1993

A Clay Modified Electrode for Ion-Exchange Voltammetry

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A CLAY MODIFIED ELECTRODE FOR ION-EXCHANGE VOLTAMMETRY

A THESIS SUBMITTED TO
THE FACULTY OF THE DIVISION OF CHEMISTRY
IN CANDIDACY FOR THE DEGREE OF
MASTER OF CHEMISTRY

DEPARTMENT OF CHEMISTRY

BY

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CHICAGO, ILLINOIS

January 1993

ACKNOWLEDGEMENTS

The author wishes to express gratitude to Dr. Alanah Fitch, for her assistance and advice during the course of this work.

The author is also indebted to Drs. William Johnston, Sumner Barenberg, and Thomas Sutliff for their support and guidance throughout this work.

The author would also like to thank Baxter Healthcare Corporation for the use of its equipment and facilities.

Lastly, the author would like to thank his wife, who picked him up when he was down, encouraged him when it was needed, and kept his vision focused.

TABLE OF CONTENTS

TABLE OF CONTENTS-Continued

LIST OF TABLES

LIST OF TABLES-Continued

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

One of the major advances in the analytical application of electrochemistry is the replacement of mercury electrodes with solid metal electrodes.

Although solid electrodes have many advantages, one disadvantage is the inability to selectively concentrate an analyte. Anodic stripping voltammetry (ASV), a common technique that has been used for many years with a mercury electrode, has this capability. In ASV, certain metals (selectivity) are absorbed (concentrated) into a mercury drop for a specified period of time, followed by detection of the absorbed metals.

One way of achieving the concentration and selectivity obtained with ASV on solid electrodes is to chemically modify the surface of the solid electrode. These chemically modified electrodes (CME's) could then serve as either a selector, concentrator, or both. CME's are an area of rapid growth in electrochemical research. For example, one CME goal is implantable glucose sensors.[1] In these sensors, a specific enzyme is sandwiched between two membranes on a platinum electrode. The outer membrane prevents the passage

of large substances, such as blood cells, from entering and reaching the enzyme. It does allow for passage of glucose, oxygen, ions, and other small molecules. A material that has been used as this outer layer with some success is a cellulose cuprophan hemodialysis membrane.[2-5]

The glucose reaching the inner region reacts with the enzyme to produce an electrochemically detectable species. The detectable species then passes through an inner membrane which excludes other, possibly interfering, species from reaching the electrode surface. A cellulose acetate membrane has been used with success as an inner membrane. These sensors demonstrate the use of modifying materials to enhance selectively and increase the lifetime of these sensors.[2,6]

Another use of modified electrodes has been to enhance electrochemical signals. Two possible ways of increasing the electrochemical signal are, a) increasing the concentration of the analyte within the modifying layer at the surface of the electrode or, b) increasing the apparent diffusion coefficient of the analyte. Both of these mechanisms will result in enhanced signals and, thus, lower detection limits. One strategy for achieving enhancement of the analyte is to employ an ion-exchange material at the electrode surface. This technique is referred to as ion-exchange voltammetry(IEV)[7,8]. For a modifying material to be a successful candidate for IEV, it must be an effective charge conductor. This can be accomplished by either retaining

conditions favorable to physical diffusion with the exchanged analyte, or by increasing the rate of electron hopping between localized substrates. The latter process relies on electron exchange to carry charge.

A modifying material that has been used to achieve ion-exchange has been Nafion®. Nafion coated electrodes have been used in determinations of cationic drugs[9] and metals such as lead.[10,11] Other ion-exchange resins have also been used with some success.[12-14] Two major drawbacks to these resins are their cost and difficulty of preparation.

A type of ion-exchange material that is readily available and easily prepared is montmorillonite clay. Montmorillonite clays are composed of an aluminum octahedral layer bonded between two silicon tetrahedral layers.[16] The individual crystal sheets can stack to form oriented layers. Isomorphous substitution of iron for silicon or magnesium results in a negative charge within the clay, which is compensated with cations intercalated between the clay sheets. Any cationic substrate can, theoretically, have an enhanced concentration within the clay modifying layer by ion-exchange with the simple intercalated cations.

As mentioned above, for the clay to be a successful enhancer, it has to be an efficient charge conductor through the film. For swollen clay films, charge conduction occurs via physical diffusion[17,18]. Electronic charge conduction can

also occur[19]. In the system that was explored here, physical diffusion is the apparent primary carrier of charge through the film.

The montmorillonite clays seem to be very good candidates as modifiers of electrode surfaces for use in ion-exchange voltammetry. The goal of this study is to prove that they can, in fact, be used for sensitive measurements of an electrochemically active analyte. In order to demonstrate this, we set certain criteria before we started. It should be noted that these criteria are not inclusive of every aspect of a good analytical method, but they incorporate the major aspects, such as reproducibility, selectivity, sensitivity, and linearity.

The first and probably most important criteria is that the clay-modified electrodes(CME) have to show a 10 fold signal enhancement.

The second criteria is that the detection limit has to be comparable to other, currently used, analytical techniques. Detection limits for Ru are 4.78×10^{2} A/M via UV-Vis[20], 9.89×10^{-7} M Ru via Atomic Absorption[21], and 9.89×10^{-8}-3.07×10^{-7} M Ru via Inductively Coupled Plasma[22].

The third criteria is that the electrodes have to be easily prepared. The usefulness of this technique would be diminished if electrode preparation required hours for modification or equilibration before use.

The fourth criteria is that one clay-modified electrode should be useable for multiple measurements over long periods of time. This requires that the electrodes must be durable and rinseable. Multiple measurement capability would eliminate measurement variability from modification to modification.

The fifth and last criteria is that clay-modified electrodes must yield reproducible results over a large linear detection range. It is our goal to thoroughly investigate this technique with the above mentioned criteria in mind. It is our hope that the resultant method could be applicable to real world samples.

CHAPTER 2

TRIAL SYSTEM

This section outlines the system we designed to answer the questions posed in the previous section.

As mentioned in the introduction, clays can theoretically serve as a good ion-exchanger. Clays were chosen because of their relatively low cost and their ease of application to the electrode surface.[23] Materials, such as Nafion®, a perfluorosulfonate ionomer(PFSI)[24], when used as electrode modifiers, have produced electrode sensors that are capable of measuring dilute solutions of certain cations.[25] Perfluorosulfonate materials are usually more expensive and the modification and equilibration of the electrode is often time consuming.[26,27]

The test ion used in this model system was $Ru(NH_3)_6^{3+}$. It was chosen because there were no reports of specific interactions of this cation with the hexagonal hole geometry of the clay face surface[23,28]. This complex should offer a true test of the ion-exchange capability of the clay.

It should be noted that detection of ruthenium might not be of great interest. The ideal situation would be to use copper hexamine or the amine complex of chromium.

Unfortunately, these compounds are not easily obtained commercially. We felt that what was learned using ruthenium hexamine could be applied to other metals that form amine complexes.

The trial system was set up to determine whether the clay is a good electrode modifier for analytical purposes. For analytical purposes, the signal development time must be minimized. The effect of clay thickness and its effect on signal development and enhancement must therefore be explored. Additionally, the electrolyte concentration must be optimized to yield the most enhancement while maintaining a rapid signal development.

It is also important to establish the linear detection range of the clay-modified electrode and to determine which potential scanning technique yields the best sensitivity. Furthermore the electrode has to have a demonstrated reproducible measuring capacity. The durability of the clay-modified electrode also needs to be measured. Finally, it should also be noted that the system is of no use unless a significant signal enhancement over the bare electrode can be demonstrated.

With the trial system and objectives in place, the trial system was explored.

CHAPTER 3

EXPERIMENTAL

In this section, general procedures used in all experiments are described.

Glassware Preparation

Since measurements of very dilute $Ru(NH_3)_6Cl_3$ solutions are made, cleanliness of glassware is a concern. The glassware used is first cleaned with a laboratory cleaner and rinsed thoroughly. It is then stored in a 50:50 (v/v) solution of concentrated nitric acid and DDI H_2O. At the time of use, the acid solution is drained from the cells and flasks, and the glassware is rinsed with at least 10 volumes of DDI H_2O. Volumetric pipettes are cleaned by pipetting a volume of acid solution, draining the acid solution, and then rinsing by pipetting 10 volumes of DDI H_20. The glassware is placed in an oven at 100°C to dry. The glassware is allowed to cool to room temperature before use. As previously mentioned in Chapter 2 the probe analyte chosen is the $Ru(NH_3)_6^{3+}$ ion. Along with the reasons outlined on page 6,

the $Ru(NH_3)_6^{3+}$ ion is also selected because it is soluble in water, and possesses a reversible redox couple. It's redox potential is suitable for measurement in aqueous solutions.

Preparation of Supporting Electrolyte

The supporting electrolyte that is most commonly used throughout the experiments is 0.01 M Na_2SO_4. It is prepared by dissolving 1.420 g of anhydrous Na_2SO_4(Aldrich or Fisher Scientific, used as received), in an acid cleaned(see above) 1 liter flask, and diluting to volume with distilled deionized(DDI) H_2O. When necessary, solutions of 0.1 M Na_2SO_4 are prepared by dissolving 14.20g of anhydrous Na_2SO_4, and preparing as described above.

Analyte Preparation

The solutions of $Ru(NH_3)_6Cl_3$ are quantitatively prepared by serial dilution from a 10mM(10^{-3}M) stock solution of $Ru(NH_3)_6Cl_3$. The stock solution is prepared by accurately weighing 77.5 mg of $Ru(NH_3)_6Cl_3$(Strem Chemicals, Newburyport, Massachusetts, used as received) into a 25 mL volumetric flask, then adding 0.01 M Na_2SO_4 to dilute to volume. The stock solution is stored away from light in a closed cabinet. The stock solution is prepared monthly and inspected prior to use.

If the stock solution becomes colored it is discarded and a new stock solution is prepared. Subsequent dilutions of the stock solution are prepared on a weekly basis. These solutions are prepared using 0.01M Na_2SO_4 as the diluent, unless otherwise noted. The solution preparations will be described in greater detail in the experiments in which they are used.

Clay Purification and Suspension Preparation

All the clay used in the electrode fabrication is SWy-1 montmorillonite[23] which is supplied by the Department of Geology at the University of Missouri at Colombia. The purification of the clay is done by suspension and sedimentation. Ten grams of the clay are stirred in 200 mL of distilled, deionized water for 48 hours. The clay is then placed into a centrifuge tube, sealed, and centrifuged for one hour at approximately 500 rpm. The liquid portion is decanted leaving a clay residue. The residual clay is then freeze dried in a lyophilizer(Flexi-dry; Model FDX-1-84; FTS Systems, Inc.)overnight.

The clay suspensions used in these experiments are all 5 g/L in concentration. These suspensions are prepared by weighing 0.250 grams of purified clay in a 100 mL beaker and adding 50 mL of distilled, deionized water. The clay is stirred for about 2 hours. The clay suspension is then transferred to 20 mL scintillation vials, which are sealed

with polypropylene lined caps and stored away from the light when not in use. The clay remains in suspension for several months. The unused purified clay is placed in a suitable beaker, covered with Parafilm®, and stored in a desiccator.

Electrodes

Two platinum electrodes are used in these experiments. One is manufactured by Bioanalytical Systems of Lafayette, Indiana. It has a geometric surface area of 2.0×10^{-2} cm^2. The second electrode is lab constructed and has an electrochemically active area of 5×10^{-3} cm^2 [23]. Before an electrode is modified with clay it is polished for 30 seconds with 0.05 micron Al_2O_3 either on a Buehler Ecomet(II) polishing wheel for the lab electrode, or by hand for the BAS electrode. The polished electrode is immersed in a beaker with sufficient DDI H_2O to cover the Pt portion of the electrode and sonicated for approximately 5 minutes. The electrode is removed from the water and dried by contact with a lint free cloth.

Clay Electrode Fabrication

Unless otherwise noted for a particular experiment, the clay modification of the electrode surface is as follows: the 5g/L clay suspension, is described on page 10, is shaken to insure proper mixing of the suspension. Using a 10 µL syringe, approximately 5 µL of clay suspension is withdrawn.

With the needle portion pointing upwards, the syringe is tapped to move any air bubbles to the surface. With the needle still pointing upwards, the syringe plunger is depressed until 1 μL of clay suspension remains in the syringe barrel. The excess clay is wiped from the needle with a lint free cloth.

With the needle pointing upward, the syringe plunger is depressed very slowly to expel the remaining clay suspension from the syringe to form a droplet. The goal is to have the 1 μL of clay form a single droplet on the end of the needle. Next, the electrode is positioned so the platinum surface faces upward. The syringe is inverted and the clay droplet is placed on the platinum area of the electrode. If the suspension does not spread across the Pt surface by itself, the needle tip is used to gently spread the drop over the Pt. The electrode is now ready for drying.

The clay treated electrode is placed, Pt surface up, into a 100 ml beaker. It is then dried at 100° C for 10 minutes. The beaker is then removed from the oven. The electrode is then removed from the beaker and allowed to cool(on a bench top) for 5 minutes.

A visual inspection of the modified electrode is made after it cools. The Pt surface of the electrode has a hazy dull appearance resulting from the dried clay. If there are any shiny areas of Pt exposed, the clay is wiped off, repolished, and the modification is repeated.

Potentiostat and Parameters

In the subsequent experiments, either a EGG PAR 273 potentiostat/galvanostat (equipped with an EGG PAR Model 0091 X-Y recorder or a BAS 100A potentiostat equipped with a H/P 7475A plotter), is used to obtain the cyclic voltammograms. Cyclic voltammetry is performed by scanning between +0.1 and -0.5 V vs Saturated Calomel Electrode(SCE) at 50 mV/s. Square wave and differential pulse voltammetry experiments are all performed on the BAS 100A system.

For the square wave experiments the parameters used are the default values of a 25 mV pulse amplitude at 15Hz superimposed on a step of 4 mV. Default values are also used for the differential pulse experiments. The pulse amplitude is 50 mV, the sample width 17 ns, pulse width 50 ms, the pulse period 200 ms, and the scan rate 20 mV/s.

Electrode Configuration

In both systems a three electrode cell is used. The working electrode is either the clay-modified lab prepared Pt electrode(EG&G Par) or the clay-modified BAS prepared Pt electrode(BAS). The EG&G Par 273 system uses a Pt wire as the counter electrode, a SCE as the reference electrode, and the lab prepared Pt electrode as the working electrode. The BAS 100A system uses Pt wire as the counter electrode, an Ag/AgCl electrode as the reference, and the BAS prepared Pt electrode as the working electrode.

Purging and Blanketing

Throughout the discussion of the experiments, reference will be made to the terms blanketing and purging. Blanketing is the procedure by which N_2 gas is passed over the surface of the solution in the electrode cell. The N_2 gas flow is adjusted until a small dimple is observed on the solution surface. The blanketing process is continued throughout the experiment when measurements are not being made.

Purging differs from blanketing in that the N_2 gas is passed through the solution. This is done by placing the tube that carries the N_2 gas into the solution. The gas is turned on until a steady bubbling action is achieved. Solutions are normally purged at the beginning of the experiments and do not need additional purging if blanketed. It should also be noted that the blanketing N_2 gas is turned off during measurements and turned back on while the solution is sitting and/or stirring.

Clay-Modified Electrode Equilibration

After the clay-modified electrode cools it is placed in the cell holder. The modified surface is submersed beneath the surface of a purged and blanketed electrolyte solution.

The electrode is then allowed to sit in this solution for 10 minutes unless otherwise noted. In some cases, while the electrode is in the electrolyte solution, the solution is stirred.

While stirring, care is taken to prohibit stir bar contact with the clay-modified surface. After any stirring, the solution is allowed to sit for 30 seconds prior to measurements.

CHAPTER 4

STEADY STATE EXPERIMENT

The first set of experiments to be described are the steady state enhancement experiments. The EGG Par 273 potentiostat/galvanostat and electrode system(page 13) are used in these experiments. The electrolyte used throughout these experiments is 0.01M Na_2SO_4(page 9). The working electrode is the laboratory prepared Pt electrode(page 11) that had been clay-modified(page 11). The electrode cell is filled with 50 mL of 0.01M Na_2SO_4, attached to the electrode holder, and purged, as described on page 14.

The counter and reference electrodes are then placed in the electrode holder, submersed in the electrolyte solution, and connected to the potentiostat. The N_2 inlet is then withdrawn from the electrolyte and placed in the blanketing position(page 14). The clay-modified Pt electrode(CME) is then carefully placed halfway into the electrolyte solution. Care is taken not to bump or touch the modified portion of the electrode against any portion of the cell.

The CME is then attached to the potentiostat, and the zero current and potential are marked on the recorder page. The N_2 is turned on to blanket the solution.

Electrolyte Background Scan

The CME is equilibrated in the blanketed electrolyte for 10 minutes(page 14)with the potentiostat in the cell off position. After 10 minutes a background cyclic voltammagram (CV) is taken(+0.2 V to --0.7 V at a scan rate of 50 mV/s). The potentiostat is set at a 10μA range and the recorder is set to 0.5 μA/inch in the Y direction and 0.1 V/inch in the X direction. The cell is turned on and a scan taken.

After the scan is taken, the cell and N_2 gas are turned off. The CME is disconnected from the potentiostat and carefully removed from the cell. The CME is next placed on its side, on a lint free paper towel, again being careful not to touch the modified surface against the towel. Approximately 10 mL of the just used electrolyte is next placed in a small vial. The CME is then, using a stopper, suspended in the vial with the clay end submersed in electrolyte. The CME is allowed to sit in the electrolyte while the test solution is being purged.

Analytical Scan of $Ru(NH_3)_6Cl_3$ Solution

The test solution is a quantitatively prepared solution of $Ru(NH_3)_6Cl_3$. Table 1(starting on page 20) lists the concentrations and how they are prepared. A 50 mL aliquot of test solution is placed into the electrode cell. The electrode cell(containing the test solution) is then attached to the electrode holder. The test solution is then purged for 5 minutes with N_2 gas(page 14). After 5 minutes the N_2 purge gas is turned off and the N_2 blanket initiated.

The CME is then removed from the electrolyte storage solution and placed into the test solution. The recorder pen is moved to a different location on the chart paper and the zero current and potential point marked as described with the electrolyte solution. An initial scan is taken with the same instrument parameters as for the electrolyte background scan. The potentiostat is placed in the cell off position after the initial scan is recorded. The N_2 is then turned on to blanket the test solution for 10 minutes.

After 10 minutes the cell is turned back on and another scan is taken with the same instrument parameters as the initial scan. This process (cell rest, scan, cell rest, scan) is repeated until two consecutive peak current measurements matched. Once two peak measurements are the same, the cell is turned off, the CME is disconnected from the potentiostat lead, and removed from the cell.

Bare Electrode Measurements

A lint free wipe is used to remove clay modification from the electrode surface. The electrode is then rinsed with DDI H_2O and polished(page 11). The cleaned Pt working electrode is inserted back into the test solution. The recorder is again zeroed and a scan is taken under the same experimental conditions for the CME. Only one scan is taken for the bare electrode measurement. The cell and N_2 gas are turned off.

The test solution is saved and the cell is cleaned (page 8). The reference and counter electrodes are thoroughly rinsed with DDI H_2O. This experiment is repeated with a freshly prepared CME for every experiment until at least two, and, when possible, three steady state results are obtained for each concentration. It should be noted that for the more dilute solutions of $Ru(NH_3)_6Cl_3$, long periods of time are needed to obtain reach steady state measurements.

TABLE 1

STEADY STATE $Ru(NH_3)_6Cl_3$ SOLUTION PREPARATIONS

Concentration $Ru(NH_3)_6Cl_3$ (M)	Preparation
6.3×10^{-3}	100.6 mg of $Ru(NH_3)_6Cl_3$ is weighed into a 50.0 mL volumetric flask and is dissolved and diluted to volume with 0.01M Na_2SO_4
4.0×10^{-3}	20.0 mL of 10mM stock diluted to 50.0 mL with 0.01M Na_2SO_4
2.5×10^{-3}	12.5 mL of 10mM stock diluted to 50.0 mL with 0.01M Na_2SO_4
1.0×10^{-3}	5.0 mL of 10mM stock diluted to 50.0 mL with 0.01M Na_2SO_4
1.0×10^{-4}	5.0 mL of 1×10^{-3} M solution diluted to 50.0 mL with 0.01M Na_2SO_4
1.0×10^{-5}	5.0 mL of 1×10^{-4} M solution diluted to 50.0 mL with 0.01M Na_2SO_4
5.0×10^{-6}	25.0 mL of 1×10^{-5} M solution diluted to 50.0 mL with 0.01M Na_2SO_4
3.0×10^{-6}	15.0 mL of 1×10^{-5} M solution diluted to 50.0 mL with 0.01M Na_2SO_4
1.0×10^{-6}	5.0 mL of 1×10^{-5} M solution diluted to 50.0 mL with 0.01M Na_2SO_4

TABLE 1-Continued

Concentration $Ru(NH_3)_6Cl_3$ (M)	Preparation
5.0×10^{-7}	25.0 mL of 1×10^{-6} M solution diluted to 50.0 mL with 0.01M Na_2SO_4
1.6×10^{-7}	8.0 mL of 1×10^{-6} M solution diluted to 50.0 mL with 0.01M Na_2SO_4
1.0×10^{-7}	5.0 mL of 1×10^{-6} M solution diluted to 50.0 mL with 0.01M Na_2SO_4

CHAPTER 5

SYSTEM OPTIMIZATION

The steady state experiments indicate that a ten-fold increase in sensitivity is possible over the bare electrode. Optimization of the system is described in this Chapter.

Electrolyte Optimization

The logical starting place in the optimization process is the electrolyte concentration and type. Two experiments are conducted to determine the best concentration and type.

Electrolyte Concentration Experiment

The purpose of these experiments is to determine the optimal electrolyte concentration that should be used for maximum enhancement. Six concentrations of Na_2SO_4 are used. For each of these concentrations, four concentrations of $Ru(NH_3)_6Cl_3$ are analyzed to ensure that enhancements are consistent with concentration. Table 2 lists the preparations and concentrations of Na_2SO_4 and $Ru(NH_3)_6Cl_3$ used in these experiments. The following is the description of the experimental procedure used for the 0.5 M Na_2SO_4

concentration. This procedure is repeated for each of the concentrations of Na_2SO_4. In the description of this experiment, the 0.5 M Na_2SO_4 will be referred to as the electrolyte solution and the $Ru(NH_3)_6Cl_3$ solutions, prepared using 0.5 M Na_2SO_4 as the diluent, as the analyte solutions.

Details of CME preparation(p.11), CV parameters(p.13), glassware preparation(p.8), and N_2 purging are given elsewhere. The sample volume used is 50 mL.

In this experiment, the CME was equilibrated in the N_2 purged electrolyte(p.17) and a background scan taken. The CME was next transferred to a N_2 purged analyte solution(pp.18-20). The solution is stirred for 10 minutes. The stirring is then stopped and a CV is then taken . This stirring and measurement process is repeated until steady state, Chapter 4, is achieved. The CME is removed from the cell and polished(page 19). The analyte solution is removed from the cell and the cell cleaned. The electrodes are rinsed with DDI H_2O.

The above experiment is then repeated until all concentrations of analyte(Table 2) and electrolyte solutions(Table 3) are measured.

TABLE 2

ELECTROLYTE OPTIMIZATION EXPERIMENT
$Ru(NH_3)_6Cl_3$ SOLUTION PREPARATION

Concentration (M)	Preparation
1.0×10^{-3}	5.0 ml of 10 mM stock solution diluted to 50.0 ml with (X)[a] Na_2SO_4
1.0×10^{-4}	5.0 mL of 1×10^{-3} M solution diluted to 50.0 mL with (X)[a] Na_2SO_4
1.0×10^{-5}	5.0 mL of 1×10^{-4} M solution diluted to 50.0 mL with (X)[a] Na_2SO_4
1.0×10^{-6}	5.0 mL of 1×10^{-5} M solution diluted to 50.0 mL with (X)[a] Na_2SO_4.

[a](X) M Na_2SO_4 is the concentration of Na_2SO_4 being examined in the experiment. For example if 0.01 M Na_2SO_4 is the electrolyte concentration being examined, the $Ru(NH_3)_6Cl_3$ is diluted with 0.01M Na_2SO_4 prepared as described on the following page.

TABLE 3

ELECTROLYTE OPTIMIZATION EXPERIMENT
Na_2SO_4 SOLUTION PREPARATION

Concentration (M)	Preparation
0.50	71.0 g of anhydrous Na_2SO_4 is dissolved and diluted to 1000.0 mL with distilled deionized water(DDI H_2O).
0.25	250.0 mL of 0.5 M Na_2SO_4 diluted to 500.0 mL with DDI H_2O.
0.18	175.0 mL of 0.5 M Na_2SO_4 diluted to 500.0 mL with DDI H_2O.
0.10	100.0 mL of 0.5 M Na_2SO_4 diluted to 500.0 mL with DDI H_2O.
0.010	50.0 mL of 0.1 M Na_2SO_4 diluted to 500.0 mL with DDI H_2O.

Salt Comparison Experiment

These sets of experiments are conducted to determine the effect of the salt concentration and type on the uptake of the $Ru(NH_3)_6^{3+}$ ion into the clay. The BAS 100a system (page 13), BAS Pt, counter and reference electrodes (page 11) are used. The CME is prepared as before(pages 11-13) and the solutions are purged and blanketed with N_2 gas (page 14).

The test solution used is 4 mM of $Ru(NH_3)_6Cl_3$. It is prepared as follows: 620 mg of $Ru(NH_3)_6Cl_3$ is accurately weighed and transferred to a 50 mL volumetric flask. The complex is dissolved and diluted to volume with DDI H_2O. This is the stock solution used throughout the experiment. 1.00 mL of this stock solution is volumetrically pipetted into a 10 mL volumetric flask and diluted to volume with the salt solution to be tested. The salt concentrations and their preparations are included in Table 4. The system is setup as before. A stir bar is used for 10 minutes to equilibrate in electrolyte and to incorporate $Ru(NH_3)_6^{3+}$ in the CME.

A fresh CME is used for each of the salt concentrations listed in Tables 4 and 5.

TABLE 4

NaCl SOLUTION PREPARATIONS FOR SALT COMPARISON EXPERIMENT

NaCl Concentration	Preparation
5.0 M	292 g of NaCl(Fisher Scientific) is weighed and transferred to a 1000 mL volumetric flask and is dissolved and diluted to volume with DDI H_2O.
4.0 M	234 g of NaCl is weighed and transferred to a 1000 mL volumetric flask and is dissolved and diluted to volume with DDI H_2O
3.0 M	175 g of NaCl is weighed and transferred to a 1000 mL volumetric flask and is dissolved and diluted to volume with DDI H_2O.
2.0 M	50 mL of 4 M NaCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
1.6 M	40 mL of 4 M NaCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
1.3 M	1.5 g of NaCl is weighed and transferred to a 200 mL volumetric flask and is dissolved and diluted to volume with DDI H_2O.

TABLE 4-Continued

NaCl Concentration	Preparation
1.0 M	20 mL of 5 M NaCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.80 M	50 mL of 1.6 M NaCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.63 M	21 mL of 3 M NaCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.50 M	10 mL of 5 M NaCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.40 M	10 mL of 4 M NaCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.30 M	10 mL of 3 M NaCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.22 M	11 mL of 2 M NaCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.

TABLE 4-Continued

NaCl Concentration	Preparation
0.15 M	5 mL of 3 M NaCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.10 M	10 mL of 1 M NaCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.

TABLE 5
KCl SOLUTION PREPARATIONS FOR SALT COMPARISON EXPERIMENT

KCl Concentration	Preparation
4.0 M	298 g of KCl(Fisher Scientific) is weighed and transferred to a 1000 mL volumetric flask and is dissolved and diluted to volume with DDI H_2O.
3.0 M	224 g of KCl is weighed and transferred to a 1000 mL volumetric flask and is dissolved and diluted to volume with DDI H_2O.
2.0 M	50 mL of 4 M KCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.

TABLE 5-Continued

KCl Concentration	Preparation
1.6 M	40 mL of 4 M KCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
1.3 M	19.4 g of KCl is weighed and transferred to a 200 mL volumetric flask and is dissolved and diluted to volume with DDI H_2O.
1.0 M	25 mL of 4 M KCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.80 M	50 mL of 1.6 M KCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.63 M	21 mL of 3 M KCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.50 M	25 mL of 2 M KCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.40 M	10 mL of 4 M KCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.

TABLE 5-Continued

KCl Concentration	Preparation
0.30 M	10 mL of 3 M KCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.22 M	11 mL of 2 M KCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.15 M	5 mL of 3 M KCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.
0.10 M	10 mL of 1 M KCl is volumetrically pipetted into a 100 mL volumetric flask and is diluted to volume with DDI H_2O.

Time Optimization

Time is the next parameter to optimize. Clay film thickness affects the time required for signal development. Signal development is also affected by CME exposure to the test solution. These two affects are explored.

Clay Film Thickness Experiment

This experiment is conducted to determine the effect of the clay film thickness on the permeability and signal enhancement. The concentration of analyte used in these experiments is 0.4 mM $Ru(NH_3)Cl_3$. It is prepared as follows: 0.0774 g of $Ru(NH_3)_6Cl_3$ is accurately weighed and transferred to a previously acid cleaned 25 mL volumetric flask. The $Ru(NH_3)_6Cl_3$ is then dissolved and diluted to volume with 0.01M Na_2SO_4 (stock solution). A 4.00 mL aliquot of the above prepared solution is volumetrically pipetted into a 10 mL volumetric flask and diluted to volume with 0.01 M Na_2SO_4(working solution). The working solution has a concentration of 0.4 mM $Ru(NH_3)_6Cl_3$. The working solution is prepared fresh daily. The stock solution is good for a week when stored in the dark.

The BAS potentiostat and electrode system as described on page 13 is used for these experiments. The electrode is polished and rinsed as outlined on page 11. Five concentrations of clay were examined in this experiment. The clay concentrations were 5 g/L, 10 g/L, 15 g/L, 20 g/L and 25 g/L. Table 6(following page) details the preparations of these electrodes.

After the electrode is prepared, it is equilibrated in 0.01 M Na_2SO_4, with stirring (page 14). All solutions used were blanketed and purged with N_2 gas (page 14). After equilibration, the electrode is transferred to the 0.4 mM $Ru(NH_3)_6Cl_3$ solution. A cyclic voltammogram is taken. This serves as the initial value. With the clay electrode in the solution, the solution is stirred for ten minutes, the stirring ceased, and another cyclic voltammogram taken under the same conditions as the initial scan. This process is repeated until the CME is exposed to the solution for 60 minutes. The experiment yields 7 cyclics (initial and six 10 minute interval scans). This experimental design is repeated for each clay concentration listed in Table 6.

TABLE 6

CLAY-MODIFIED ELECTRODE PREPARATIONS FOR CLAY FILM THICKNESS EXPERIMENT

Number of 1 µl Aliquots of 5 g/L Clay Suspension	Number of Heating and Cooling Cycles	Clay Concentration (g/L)
1	1	5
2	2	10
3	3	15
4	4	20
5	5	25

Signal As A Function Of Time Experiment

In the steady state experiments it is noted that a measurable peak current is seen in as little as ten minutes. These experiments are designed to monitor the peak current as a function of time. From these measurements an optimum measurement time is identified.

Five $Ru(NH_3)_6Cl_3$ solutions of concentrations; 1 x 10^{-3}, 1 x 10^{-4}, 1 x 10^{-5}, 1 x 10^{-6} and 1 x 10^{-7} M are prepared (Table 7). All glassware used is acid washed volumetric glassware(page 8). The potentiostat system used is the EG&G Par system(page 13). The clay-modified electrode is prepared using the lab made Pt electrode (page 11). After preparation the clay electrode is equilibrated with stirring in 0.01M Na_2SO_4 (page 14). The $Ru(NH_3)_6Cl_3$ solutions are purged and blanketed with N_2(page 14).

The electrodes are connected to the cell(Chapter 4) and an initial cyclic voltammogram is taken(page 16). The solution is then stirred for 10 minutes and the above procedure repeated. This stirring, measurement, stirring procedure is repeated until the peak current measurements showed little change or until 100 minutes had passed from the beginning of the experiments. This procedure is repeated for every $Ru(NH_3)_6Cl_3$ solution.

Linear Concentration Range and Method Optimization

The following experiments are conducted to determine the linear concentration range of the system and to determine which of the three scanning techniques yields the best sensitivity.

The BAS 100A potentiostat, and the BAS manufactured Pt, counter and reference electrodes are used (pages 11 and 13). The glassware(page 8), BAS Pt working electrode(page 11), and solution purging(page 14) have been described. The scan parameters for the cyclic(CV), square wave(SWV) and differential pulse voltammagrams(DPV) are listed on page 13. The concentrations of $Ru(NH_3)_6Cl_3$ and their preparations are included in Table 7. Ten mL of sample is used.

The clay-modified electrode is connected to the cell and equilibrated with stirring(page 14). After equilibration, the electrodes are rinsed with a squirt bottle containing DDI H_2O. A cell containing a purged 1×10^{-3} M $Ru(NH_3)_6Cl_3$ solution, listed in Table 7, is attached to the electrode holder. A stirring bar is then added to the solution. The solution is stirred for 10 minutes. The stirring is then stopped and the solution allowed to settle for 30 seconds. A CV is then taken. Once the CV is taken, the solution is allowed to sit for 15 seconds and a square wave voltammagram taken. The solution is again allowed to sit for 15 seconds after the SWV and a DPV is taken.

TABLE 7

CONCENTRATION/METHOD OPTIMIZATION EXPERIMENT
$Ru(NH_3)_6Cl_3$ SOLUTION PREPARATIONS

$Ru(NH_3)_6Cl_3$ Concentration (M)	Preparation
3.0×10^{-3}	15 mL of 10mM stock diluted to 50 mL with 0.01M Na_2SO_4.
1.0×10^{-3}	5 mL of 10mM stock diluted to 50 mL with 0.01M Na_2SO_4.
3.0×10^{-4}	5 mL of 3×10^{-3} M solution diluted to 50 mL with 0.01M Na_2SO_4.
1.0×10^{-4}	5 mL of 1×10^{-3} M solution diluted to 50 mL with 0.01M Na_2SO_4.
3.0×10^{-5}	5 mL of 3×10^{-4} M solution diluted to 50 mL with 0.01M Na_2SO_4.
1.0×10^{-5}	5 mL of 1×10^{-4} M solution diluted to 50 mL with 0.01M Na_2SO_4.
1.0×10^{-6}	5 mL of 1×10^{-5} M solution diluted to 50 mL with 0.01M Na_2SO_4.
1.0×10^{-7}	5 mL of 1×10^{-6} M solution diluted to 50 mL with 0.01M Na_2SO_4.

TABLE 7-Continued

$Ru(NH_3)_6Cl_3$ Concentration (M)	Preparation
1.0×10^{-8}	5 mL of 1×10^{-7} M solution diluted to 50 mL with 0.01M Na_2SO_4.
1.0×10^{-9}	5 mL of 1×10^{-8} M solution diluted to 50 mL with 0.01M Na_2SO_4.

This process yields three data points, one for each of the scanning methods for this concentration. This whole process is repeated a total of three times, each time using a freshly prepared CME. $Ru(NH_3)_6Cl_3$ concentrations are listed in Table 7.

Electrode Rinsing Method

For this one method to have real use, one CME should be capable of making multiple measurements. This requires that the electrode be easily rinsed. The following rinsing method is used in the subsequent experiments: the previously $Ru(NH_3)_6^{3+}$ exchanged clay electrode is placed in a solution of 0.1M Na_2SO_4 for 5 minutes, then transferred to a fresh solution of 0.01M Na_2SO_4, and stirred for five minutes. The CME is then transferred to the $Ru(NH_3)_6Cl_3$ solution to be tested.

Electrode Precision

The following experiments compare the precision of measurements from freshly prepared electrodes and a single modified electrode rinsed between measurements.

Repreparation Experiment

In this set of experiments, a new clay-modified electrode is prepared for each measurement. The BAS 100A Potentiostat, counter, reference, and Pt working electrode are used in these experiments(pages 11 and 13). The preparation of the clay-modified electrode is outlined on page 11. The test solution is a $Ru(NH_3)_6Cl_3$ solution of concentration 3 x 10^{-6} M (see Table 1, page 20). All the solutions are purged and blanketed during the experiment with N_2 as outlined on page 14.

The clay-modified electrode is inserted into the cell holder along with the counter and reference electrodes. The CME is equilibrated, with stirring, in a solution of 0.01M Na_2SO_4. The CME is then transferred, submersed in the 3 x 10^{-6} M $Ru(NH_3)_6Cl_3$ solution, and stirred for 10 minutes. The CME is then scanned using Square Wave Voltammetry(page 13). The peak current obtained is recorded. The electrode is then

removed from the cell, polished, and reprepared as before and experiments repeated. A total of 5 electrode preparations are made and their resulting Square Wave Voltammetry(SWV) peak currents were recorded.

Rinsing Experiment

This experiment is a continuation of the precision experiments. In these experiments, one CME is prepared and used to make five peak current measurements using the rinsing technique outline above.

Again the electrode is polished and prepared as detailed on page 11. The same potentiostat, electrodes, $Ru(NH_3)_6Cl_3$ solution, are used as in the electrode repreparation experiment above. Once the CME is ready for use, it is inserted into the cell holder along with the counter and reference electrodes. The electrode is then equilibrated, with stirring, in a solution of 0.01M Na_2SO_4 (page 16).

The CME is then transferred, submersed in the 3×10^{-6} M $Ru(NH_3)_6Cl_3$ solution, and stirred for 10 minutes. It is then scanned using Square Wave Voltammetry(page 13). The peak current obtained is recorded. The solutions are purged prior to use and blanketed while they are stirred.

The CME is then rinsed by the procedure described above and placed back in the cell that contained the 3 x 10^{-6} M $Ru(NH_3)_6Cl_3$ solution. The solution is stirred for 10 minutes and another SWV is taken with the same parameters as before. This rinsing process is repeated three more times to achieve a total of five peak current measurements.

Electrode Carryover

The last set of experiments are set up to determine whether there is any analyte carryover in the electrode from analyte solutions of differing concentrations.

Low To High Concentration Experiment

The following experiment is designed to determine if there is any carryover effect when a CME is used for measurements of solutions of increasing concentrations. The CME is prepared for use as described on page 11. The potentiostat and electrode system is the BAS 100a system (pages 11 and 13). All the solutions used are purged and blanketed with N_2 gas during the experiments. The electrolytes used in this experiment were 0.01M Na_2SO_4 and 0.1 M Na_2SO_4 (page 9).

The concentrations of $Ru(NH_3)_6Cl_3$ used are 1 x10^{-5}, 3 x10^{-6}, 1 x10^{-6}, and 3 x 10^{-7} M. The preparation of these solutions is described in Table 1(page 20) except for the 3 x 10^{-7} M solution which is prepared by volumetrically pipetting

1.00 mL of the 3 x 10^{-6} M into a 10 mL volumetric flask and diluting with 0.01 M Na_2SO_4. The amount of analyte used for the experiments is 10.00 mL. The analyte solution is transferred to the cell with a 10.00 mL volumetric pipette. All the glassware is cleaned prior to use as described on page 8. Differential Pulse Voltammetry (page 13) is used for peak current measurements in these experiments.

After the CME is prepared it is equilibrated with stirring (page 14) for 5 minutes. At this time, the cell containing the 0.01 M Na_2SO_4 is replaced with a cell that contains the 3 x 10^{-7} M solution of $Ru(NH_3)_6Cl_3$. The solution is stirred for 10 minutes. A DPV is next taken. The cell containing the $Ru(NH_3)_6Cl_3$ solution is removed and the electrodes are rinsed with a DDI H_2O using a squirt bottle. The CME is then rinsed using the rinsing procedure described above.

After the rinsing procedure is completed, the next highest concentration of ruthenium is analyzed using the same procedure. This measurement, rinsing, measurement procedure is repeated until all four solutions had been analyzed.

High To Low Concentration Experiment

The experiment described above is repeated with a freshly prepared CME. In this case, we start with the highest concentration solution (1×10^{-5} M) . The solutions are then analyzed in order of descending concentration, until the four solutions had been analyzed.

CHAPTER 6

DISCUSSION OF RESULTS

The experiments described in Chapter 5 were conducted to investigate the clay-modified electrode system for its signal enhancement capacity. To achieve this goal the electrolyte and clay film thickness had to be optimized. The time for signal enhancement had to be studied to determine the minimum time in which a measurable peak current could be detected. The linear detection concentration range of the system and the best scanning technique for measurement had to be determined. The clay-modified electrode also had to be studied for its ruggedness and reusability. The following discussion, describes the results of the experiments.

Discussion of Signal Enhancement in the Steady State Experiment

The steady state experiments were conducted to determine if any significant enhancement could be seen from a bare electrode to the clay-modified electrode. We initially theorized that the cation exchange capacity of the clay could result in the uptake and concentration of $Ru(NH_3)_6^{3+}$ ion.

If measurements were made such that the diffusion layer remained within the thickness of the clay film, an enhancement of the $Ru(NH_3)_6^{3+}$ ion over the bare electrode would be seen.

This experiment was designed to determine if a significant enhancement could be detected and the concentration range that would give the greatest enhancement over the bare electrode. The results obtained are listed in Table 8 and plotted in Figure 1. At concentrations of 6.3 and 4.0×10^{-3} M, the bare electrode and clay electrode peak currents weren't significantly different. At a concentration of 2.5×10^{-3} M the ratio of the clay and bare electrode currents was 1.8. At this concentration, enhancement, although not large was seen. The next concentration is 1×10^{-3} M. At this concentration the ratio is 2.0. This still isn't a significant enhancement, but it is increasing. When the 1×10^{-4} M concentration is analyzed, a ratio of 14.8 is found. This is a significant enhancement. What is also found is that concentrations below 1×10^{-4} M were not detectable with the bare electrode. The concentration of $Ru(NH_3)_6Cl_3$ is lowered until it isn't measurable at the clay electrode. The lowest concentration measurable is 1×10^{-7} M.

TABLE 8

STEADY STATE EXPERIMENT RESULTS

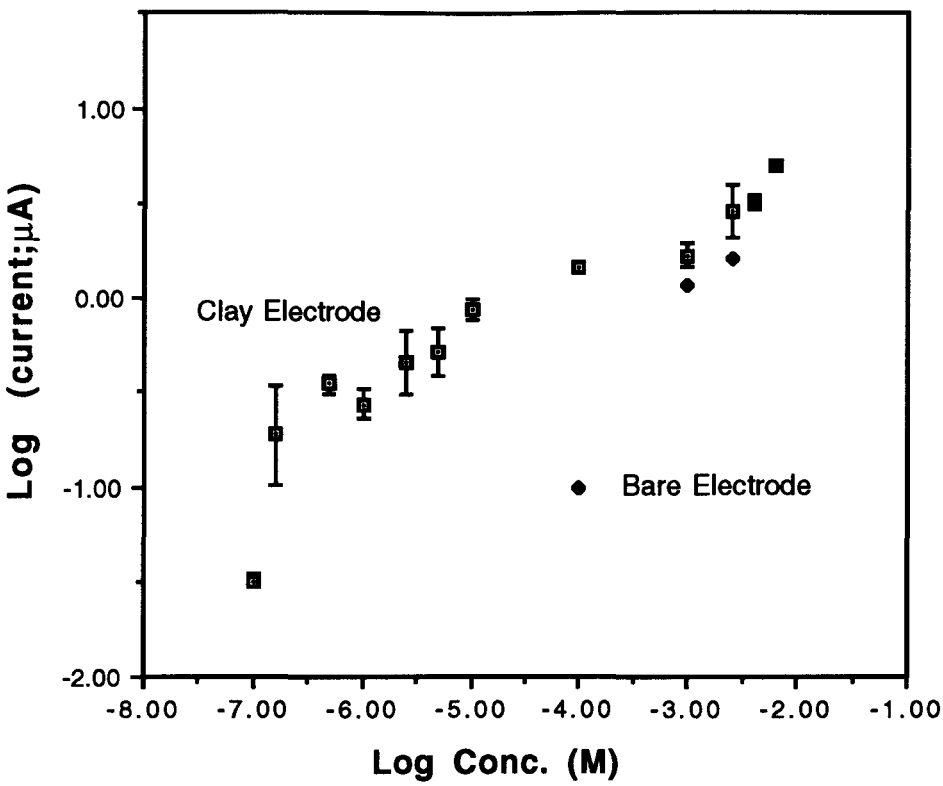
Concentration $Ru(NH_3)_6Cl_3$ (M)	Clay-Modified Electrode Peak Current (μA)	Bare Electrode Peak Current (μA)
6.3×10^{-3}	4.80 4.90 5.30	5.00
4.0×10^{-3}	3.50 3.00 3.10	3.20
2.5×10^{-3}	4.00 2.20 2.50	1.60
1.0×10^{-3}	1.40 1.80 1.85	0.85
1.0×10^{-4}	1.49 1.45 1.50	0.10
1.0×10^{-5}	0.95 0.90 0.75	Not Detected
5.0×10^{-6}	0.39 0.48 0.70	Not Detected
2.5×10^{-6}	0.40 0.30 0.80 0.66	Not Detected
1.0×10^{-6}	0.28 0.22 0.32	Not Detected

TABLE 8-Continued

Concentration $Ru(NH_3)_6Cl_3$ (M)	Clay-Modified Electrode Peak Current (μA)	Bare Electrode Peak Current (μA)
5.0×10^{-7}	0.38 0.31 0.35	Not Detected
1.5×10^{-7}	0.33 0.10 0.20	Not Detected
1.0×10^{-7}	0.035 0.032 0.030	Not Detected
5.0×10^{-7}	0.045 0.045	Not Detected

Figure 1

Plot of Steady State Results



This set of experiments indicated that at concentrations higher than 1 x 10^{-3} M, the clay was saturated and consequently, the enhancement wasn't as large as at lower concentrations. It also indicated that the clay was a very good concentrator of $Ru(NH_3)_6^{3+}$ at low $Ru(NH_3)_6^{3+}$ concentrations.

These experiments raised some questions. 1) What type and concentration of electrolyte gives the maximum enhancement? The 0.01M Na_2SO_4 used in the steady state experiments was chosen based on other work done with the clays, however it's effect on enhancement had not been tested. 2) What effect does the thickness of the clay film have on the enhancement? 3) Can the time of the experiments be reduced? (The time to steady state at the lower concentrations of $Ru(NH_3)_6Cl_3$ was very long, in some cases over 72 hours.) 4) Will electrochemical pulsing techniques yield lower detection limits? (Cyclic voltammetry is not a very sensitive technique, square wave and differential pulse voltammetry are known to be more sensitive.) 5) Can a clay electrode be rinsed and used for multiple measurements without any carryover effects? (The repreparation of the clay electrode for each measurement is a very large drawback in the viability of this system.)

In addition, it was seen that long periods of time were needed for the dilute solutions to reach equilibrium. It was thought that if the solution was stirred, this process could be shorten. At this point in the study, stirring was incorporated.

Discussion of System Optimization

In an effort to answer some of the questions posed above, experiments were designed to optimize the experimental system. The following is a discussion of these experiments and the results obtained.

Discussion of Electrolyte Effects

As mentioned previously, the effect of electrolyte concentration on enhancement had to be studied. The following discusses the experiments conducted to examine the electrolyte and its effect on signal enhancement.

Discussion of Electrolyte Concentration Experiments

The purpose of this experiment was to determine what concentration of Na_2SO_4 would yield the maximum reduction peak current. Five concentrations of Na_2SO_4 and $Ru(NH_3)_6Cl_3$ were analyzed. Reduction peak currents were recorded for both the clay and bare electrodes(Tables 9 and 10). The results are plotted in Figure 2. The shaded area represents the difference in the maximum peak currents between the clay and

bare electrode. These results indicate that the signal enhancement is greatest at the lowest electrolyte concentration, 0.01M Na_2SO_4. These results were expected from consideration of both the ion-exchange reaction and the clay film structure. To determine whether the loss of enhancement with increased electrolyte concentration was due to the clay film porosity(this effect is described in detail in the next section) or to competition from Na^+, another experiment was designed.

TABLE 9

ELECTROLYTE OPTIMIZATION EXPERIMENT
CLAY MODIFIED ELECTRODE RESULTS

	Na_2SO_4 Concentration(M)				
$Ru(NH_3)_6Cl_3$ Concentration(M)	0.01	0.10	0.18	0.25	0.50
1.0×10^{-3}	1.70uA	1.85uA	1.70uA	1.50uA	0.78uA
1.0×10^{-4}	1.50uA	0.95uA	0.35uA	0.40uA	0.10uA
1.0×10^{-5}	0.85uA	0.55uA	0.14uA	0.29uA	ND[a]
1.0×10^{-6}	0.28uA	0.32uA	ND[a]	ND[a]	ND[a]

[a]ND signifies that no current was detected. This value for the graphing of this data was assigned as zero current.

TABLE 10

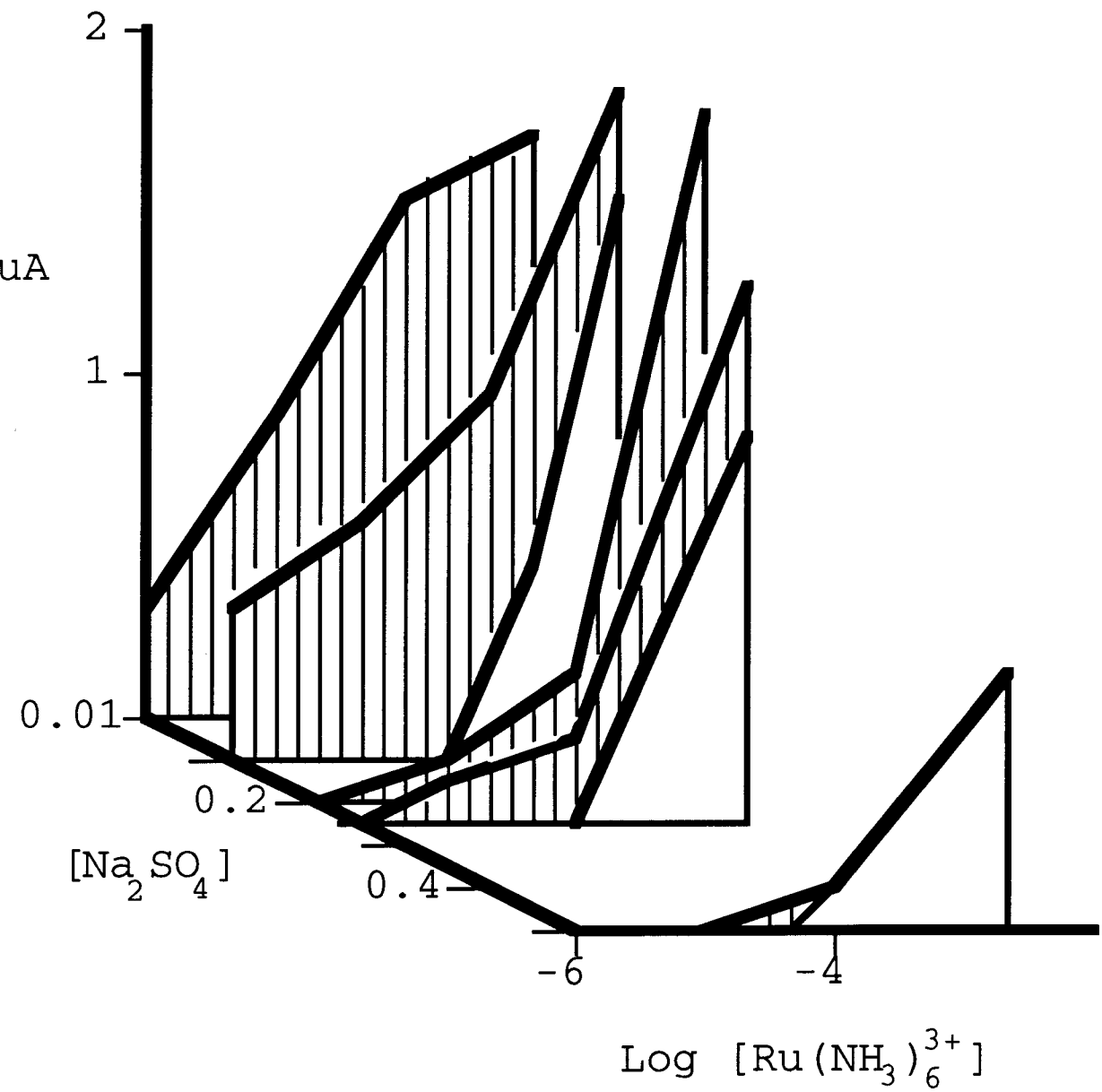
ELECTROLYTE OPTIMIZATION EXPERIMENT
BARE ELECTRODE RESULTS

	Na_2SO_4 Concentration (M)				
$Ru(NH_3)_6Cl_3$ Concentration (M)	0.01	0.10	0.18	0.25	0.50
1.0×10^{-3}	0.85uA	1.50uA	1.00uA	0.80uA	0.75uA
1.0×10^{-4}	0.01uA	0.18uA	0.35uA	0.17uA	0.08uA
1.0×10^{-5}	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
1.0×10^{-6}	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]

[a]ND signifies that no current was detected. This value for the graphing of this data was assigned as zero current.

Figure 2

Plot of Electrolyte Concentration Results



Discussion of Salt Comparison Results

In the previous experiment, it was noticed that at high electrolyte concentrations, signal enhancements decreased. To determine if the decrease in signal is a function of the ion-exchange reaction or a function of the porosity of the clay film[17,18], the signal of a 4 mM solution of $Ru(NH_3)_6Cl_3$ was analyzed as a function of NaCl and KCl concentration. Tables 11 and 12 list the results of these experiments. Figure 3 is a plot the ratio of the maximum reduction current for 4 mm $Ru(NH_3)_6^{3+}$ obtained at a clay-modified electrode to the maximum reduction current obtained at a bare electrode as a function of -Log[M], where M is either NaCl or KCl concentrations.

There are three regions of interest in the NaCl results(Figure 3). From 5 to 1.6 M Na^+ the ratio is less than one. The suggests that the $Ru(NH_3)_6^{3+}$ is being excluded from the clay film. From 1.6 to about 0.8 M Na^+ the ratio rises to approximately 1, indicating that neither enhancement nor exclusion occurs. The third region, $[Na^+] < 0.8$ M the ratio progressively increases with dilution of the sodium ion indicating that enhancement is occurring. The results obtained for the KCl are somewhat different. The $Ru(NH_3)_6^{3+}$ ion is excluded from the clay film in the high electrolyte

regime, $[K^+] > 1.6$ M, as was seen with the NaCl. But, instead of two sharp increases in the current ratio upon dilution, as was seen with the NaCl, the current ratio gradually increases over a broader range.

TABLE 11

SALT COMPARISON NaCl RESULTS

NaCl Concentration (M)	Clay Electrode Peak Current (uA)	Bare Electrode Peak Current (uA)	Clay/Bare Electrode Ratio
5.0	4.54	13.02	
	4.75	13.32	0.34
	4.47	13.74	
4.0	5.46	14.38	
	5.13	14.29	0.37
	5.32	14.28	
3.0	7.25	15.49	
	6.81	15.98	0.44
	6.81	15.74	
2.0	8.41	16.85	
	8.78	14.31	0.58
	9.70	15.65	
1.6	9.69	16.39	
	10.09	16.30	0.60
	9.42	16.28	
1.3	15.44	17.02	
	14.77	17.23	0.86
	14.43	17.44	

TABLE 11-Continued

NaCl Concentration (M)	Clay Electrode Peak Current (uA) μ	Bare Electrode Peak Current (uA)	Clay/Bare Electrode Ratio
1.0	18.57	16.81	
	17.85	16.88	1.08
	18.63	17.22	
0.80	19.65	16.94	
	19.19	16.84	1.14
	19.43	17.17	
0.63	18.70	15.52	1.20
0.50	28.90	17.53	
	26.71	16.55	1.66
	29.31	17.21	
0.40	29.76	16.70	1.78
0.30	32.86	17.87	
	32.06	17.87	1.81
	31.94	17.79	
0.22	29.62	17.17	1.73
0.15	30.54	16.72	1.83
0.10	33.62	18.06	
	35.24	18.07	1.89
	33.86	18.33	

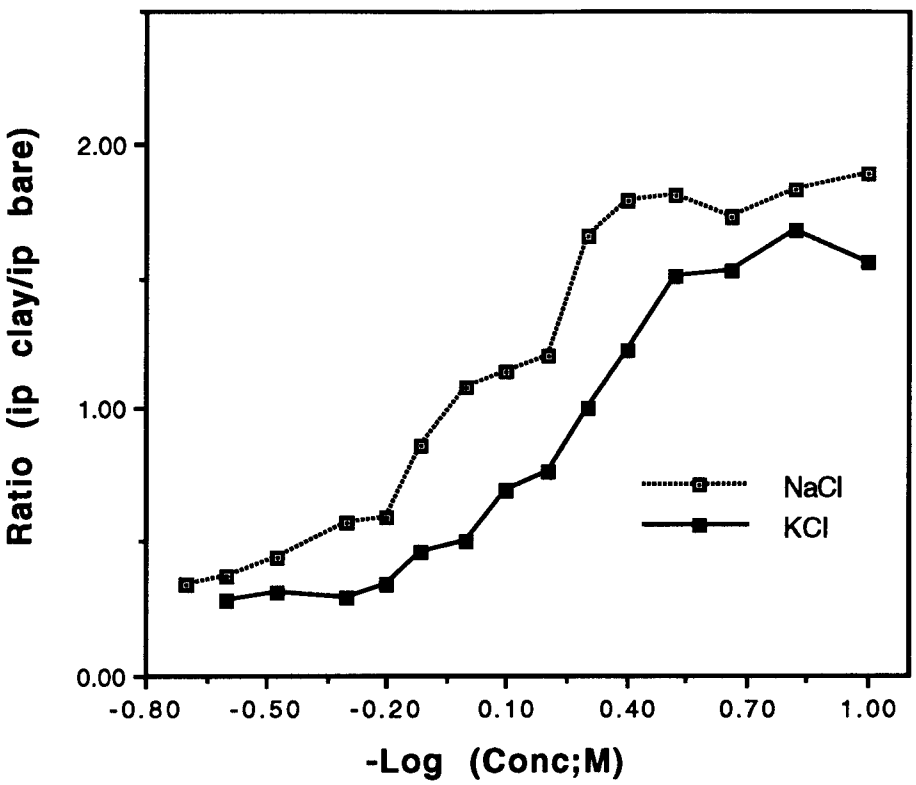
TABLE 12

SALT COMPARISON KCl RESULTS

KCl Concentration (M)	Clay Electrode Peak Current (uA)	Bare Electrode Peak Current (uA)	Clay/Bare Electrode Ratio
4.0	4.38	15.41	0.28
3.0	5.02	16.04	0.31
2.0	4.98	17.08	0.29
1.6	6.01	17.42	0.34
1.3	7.73	16.86	0.46
1.0	8.80	17.60	0.50
0.80	11.85	17.18	0.69
0.63	11.38	14.98	0.76
0.50	17.60	17.56	1.00
0.40	19.33	15.89	1.22
0.30	26.86	17.75	1.51
0.22	22.87	16.99	1.35
0.15	27.71	16.48	1.68
0.10	27.76	17.78	1.56

Figure 3

Plot of Salt Comparison Results



These observations can be explained by reference to change in the clay structure as a function of electrolyte concentration. The inter-layer distances between two clay platelets are determined by the counter-balancing of (1) clay face-face inter-layer distance collapse driven by van der Waals attractive forces when the negatively charged plates are well shielded in high electrolyte solutions, and, (2) the energy required to dehydrate the intercalated cations[29-31]. Since KCl has a low energy of hydration, a single inter-layer clay platelet spacing of 3.4Å predominates over the entire concentration regime of 6-0 M KCl[32].

For the NaCl, three different spacing regions can be observed by X-ray diffraction. From 6 to 1 M NaCl the inter-layer spacing is 5.5Å, corresponding to a single layer of hydration of Na^+. From 1 to approximately 0.3 M NaCl the inter-layer spacing is 9.5Å, corresponding to two layers of hydration of Na^+. At 0.3 M NaCl, there is a three-layer hydrate, which then expands in a continuous fashion with increasing dilution of the electrolyte. This expansion is attributed to osmotic swelling[29].

These spacing differences affect the overall porosity of the film and are readily observable in the conductivity of the film with respect to the anion $Fe(CN)_6^{3-}$[17,18]. Thus, we expect that the conductivity of the CME with respect to $Ru(NH_3)_6^{3+}$ may differ in the presence of KCl and NaCl,

depending on whether simple ion exchange, pore size, or both, affect the observed currents. The data can be interpreted in light of these spacing effects. For 1.6 < [Na^+] < 5 M the inter-layer spacing is predicted to be 5.5Å, hence the $Ru(NH_3)_6^{3+}$ is excluded from the inter-layer region.

In Na^+ concentrations between 1.6 and 0.6 M, the spacing is expanded to 9.5Å as the hydration of Na^+ increases from a single to a double layer. As a consequence, the current ratio of the clay-modified and bare electrode rises, as the accessible surface area increases. In Na^+ concentrations below 0.6 M, the inter-layer spacing is greater than 9.5Å, the ratio increases indicating the ion-exchange reaction of $Ru(NH_3)_6^{3+}$ for Na^+ is occurring.

As mention earlier, the results obtained for KCl are somewhat different. The results, though, are consistent with the fact that there are no hydrational changes in K^+ exchanged montmorillonite with dilution of K^+. In the absence of removal of K^+ via an ion-exchange reaction, there is a single pore dimension in the film associated with K^+ over the entire concentration range of the electrolyte. This pore dimension is smaller than that for Na^+ (3.4 versus 5.5 angstroms)[29,31]. Thus, there should be a single region of exclusion that is followed by enhancement of the signal as ion exchange proceeds, as is observed.

This information, coupled Åwith the previous results, indicates that the choice to use 0.01 M Na_2SO_4 was a good decision. This statement is based on the observations that at this concentration, the mechanism for enhancement is ion-exchange and at low electrolyte concentrations, enhancement is the greatest. This concentration of electrolyte was then used throughout the rest of the experiments.

Discussion of Time Optimization Experiments

The experimental time frame was an important factor that had to be considered in the development of this method. The signal was seen to increase over time until the analyte and clay reached equilibrium. The following discussion addresses the effect of the clay film thickness on the signal development time and also examines the results of an experiment designed to monitor the signal development as a function of time.

Clay Film Thickness Experiment Results

These experiments were carried out to determine the effect of the clay film thickness on signal enhancement and time to maximum current. Table 13 lists the results obtained from these experiments. These results are expressed graphically in Figure 4, which is a plot of the ratio of the reduction current of a 0.4 mM $Ru(NH_3)_6^{3+}$ solution obtained at a clay-modified electrode to the reduction current of a bare

electrode as a function of immersion time and clay concentration. The results show that current rises to a maximum within 10 minutes and also that the largest enhancement (as indicated by the greatest ratio) is obtained by drying 1 uL of a 5 g/L suspension on the electrode surface. It should be mentioned that working with clay concentrations below 5 g/L becomes very difficult. Inconsistent coverage of the electrode surface and the durability of the clay-modification were two reasons lower clay concentrations were not explored in these experiments.

TABLE 13

CLAY FILM THICKNESS RESULTS

5 g/L Clay Film

Time(min)	Cathodic Peak Current (uA)
0	1.54
10	7.31
20	7.38
30	7.50
40	7.54
50	7.61
60	7.78
Bare Electrode	1.77

10 g/L Clay Film Results

Time(min)	Cathodic Peak Current (uA)
0	1.06
10	3.58
20	3.58
30	3.61
40	3.62
50	3.64
60	3.66
Bare Electrode	2.00

TABLE 13-Continued

10 g/L Clay Film Results

Time(min)	Cathodic Peak Current (uA)
0	1.45
10	2.17
20	2.21
30	2.20
40	2.21
50	2.24
60	2.25
Bare Electrode	2.29

20 g/L Clay Film Results

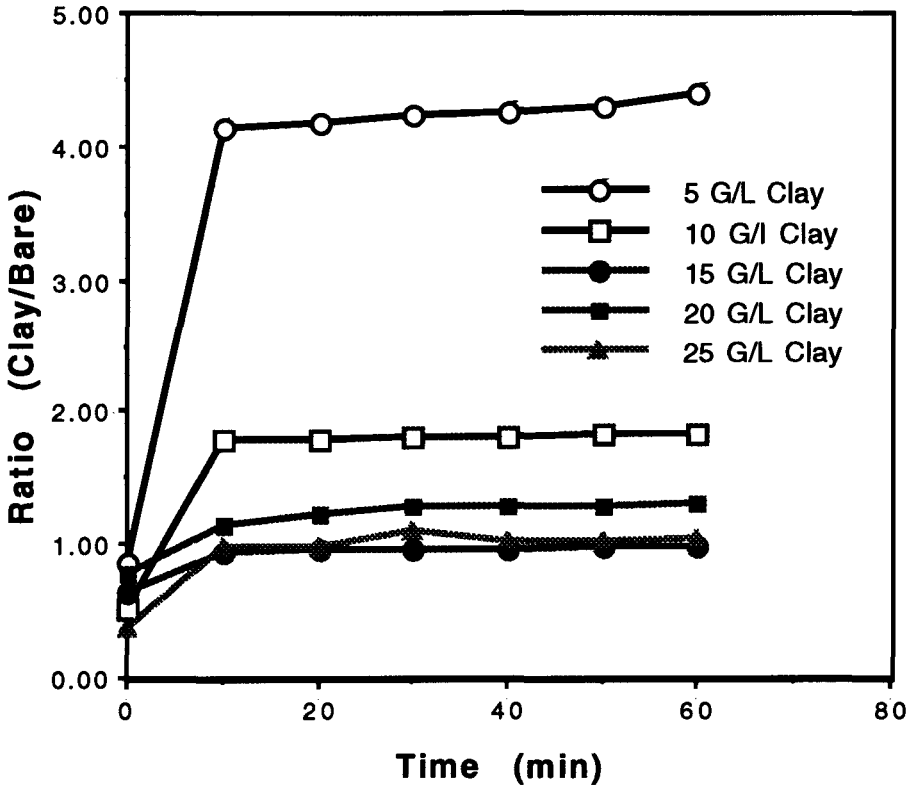
Time(min)	Cathodic Peak Current (uA)
0	1.61
10	2.37
20	2.60
30	2.63
40	2.65
50	2.65
60	2.67
Bare Electrode	2.06

25 g/L Clay Film Results

Time(min)	Cathodic Peak Current (uA)
0	0.82
10	2.09
20	2.09
30	2.12
40	2.15
50	2.17
60	2.20
Bare Electrode	2.10

Figure 4

Plot of Clay Film Thickness Results



Discussion of Signal as a Function of Time Experiment Results

These experiments were conducted to optimize the signal in terms of the immersion time. The experiment measured five concentrations of $Ru(NH_3)_6Cl_3$ over immersion time. The results obtained in these experiments are listed in Table 14. Figure 5 shows a plot of the current observed at any given immersion time divided by the maximum current observed for that solution as a function of immersion time. As expected, the higher the concentration, the more rapidly the maximum current is achieved. At lower concentrations, the time to reach maximum current is lengthened. These results also indicate that a sizeable current is measured at 10 minute immersion even in the most dilute solutions. With the results of these two experiments, a 10 minute sampling period was chosen.

TABLE 14

SIGNAL vs TIME EXPERIMENT

1×10^{-3} M $Ru(NH_3)_6Cl_3$ Results

Time (minutes)	Cathodic Peak Current (uA)	Ratio (Present/Last)
0	18.5	1.00
10	18.5	1.00
20	18.5	1.00
30	18.5	1.00

Table 14-Continued

1×10^{-4} M $Ru(NH_3)_6Cl_3$ Results

Time (minutes)	Cathodic Peak Current (uA)	Ratio (Present/Last)
0	4.0	0.27
10	12.0	0.81
20	13.2	0.89
30	14.2	0.96
40	14.8	1.00
50	14.8	1.00

1×10^{-5} M $Ru(NH_3)_6Cl_3$ Results

Time (minutes)	Cathodic Peak Current (uA)	Ratio (Present/Last)
0	0.88	0.23
10	3.75	0.38
20	7.00	0.72
30	8.15	0.84
40	8.75	0.90
50	9.00	0.92
60	9.25	0.95
70	9.50	0.97
80	9.75	1.00

1×10^{-6} M $Ru(NH_3)_6Cl_3$ Results

Time (minutes)	Cathodic Peak Current (uA)	Ratio (Present/Last)
0	0.10	0.025
10	2.00	0.51
30	2.25	0.57
40	2.62	0.66
50	3.00	0.76
60	3.12	0.79
70	3.25	0.82
80	3.38	0.86
90	3.87	0.98
100	3.95	1.00

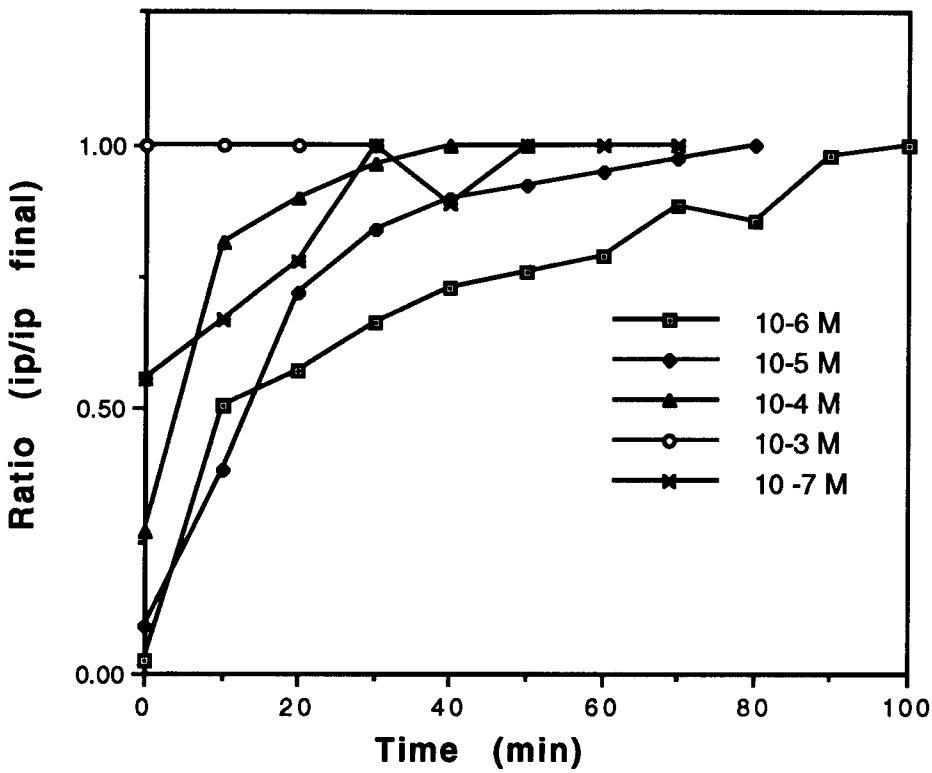
TABLE 14-Continued

1×10^{-7} M $Ru(NH_3)_6Cl_3$ Results

Time (minutes)	Cathodic Peak Current (uA)	Ratio (Present/Last)
0	0.25	0.56
10	0.30	0.67
20	0.35	0.78
30	0.45	1.00
40	0.40	0.89
50	0.45	1.00
60	0.45	1.00
70	0.45	1.00

Figure 5

Plot of Signal vs Time Experiment



Discussion of Linear Concentration Range and Method Optimization

The purpose in conducting these experiments was to determine the linear detection range and to determine which scanning technique yielded the most sensitivity. The three methods employed were cyclic voltammetry(CV), square wave voltammetry(SWV), and differential pulse voltammetry(DPV). All three techniques yielded similar results. The two pulse techniques(SWV and DPV) were able to sense concentrations of analyte at 1 x 10^{-9} M. The CV technique only was able to sense analyte concentrations down to 1 x 10^{-8} M. Table 15 lists the results of these experiments.

These results are also graphically represented in Figures 6-8. In those plots it was noted that there is an initial plateau like region followed by a linear region followed by a second plateau like region. The second plateau region corresponds to the saturation of sites where the enhancement over the bare electrode is very small. The linear region from 10^{-5} to 10^{-8} M $Ru(NH_3)_6^{3+}$ in the pulse techniques and 10^{-5} to 10^{-7} M $Ru(NH_3)_6^{3+}$ in the cyclic voltammetry experiments, yields currents an order of a magnitude greater than the bare electrode.

In the linear region of the peak height plot, the best set of data arises from the differential pulse voltammetry experiments. The equation obtained from these experiments is given by $\log(uA)=3.94 + 0.663 \log [Ru(NH_3)_6^{3+}]$; the

correlation coefficient is 1.00. At 10^{-8} M $Ru(NH_3)_6Cl_3$ (3.26 x 10^{-9} M Ru), for a 10 mL solution volume, the system is detecting 100 pmol of $Ru(NH_3)_6Cl_3$. This detection limit is 300 times lower than AA and 30 times lower than ICP techniques.[21,22]

TABLE 15

Concentration/Method Optimization Results

Cyclic Voltammetry Results

$Ru(NH_3)_6Cl_3$ Concentration (M)	Clay Electrode Current (uA)	Bare Electrode Current (uA)
1.0 x 10^{-3}	15.28	3.79
	13.89	3.91
	11.96	3.79
3.0 x 10^{-4}	7.34	1.35
	9.24	1.11
	9.18	1.06
1.0 x 10^{-4}	6.80	0.41
	8.78	0.41
	7.92	0.33
3.0 x 10^{-5}	5.39	0.15
	4.49	0.12
	4.11	0.18
1.0 x 10^{-5}	4.09	0.0090
	3.10	0.0073
	3.97	0.022
1.0 x 10^{-6}	1.12	
	0.45	Not Detected
	0.92	
1 x 10^{-7}	0.13	
	0.091	Not Detected
	0.12	

TABLE 15-Continued

$Ru(NH_3)_6Cl_3$ Concentration (M)	Clay Electrode Current (uA)	Bare Electrode Current (uA)
1×10^{-8}	0.065	
	0.019	Not Detected
	0.053	

Square Wave Voltammetry Results

$Ru(NH_3)_6Cl_3$ Concentration (M)	Clay Electrode Current (uA)	Bare Electrode Current (uA)
1.0×10^{-3}	20.73	11.18
	21.47	7.26
	21.33	11.61
3.0×10^{-4}	17.47	4.27
	16.06	3.93
	17.91	2.13
1.0 x 10-4	15.64	1.44
	14.58	1.37
	18.66	1.23
3.0×10^{-5}	10.12	0.22
	12.14	0.63
	10.37	0.31
1.0×10^{-5}	6.60	0.055
	7.61	0.011
	12.10	0.11
1.0×10^{-6}	3.53	
	1.06	Not Detected
	1.80	
1.0×10^{-7}	0.51	
	0.18	Not Detected
	0.33	
1.0×10^{-8}	0.031	
	0.19	Not Detected
	0.077	

TABLE 15-Continued

$Ru(NH_3)_6Cl_3$ Concentration (M)	Clay Electrode Current (uA)	Bare Electrode Current (uA)
1.0×10^{-9}	0.53	
	0.066	Not Detected
	0.017	

Differential Pulse Voltammetry Results

$Ru(NH_3)_6Cl_3$ Concentration (M)	Clay Electrode Current (uA)	Bare Electrode Current (uA)
1.0×10^{-3}	17.77	6.86
	18.04	6.13
	20.02	7.26
3.0×10^{-4}	15.21	2.80
	14.39	2.40
	15.01	1.65
1.0 x 10-4	11.98	0.87
	12.42	0.86
	11.90	0.79
3.0×10^{-5}	7.02	0.31
	10.04	0.29
	8.40	0.25
1.0×10^{-5}	4.62	0.048
	2.32	0.012
	6.95	0.057
1.0×10^{-6}	0.73	
	0.81	Not Detected
	1.44	
1.0×10^{-7}	0.16	
	0.27	Not Detected
	0.21	
1.0×10^{-8}	0.020	
	0.10	Not Detected
	0.026	
1.0×10^{-9}	0.35	
	0.062	Not Detected
	0.011	

Figure 6

Plot of Cyclic Voltammetry Results

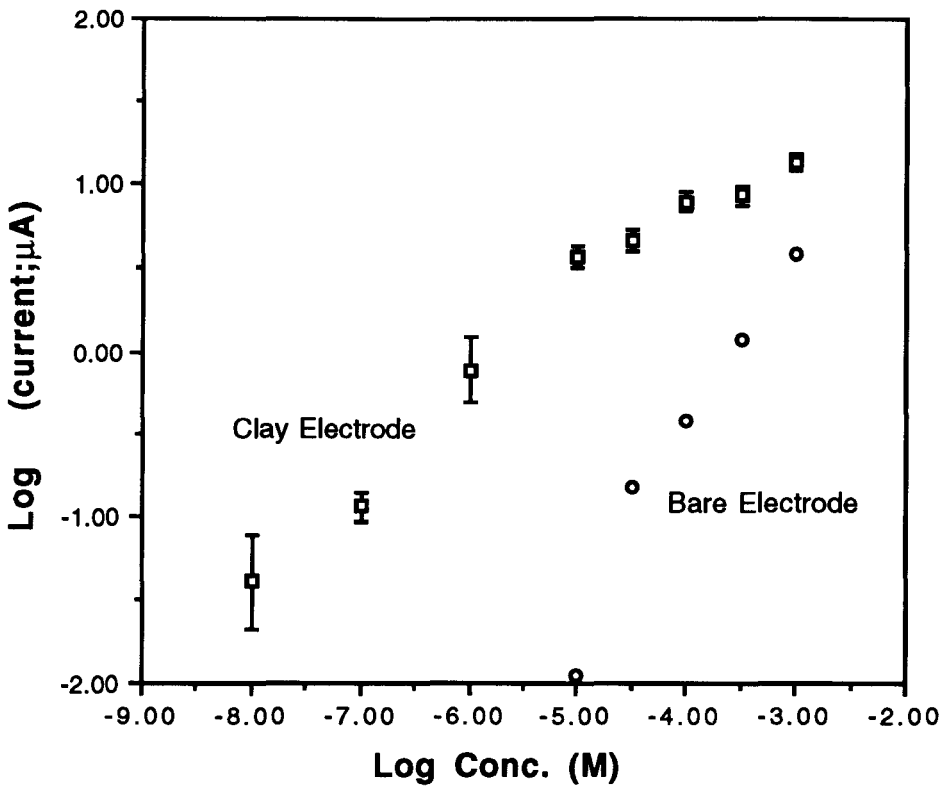


Figure 7

Plot of Square Wave Voltammetry Results

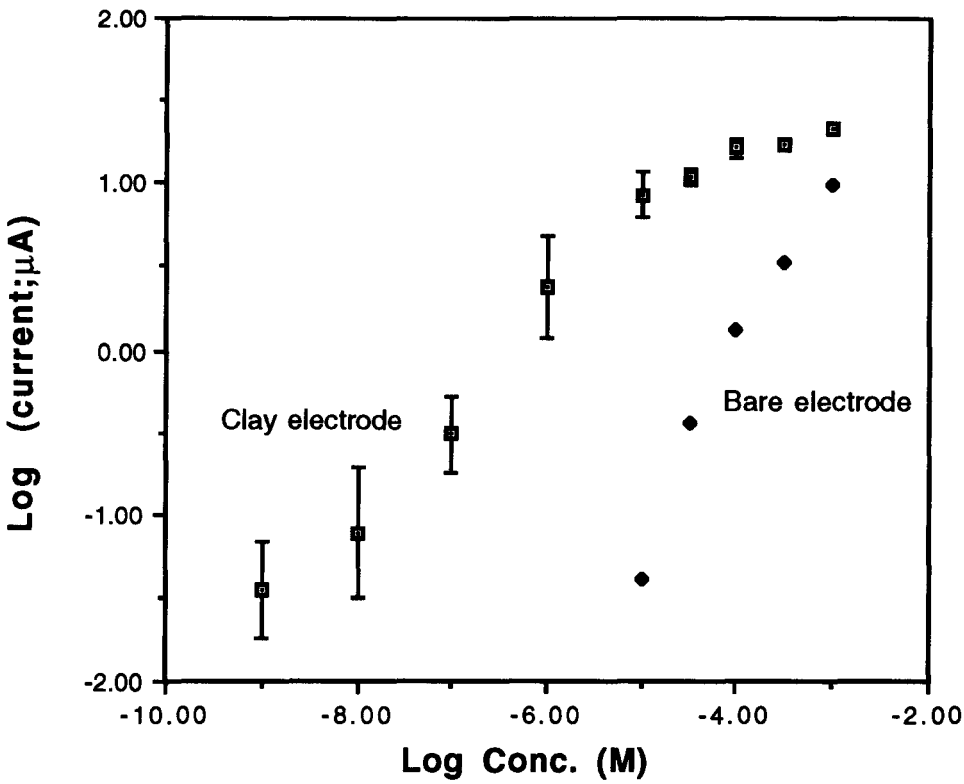
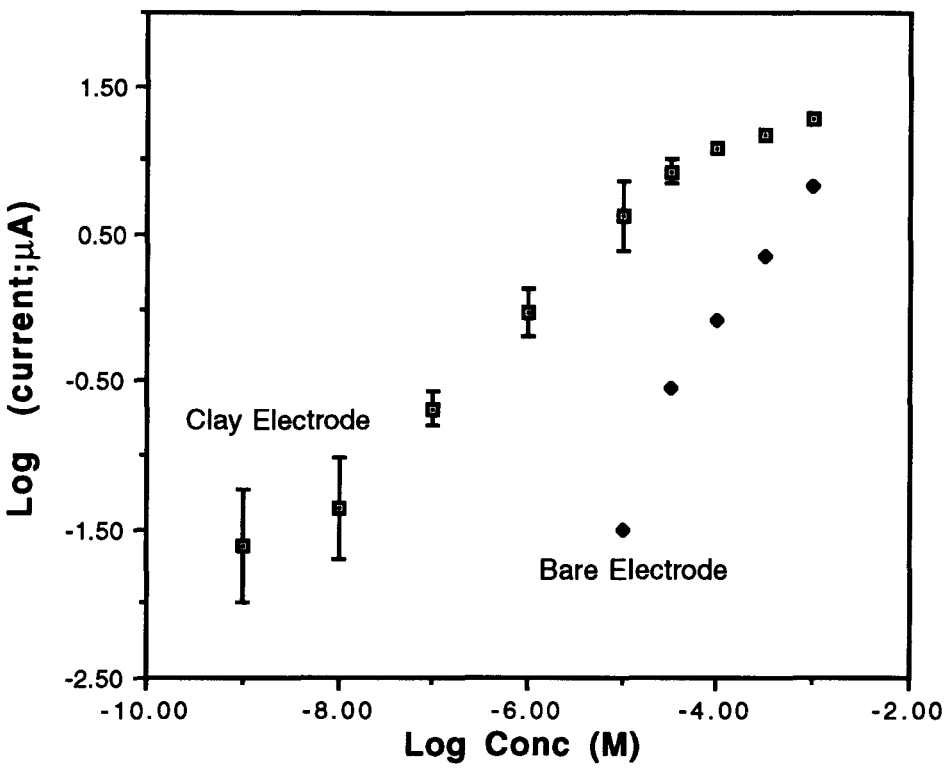


Figure 8

Plot of Differential Pulse Voltammetry Results



Discussion of Electrode Rinsing Method

In all the experiments carried out thus far, a new CME was prepared for each experiment. Although the preparation of the electrode isn't necessarily that lengthy, it would be advantageous to be able to use the same electrode for multiple measurements. This would reduce the length of the experiment and eliminate experimental variations that arise in different electrode preparations.

From previous experiments dealing with the salt concentrations, it was felt that the $Ru(NH_3)_6^{3+}$ could be exchanged in the clay if the salt concentration was high enough. The problem was that if the salt concentration was too high, collapse of the platelets would occur and the enhancement would be diminished when placed in the analyte solution.

What was proposed was an immersion of the CME in a 0.1 M Na_2SO_4 solution for 5 minutes followed by a conditioning immersion in 0.01 M Na_2SO_4 for 5 minutes under stirring. It was thought that the initial immersion would exchange the $Ru(NH_3)_6^{3+}$ with Na^+. The immersion in the 0.01 M Na_2SO_4 would then allow the clay to expand, if it had collapsed in the initial immersion, and allow for maximum uptake when placed into the analyte solution. This rinsing procedure was tested in the following experiments.

Discussion of Electrode Precision Results

These experiments were conducted to determine if there was any difference in the precision of rinsed electrodes compared to freshly prepared electrodes. Table 16 contains the results obtained. As shown in this data, the average square wave peaks heights were 2.4 +/- 0.7 uA for the freshly prepared electrode and 2.9 +/- 0.7 uA for the rinsed electrodes. The results show that the standard deviations for the rinsed electrode are the same as the freshly prepared electrode. Also, the rinsed electrode shows a larger average signal, although the average signal of either method falls within a standard deviation of each other. These data suggest that rinsing is viable for measurements made with a single analyte concentration. The following discussion addresses the subject of analyte carryover.

TABLE 16

ELECTRODE PRECISION RESULTS

Electrode Preparation Number	Rinse Peak Current (uA)	Repreparation Peak Current (uA)
1	3.71	1.98
2	1.81	1.66
3	3.27	2.85
4	2.90	3.31
5	2.90	2.18
Average	2.92	2.40

Discussion of Electrode Carryover Results

These experiments address the question of analyte carryover using the rinsed electrode. Four concentrations of $Ru(NH_3)_6^{3+}$ that fell within the linear region of the electrode were used to test for any memory effects of the clay. The results are shown in Table 17 and graphically expressed in Figure 9, which is a plot of the data obtained using differential pulse voltammetry. It should be noted that the correlation coefficient for the standard curve, when going from high to low concentrations, was 0.987 and, when going from low to high was 0.989. From these results, it was concluded that carry over was not a problem and also it indicated that the electrode was sufficiently robust to handle repeated rinsing over a long period of time.

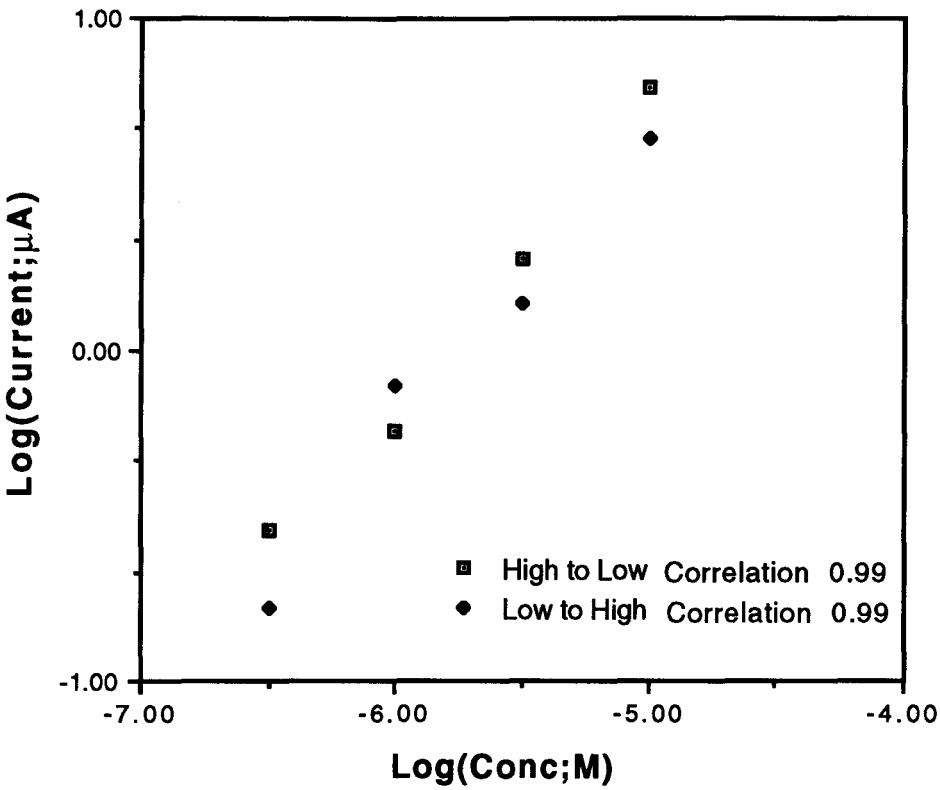
Table 17

ELECTRODE CARRYOVER RESULTS

$Ru(NH_3)_6Cl_3$ Concentration (M)	High to Low Peak Current (uA)	Low to High Peak Current (uA)
1.0×10^{-5}	6.16	4.37
3.2×10^{-6}	1.89	1.38
1.0×10^{-6}	0.57	0.77
3.2×10^{-6}	0.29	0.17

Figure 9

Plot of Electrode Carryover Results



CHAPTER 7

CONCLUSIONS

The previously reported results have shown that ion-exchange voltammetry can be performed at clay-modified electrodes. The clay-modified electrode was capable of sensing 100 picomoles of $Ru(NH_3)_6Cl_6$ and had a linear range covering four orders of magnitude (10^{-5}-10^{-8} M). The signal enhancement seen occurs via an ion-exchange reaction and physical diffusion of the complex within the film.

The enhancement was found to be dependent on electrolyte concentration and time of immersion in the analyte solution. Measurable amounts of the complex were sensed at 10 minute immersion times using 0.01 M Na_2SO_4 as the electrolyte. At ten minute immersion times, an electrode prepared from a 5 g/L clay suspension yielded the greatest enhancement. The clay film was found to be rinseable and robust enough to handle repeated measurements without having to prepare new electrodes for each measurement.

The use of the clay-modified electrode technology to sense other amine forming complexes is the next logical step. Metals such as copper and chromium form amine complexes and

might be good candidates for further exploration of this technique. Also additional optimization of the pulse techniques utilized might yield detection in the sub 100 pmole range.

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APPROVAL SHEET

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The final copies have been examined by the director of the thesis and the signature which appears below verifies the fact that any necessary changes have been incorporated and the thesis is now given final approval by the committee with reference to content and form.

The thesis is, therefore, accepted in partial fulfillment of the requirements for the degree of **Master of Science**.

12/29/92
Date

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