electroactive. The oxidation and reduction peak potential for quinine in alstonia scholaris appeared at 0.540V and 0.225V in 1M H2SO4 and 0.525V and 0.330 V in HCl. The malbet appears to ingress into bentonite lattice and is pre-concentrated in the bentonite hence, giving enhanced redox signals. The electrochemical signal obtained in malbet is attributed to quinine in Alstonia scholaris.

Key Words: Cinchona, Malbet, unconventional (herbal) drug, surface modified electrode

I. Introduction:

A drug may be defined as any substance that brings about a biological response through its chemical action on a biological system. The drug molecule normally interacts with a specific molecule in the biological system that plays a regulatory role. The targets sites of drugs include lipids, proteins (enzymes and receptors), and deoxyribonucleic acid (DNA). When this occurs the shape of the substrates active site changes which can lead to activation or deactivation of the enzyme. A drug can also act on receptors by opening ion channels or closing them.

For effective drug action, the drug molecule must have the appropriate size, electrical charge, shape, and atomic composition. A useful drug must have the necessary properties to be transported from its site of administration to its site of action. A practical drug should be inactivated or excreted from the body at a reasonable rate so that its action will be of appropriate duration. A drug may be solid at room temperature, liquid, or gaseous. The molecular size of drugs can be very large such as cataplasm t-pA, a protein of MW 59,050. However the vast majority of drugs have MW between 100 and 1000.

Malaria is an infectious disease caused by a one-celled parasite known as Plasmodium which is transmitted to humans by the bite of the female Anopheles mosquito.

Unconventional drugs have been used in the past to treat malaria due to microorganisms such as bacteria, fungi or parasites developing resistance to the traditional antimalarials i.e., unaffected by the drug.

The evolution and spread of multidrug-resistant Plasmodium falciparum malaria have prompted the need to use combinations of antimalarial drugs and herbal medicines.

Quinine

Quinine is derived from the bark of the cinchona tree, a traditional remedy for intermittent fevers from South America.

Family: Rubiaceae
Genus: Cinchona
Species: officinalis, ledgeriana, succirubra, calisaya
Synonyms: Quinaquina officinalis, Quinaquina lancifolia, Quinaquina coccinea
Common names: Quinine bark, quina, quinine, kinakina, China bark, cinchona bark, yellow cinchona, red cinchona, Peruvian bark, Jesuit's bark, quina-quina, calisaya bark, fever tree
Parts Used: Bark, wood.

The alkaloid quinine was purified from the bark in 1820, and it has been used in its chloride or sulphate form in the treatment and prevention of malaria since that time. Cinchona trees remain the only practical source of quinine (1-16)
Sodium Thiosulphate, a Novel Electrocatalyst in the Electro-synthesis of Electronically Conducting Polymer-Polythiophene.

Duke Orata*, Hellen Njenga, Marina Mukabi, Amir Yusuf
Department of Chemistry University of Nairobi P. O. Box 30197-00100 Nairobi, Kenya

Abstract: In this paper we report on the electrosynthesis of polythiophene from aqueous media with sulphuric acid as the supporting electrolyte. The redox features of polythiophene on a bare carbon graphite working electrode and on a clay montmorillonite host matrix is also reported. Co-polymerisation of polythiophene and polyaniline from an electrolyte media containing both aniline and thiophene monomers reveal that, the redox centres of the two polymers are independent, hence suggesting the formation of a bilayer, even though no charge rectification is observed. The role of sodium thiosulphate as a novel electrocatalyst which has led to a tremendous improvement in the polythiophene faradaic/redox process is also reported.

Key Words: Polythiophene, electronically conducting, clay montmorillonite (bentonite), electrocatalyst.

I. Introduction:
Polyaniline, polythiophene, and polypyrrole are amongst the most well researched of electronically conducting polymers. They have received much in research because of their known unique properties such as low density, well behaved electrochemistry, versatility in methods of production, high anisotropy of electrical conduction, and non-metallic temperature dependence of conductivity.

Electrochemical methods have played a significant role in the characterization and synthesis of these materials. The major advantage of these electrochemical techniques lies in the fact that, they are especially well-suited to the controlled synthesis of these compounds and for the tuning of a well-defined oxidation state.

Despite all the advances made in the study of these novel materials, the preparation, characterization and application of these electronically conducting polymeric systems are still largely un-understood, hence still a major focus of research activity in electrochemistry. The key areas where gaps still exist include understanding the behavior of these systems, in particular on the mechanism of charge transfer and on charge transport processes that occur during redox reactions of conducting polymeric materials. On the applications frontier, research continues on how to perfect their use/application in the fields of energy storage, electrocatalysis, organic electrochemistry, bio-electrochemistry, photo-electrochemistry, electro-analysis, sensors, electrochromic displays, microsystem technologies, electronic devices, microwave screening and corrosion protection etc.

The intensity of research geared towards understanding the electrosynthesis, charge transfer mechanism and possible applications domain for these polymers is captured in the litany of references listed (1-61) and the references therein.

In this paper we report on the electrosynthesis of polythiophene from aqueous media with the mineral acids as supporting electrolyte. This is in contrast to the much used non-aqueous media with large organic salts as supporting electrolyte. We also report on the novel role of sodium thiosulphate as an electro-catalyst in the polythiophene redox process leading to tremendous improvement in the film electrode transfer kinetics/faradaic process.

II. Experimental Section:
Analytical grade acids were used as received without further purification. The thiophene and aniline monomers were triply distilled until a colorless liquid was obtained prior to use. The liquids were purged using an inert gas and stored under nitrogen.

Triply distilled water or de-ionised water from a Millipore-purification system was used, in preparation of the electrolyte solutions.

The cyclic voltammmograms were generated from a potentiostat/galvanostat used in conjunction with a universal programmer which generated the cyclical potential waves. The signals were then fed into an x-y recorder.

The modification of the carbon graphite working electrode was achieved by cycling the potential of the working electrode within a given potential window in an electrolyte solution containing thiophene or aniline monomer. The clay montmorillonite modification of the carbon graphite working electrode surface was achieved as discussed by Orata and Segor (62-63).
Polyaniline and Polythiophene Modified Electrodes in Energy Storage Units with Hydrocarbon Gel/Bentonite/Sodium Chloride as Electrolyte Gel.

Duke Orata *1, Hellen Njenga2, Marina Mukabi3, Yusuf Amir4, Damaris Mbui5

12345Department of Chemistry, P.O. Box 30197-00100, Nairobi., University of Nairobi

Abstract: In this paper we present results obtained for energy storage units developed using polyaniline and polythiophene modified electrodes. The voltage potential profiles for recharge/discharge are either linear or exponential. Nucleation over-potential has been observed in some profiles where there is a phase transition. It is observed that hydrocarbon gel: bentonite electrolyte mixtures yielded relatively high initial voltages and that, this voltage also depended on the hydrocarbon: bentonite ratio. The potential decay profile for potential at 1/2Vo, 1/3Vo yielded linear and exponential curves for various hydrocarbon:bentonite mixtures. The capacity (C) were 0.0014 Ah, for the 2:1 energy unit and 0.00035 Ah for the 3:1 energy unit. The electric storage density (ESD) for the 2:1 and 3:1 energy units were 4.7 × 10⁻⁴ Ah/g and 8.8 × 10⁻⁵ Ah/g

Key words: Electronically conducting polymers, Bentonite, Hydrocarbon gel, discharge profile

I. Introduction:

Research in electronically conducting polymers as continued unabated since the discovery of the highly conducting polyaniline. The discovery of other electronically conducting polymers such as polyaniline, polypyrrole and polythiophene has even widened the frontiers of research with regards to this conducting 'plastics' (1-12).

These conducting polymers are already being used as electrochromic display devices, components of rechargeable batteries just to mention a few (12-16). Intense research in the use of these polymers in rechargeable batteries is on-going (17-22). These polymers have drawn much attention given that their specific weight is significantly lower than that of ordinary inorganic materials and they are environment friendly.

Rechargeable batteries are batteries which can be restored after complete discharge. Examples include Li-ion and Ni-MH. These batteries had almost the same energy storage capacity as that of the primary alkaline cell.

Earlier reported studies on the use of conducting polymers in battery studies, is represented by the case where p-doped (oxidized) polyaniline was used as the cathode and Li as anode. Ni-Cd batteries had a better energy storing capacity and high performance compared to lead-acid batteries. These Ni-Cd batteries can withstand high current surges and tolerate adverse conditions without any damage. The major disadvantage is that, the negative electrode cadmium is a toxic material, hence not environment friendly.

Lithium ion batteries are commonly used given that, they have a low self-discharge, energy-to-weight ratio and no memory loss.

Research has been on-going in attempts to develop new rechargeable batteries using conjugated conducting polymers. The batteries christened 'plastic batteries' has traditionally involved the polymer material being doped by specific dopant material to convert it to a semi-conductor, with the lithium as one of the electrode in rechargeable battery (16-17).

Batteries with polymer as both the electrodes have been developed. Polypyrrole and styryl-substituted dialkoxyterthiophene (poly (OC10DASTT). The batteries of these combinations showed as high as 94% discharge efficiency and a discharge capacity of 39.1 mAhg⁻¹ (18). Other studies on polymer based batteries have been done by Killian (15).

In this paper we have used polyaniline, and polythiophene modified electrodes in the energy storage unit.

Bentonite a clay montmorillonite which has octahedral (O₆) and tetrahedral sites (T₄)/layers, with exchangeable cations being found in the octahedral layer has been used, singularly or with hydrocarbon gel/sodium chloride in known ratios (mass/mass). In the energy storage units discussed in this work, the bentonite/hydrocarbon gel/sodium chloride serve both as an electrolyte and/or an electrode i.e., source of dopant ions and a participant in the faradaic process.