AN INVESTIGATION OF THE OXIDATION OF ALCOHOLS USING ATTENUATED TOTAL REFLECTANCE SPECTRO-ELECTROCHEMISTRY

by

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Advisor Date

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Dean of the Graduate School Date

YOUNGSTOWN STATE UNIVERSITY

Graduate School

THESIS

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For the Degree of Master of Science

TITLE "An Investigation of the Oxidation of Alcohols
Using Attenuated Total Reflectance Spectro-Electrochemistry"

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ABSTRACT

Considerably more information can. be obtained by simultaneous electrochemical and spectroscopic observation of a chemical reaction than by either technique alone. In this work the oxidation of 2–propanol to acetone has been studied by the combined technique. The electrochemical reaction, occurring on a gold' electrode formed near the surface of a ZnSe circular attenuated total reflectance crystal, has been monitored by IR spectroscopy. The design of an electrochemical cell to carry out the reaction of the solutions near an ATR crystal is given. Results of the spectroscopy show that acetone can be observed and that the intensity of the spectroscopic peak is proportional to the oxidation of 2–propanol.

Acknowledgements

I would like to express my sincere gratitude to Professor Daryl Mincey for his guidance and encouragement in this project. I would also like to thank Dr. Richard Philips and Dr. Francis Smith for their valuable suggestions to this work.

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LIST OF SYMBOLS

SYMBOL	DEFINITION
A	Area of Electrode
C_{ox}, C_o	Concentration of Oxidizer
C_{red}	Concentration of Reducer
D_o	Diffusion Coefficient of Oxidizer
4	Penetration Depth
E^o	Standard Electrode Potential
e-	Charge on Electron
E_{INDIC}	Indicated Electrode Potential
E_{PK}	Peak Potential
$E_{PK/2}$	Half-Peak Potential
E_{REF}	Reference Electrode Potential
F	Faraday Constant
i	Current
k	Force Constant
m_e	Mass of Electron
$\mathcal{N}$	Molecular Number Density
n	Moles of Electrons
n_c	Concentration Overpotential
N_e	Number of Electrons
n_{sp}	Ratio of Refractive Indices
n_t	Charge Potential Overpotential
n_1, n_2, n_r	Refractive Index
t	Time
v	Sweep Rate
x	Displacement

ϵ_0	Permittivity
λ	Wavelength
ϕ	Angle of Reflectance
θ	Angle of Incidence
ν	Frequency

LIST OF FIGURES

INTRODUCTION

The use of electrochemistry to analyze substances started with the invention of polarography by Heyrovsky.[1] This technique used a dropping mercury electrode (DME) inserted in the solution to be tested. The current was measured as the voltage was changed with respect to a reference electrode.

The use of the dropping mercury electrode decreased with the introduction of other more accurate non-electrochemical tests. It was not until the advent of microelectronics that interest in electroanalytical techniques was revived. Modern electronic devices and techniques allow the measurement of smaller currents more accurately than ever before. These devices along with newer materials make electrochemistry one of the most sensitive and versatile analytical techniques.

The classical electrochemical techniques include DC polarography, TAST polarography, and cyclic voltammetry (CV). Newer techniques include normal pulse, differential pulse, differential normal pulse, and square wave voltammetry.[2,3] All of these techniques can be used with a variety of electrode types. These electrode types include membrane (glass), solid state, liquid membrane, ion-exchange, and enzyme.

Even though electroanalytical techniques are among the most sensitive they all suffer from the same drawback. The techniques are not very chemically or structurally specific so can only be used for detection of electroactive substances. The ideal analytic technique would possess the ability to detect very low levels of a specific substance. This can be accomplished by combining a highly specific technique like IR, UV, or NMR spectrometry with the low level detectability of electroanalytical methods.[4]

In this thesis I will present some preliminary findings of the combination of fourier transform infrared spectroscopy (FTIR) with cyclic voltammetry and potential step electrochemical techniques. With this combination I will study the ability of this technique to detect intermediates or products generated by the electrochemical oxidation of 2-propanol. A proposed mechanism will be presented that may account for the observed spectra.

THEORY

The oxidation and reduction of organic compounds has been studied for some time. Alcohols are particularly interesting because of their use as fuels in electrochemical fuel cells. Fuels are reacted at electrodes to convert chemical energy directly to electrical energy. Alcohols are good fuel sources because of their relative non-toxicity, ease of transportation, and low pollution from the reaction.

The problem with the use of alcohol fuels is that very little is known about the reaction mechanism itself. Because not very much is known about the reaction mechanism, the current techniques of using alcohols as electrochemical fuel sources are far from optimum. What is known shows that there is a great deal of concern about the poisoning of electrode surfaces by reaction intermediates.[5,6] Some reaction intermediates may also catalyze the reaction.[7] To optimize the electrochemical uses of alcohols as fuels, it is necessary to determine the reaction mechanism. Various studies of the interfaces between an electrolyte solution and an electrode have been carried out using infrared spectroscopy.[8-14] Studies carried out previously obtained IR spectra by transmission through the solution. The electrochemistry was performed between transparent electrodes. This required the use of non-aqueous solvents since water is opaque to IR radiation. These techniques also suffer from the problem of low light throughput that requires the use of very thin samples. Non-aqueous solvents are a problem because they negate some of the good attributes of alcohols as fuel sources. They are often toxic and hazardous to the environment. Water as a solvent in electrochemical reactions has some very important qualities. Water's high dielectric strength and high polarity make it a very good solvent for the electrochemical oxidation of alcohols. Therefore the study of the reaction mechanisms of the electrochemical oxidation of alcohols should be performed in aqueous solvents because that is the solvent that would be used in a fuel cell. The techniques that have been used in the past to study the interface have all relied on the transmission of the infrared light through the electrochemical solution. If water is used as a solvent, very little light will be transmitted by the solution because water absorbs infrared radiation. In order to overcome these problems a new infrared method, called attenuated total reflectance, can be used.

ATTENUATED TOTAL REFLECTANCE

When radiation strikes an interface between two materials of different refractive index it is either transmitted or reflected. This is governed by Snell's law

$$n_1 \sin\theta = n_2 \sin\phi$$

where n_1 and n_2 are the refractive indices of the respective media and θ and ϕ are the angles of incidence and transmittance. If $n_2 < n_1$ then there exists some critical angle where ϕ is 90° and no radiation is transmitted through the interface. For angles greater than this critical angle all radiation is reflected: total internal reflectance. This is different from reflection from a mirror where several percent is absorbed by the surface in the reflection. No radiation is propagated accross the interface in total internal reflectance so a beam of radiation can be reflected indefinitely. However this does not imply that no energy passes into the second medium. This energy, called the evanescent wave, passes a short distance into the second medium. If the second medium can absorb the radiation it will attenuate the beam. This is attenuated total reflectance. This evanescent wave penetrates the second medium to a depth given by[15]

$$d_p = \frac{\lambda}{2\pi\left|\sin^2\theta - n_{sp}^2\right|^{1/2}}$$

where λ is the wavelength in the crystal (λ/n_1), θ is the angle of incidence, and $n_{sp}=n_2/n_1$.

The calculation of the penetration depth requires knowledge of the index of refraction of the solution. The index of refraction can be calculated by [16]

$$\frac{n_r^2 - 1}{n_r^2 + 2} = \frac{1/2\left(-\frac{e^2}{m_e\omega^2}\right) N_e \mathcal{N}}{\epsilon_o}$$

where n_r is the refractive index, e– is the charge on an electron, m_e is the mass of the electron, ω is the frequency of the radiation, N_e is the total number of electrons in the molecule, ϵ_0 is the permittivity, and N is the molecular number density. From this equation the index of refraction is calculated to be 1.4142 for a solution of water and 2-propanol at 1500 cm^{-1}. The penetration depth is then calculated to be about 3×10^{-4} cm or approximately a half-wavelength.

A typical attenuated total reflectance (ATR) cell is shown in Figure 1. The infrared radiation passes into and through a crystal of zinc selenide. The radiation enters the crystal at a 45° angle, and is reflected off the sides of the crystal as it travels down the length of the crystal. The radiation is reflected ten times for a crystal 0.25 in. in diameter and 2.50 in. in length. The crystal is supported by a stainless steel boat that is used to hold the solution that is being analyzed

MECHANISM OF REACTION

Before describing the spectroscopic; theory of this work it is desirable to discuss the mechanism of the oxidation of 2-propanol. The oxidation of some alcohols has been described in the literature and the ideas presented should apply equally well to 2-propanol.[5,6,7,12,17,18] There are a number of alternate mechanisms that propose different intermediates. There are, however, three steps to the process of oxidation of

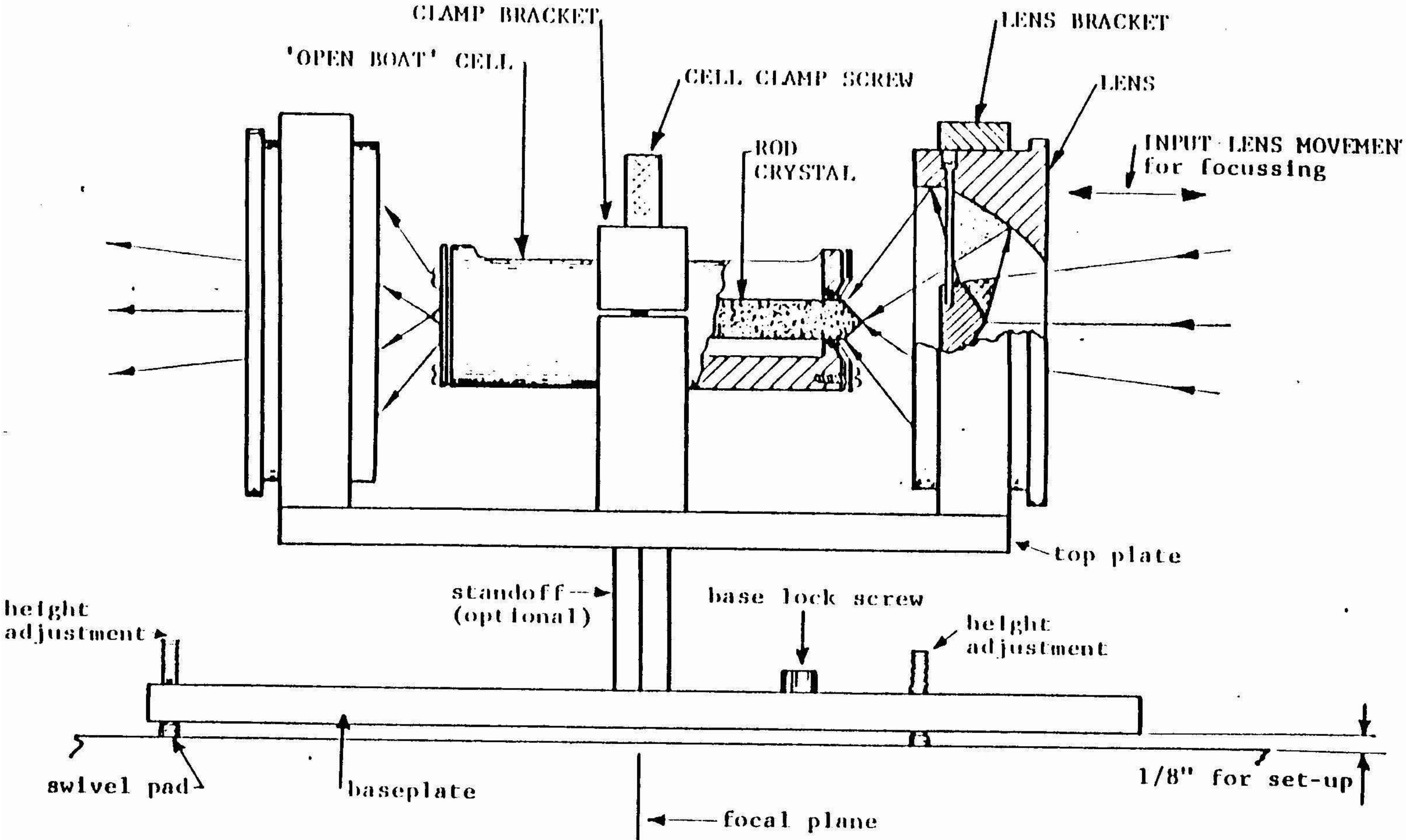

Figure 1. Attenuated Total Reflectance cell.

any substance on the surface of an electrode. These steps are adsorption, reaction, and desorption.

The process of adsorption is little understood but can be thought of as a displacement of solvent molecules at the surface. There are many relationships that relate the surface coverage of an electrode to the properties of the bulk solution.[19] All models used today are empirical and are related to Langmuir's equation. The surface coverage can also be related to the solubilities of the materials in the solvent.[20]

The mechanism of the oxidation of 2-propanol to acetone is only part of the reaction mechanism that takes 2-propanol to CO_2 and H_2O. The reaction can be written as

$$(CH_3)_2CHOH \text{ --> } (CH_3)_2C{=}O + 2e^- + 2H^+$$

As the molecule is adsorbed onto the surface it will lose hydrogen.[6,12,17,18] Under the conditions of the experiments carried out here it appears that the alpha hydrogen is removed in an oxidative addition type reaction.[25] Once the molecule is bound to the surface, the electrode can then remove electrons to oxidize the bound intermediates to acetone. The acetone then must desorb from the surface. Very little is known about the desorption of molecules from the surface. As with absorption the available equations are for steady state not dynamic systems. If the acetone does not desorb it will be oxidized to other intermediates that may also desorb or, ultimately, be oxidized to CO_2 and water. These other intermediates may include CO, COH, HCO, C_2H_xO, CH, and others,

INFRARED SPECTROSCOPY

A description of attenuated total reflectance was given above., How infrared.(IR) spectroscopy can be used for analysis is discussed here. The frequencies of IR are such that only molecular vibrations have the right characteristics to be observed. These vibrations are IR active if the vibration leads to a change in the electric dipole moment of the molecule.[21]

The absorption of IR radiation can be illustrated by considering that the molecules are a series of charged point sources connected by springs. The force between two atoms is given by Hooke's law

$$F = 1/2\ k\ x^2$$

where k is a force constant, x is the displacement of the atoms from equilibrium, and m is the reduced mass of the system. The frequency of such a vibration is given by

$$\nu = \frac{1}{2\pi}\sqrt{k/m}$$

These equations give acceptable answers for diatomic molecules. For polyatomic molecules the vibrations of all the molecules must be accounted for. It is more convenient in these cases to use internal coordinates rather than cartesian coordinates.[22] The internal coordinates are bond stretching, bond bending, bond torsion, and out-of-plane bending. The spectrum of a system would show these modes of vibration. A correlation of the observed spectra with the frequencies of the internal modes of vibration would identify the species. The adsorption onto a surface as well as solvent effects may shift the frequencies from their calculated values.

A spectrum of acetone would show peaks that correspond to the normal modes of vibration. There are peaks at about 3000 cm^{-1} from the C–H stretch of the CH_3 groups. Around 1400 cm^{-1} are the bending vibrations of the CH_3 groups. The C=O stretch yields a peak at about 1730 cm^{-1}. While the C–C bond stretches at about 1165 cm^{-1}.[22] IR spectroscopy allows us to differentiate between acetone and 2-propanol. 2-propanol would not have the peak corresponding to the C=O stretch. It would have additional peaks for the alcoholic oxygen and the C–H stretch of the alpha hydrogen.

ELECTROCHEMISTRY

Electrochemistry requires at least a pair of electrodes in contact with a solution. These electrodes are connected to electronic devices to set the conditions at the. electrodes and measure the conditions at the electrodes. When the electrode conditions are set the solution organizes itself in a fundamental way first proposed by Stern. This model consists of an Inner Helmholtz Plane (IHP), an Outer Helmholtz Plane (OHP), and a Diffusion layer. The IHP is that plane that contains the centers of the ions actually in contact with the electrode. These ions are usually the same charge as the electrode. The OHP is that plane that contains the centers of the ions plus their hydration layer. These ions are of opposite charge as the electrode. The Diffusion layer is the transition layer between the OHP and the bulk solution. It is a mixture of ions diffusing into and away from the electrode. These three layers form a capacitor whose capacitance is proportional to the concentration of the electroactive species in the bulk solution. To minimize the effect of the bulk solution on the electrode capacitance an inert supporting electrolyte is added to the solution. This electrolyte, usually added in 0.1 M concentrations, aids the transport of electric current but is electrochemically inactive. This three-layer model is shown schematically in Figure 2.[23]

The ideal case in measuring the potential of a system is to measure the potential with no current flow. This is a situation not found in the real world and all potential measurements require some current flow. Because of this small current flow there is a voltage drop through the solution due to its resistance; i.e., IR drop. There is also a change in potential due to the electrode itself. One of these effects is the concentration overpotential (n_c). It causes a change in potential of an electrode as a redox reaction occurs. Another effect is a charge-potential overpotential (n_t). It causes a change in potential of an electrode due to the necessity of accelerating a reaction to the desired state. Combining all of these effects gives the expression for the voltage of a cell as

$$E_{CELL} = E_{INDIC} - E_{REF} = E^{\circ} + (0.059/n) \log(C_{OX}/C_{RED}) + n_C + n_t + IR) - E_{REF}$$

where E_{indic} is the measured voltage, E_{ref} is the voltage of the reference cell, E^{o} is the half cell voltage versus a standard hydrogen electrode (SHE), n is the number of moles of electrons involved in the reaction, and C_{ox} and C_{red} are the bulk concentrations of the oxidant and reductant. The variables n_c, n_t, and IR are additive corrections to the Nernst equation. They can be treated as constants if the conditions of

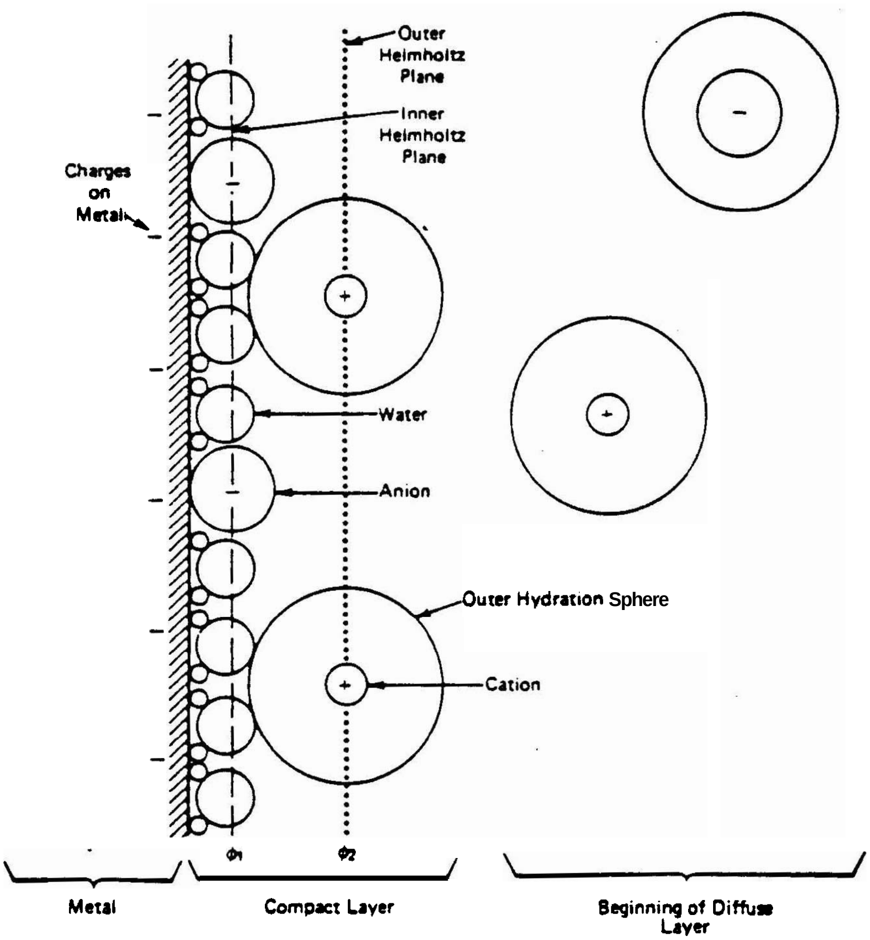

Figure 2. The Electrical Double Layer.

the cell do not change much. This is ensured by the presence of a supporting electrolyte. Thus the above equation reduces to an equation that relates the cell voltage to the ratio of oxidant and reductant concentrations.

The electrochemical cell used here is a conventional three-electrode cell. It consists of a working electrode, an auxilliary electrode, and a reference electrode. The setup is shown schematically in Figure 3. The electrochemical reaction of interest occurs at the working electrode. The reference electrode is used to monitor the voltage and feedback to the controlling electronics. The controlling electronics adjust the conditions at the electrodes to maintain the desired voltage or voltage versus time relationship.

Two techniques were used in these experiments. They are cyclic voltammetry (CV) and potential step. In potential step the voltage is stepped from one voltage to another. The current response is a decaying curve with the current given by the Cottrell equation

$$i = nFA\left(\frac{D_O}{\pi t}\right)^{1/2} C_O$$

where i is the current, A is the electrode area, t is the time, D_O is the diffusion coefficient of the oxidizer, C_O is the bulk concentration of the oxidizer,

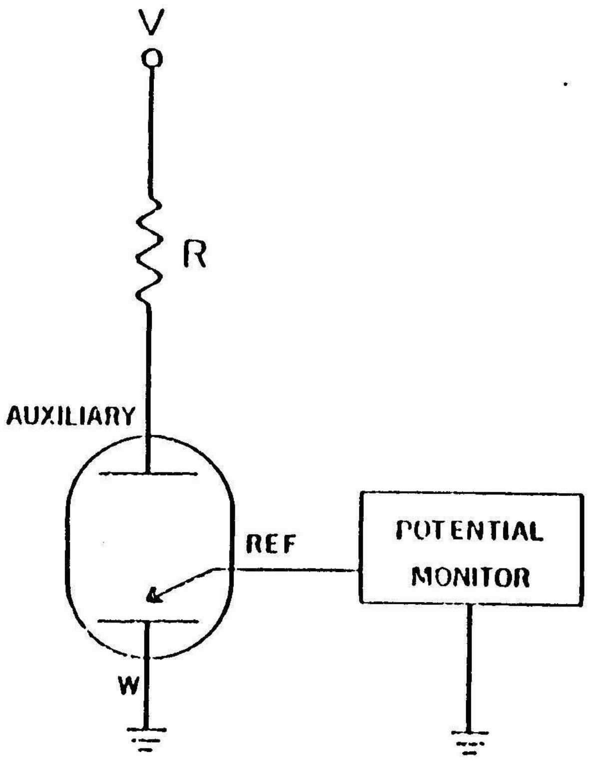

Figure 3. Three Electrode Cell Schematic.

F is the Faraday constant, and n is the number of electrons involved in the reaction. In cyclic voltammetry the voltage is swept linearly between two voltages while the current is monitored. The cell is swept continuously between two voltages which set up both oxidizing and reducing conditions at the working electrode. A typical current versus voltage response is shown in Figure 4. In a reversible system two peaks are seen: a cathodic and an anodic peak. The current of the peak is given by the Randles and Sevcik equation

$$i_{PK} = (\text{const.})\, n^{3/2} A (D_O v)^{1/2} C_{OX}$$

where v is the sweep rate in volts per second. The peak voltage is given by

$$E_{PK} = E_{PK/2} \pm \frac{56.5}{n}\ \text{mV}$$

where the plus sign is for the cathodic peak and the minus sign is for the anodic peak. $E_{pk/2}$ is the potential at half peak height. So the anodic and cathodic peaks are separated by 57/n mV for a reversible system. Irreversible systems can also show two peaks but they are usually separated by more than 57/n mV.

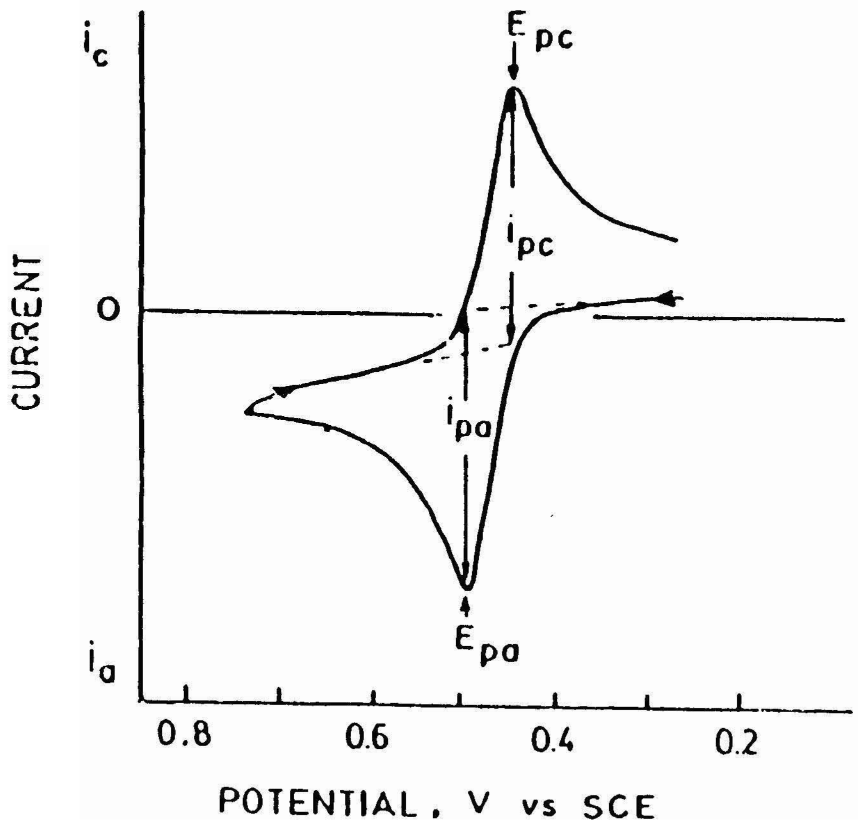

Figure 4. Typical CV Output.

EXPERIMENTAL

ELECTROCHEMISTRY

The electrochemical experiments were carried out using a BAS CV27 model electrochemical controller with a three-electrode cell. The working electrode was a gold electrode. The auxiliary electrode was a platinum wire electrode. The reference electrode was a silver/silver chloride electrode in a saturated (approximately 4 M) KC1 solution. The potential step experiments were carried out by applying a voltage step to the working electrode. These voltage steps were from 0 V to either -0.5 V or -1.0 V. The CV analysis was carried out by applying a linear voltage sweep to the working electrode. The sweep ran from 1 V to -1 V at a sweep rate of 100 mv/sec.

SPECTRO-ELECTROCHEMISTRY

The spectroscopic studies were carried out on a IBM IR/32 Fourier Transform Infrared (FTIR) spectrometer. A circle cell attenuated total reflectance attachment was modified to allow electrochemistry to be performed near the zinc selenide crystal. The modifications are shown in Figure 5. Two types of working electrodes were tried. The first was a vapor deposited gold coating.

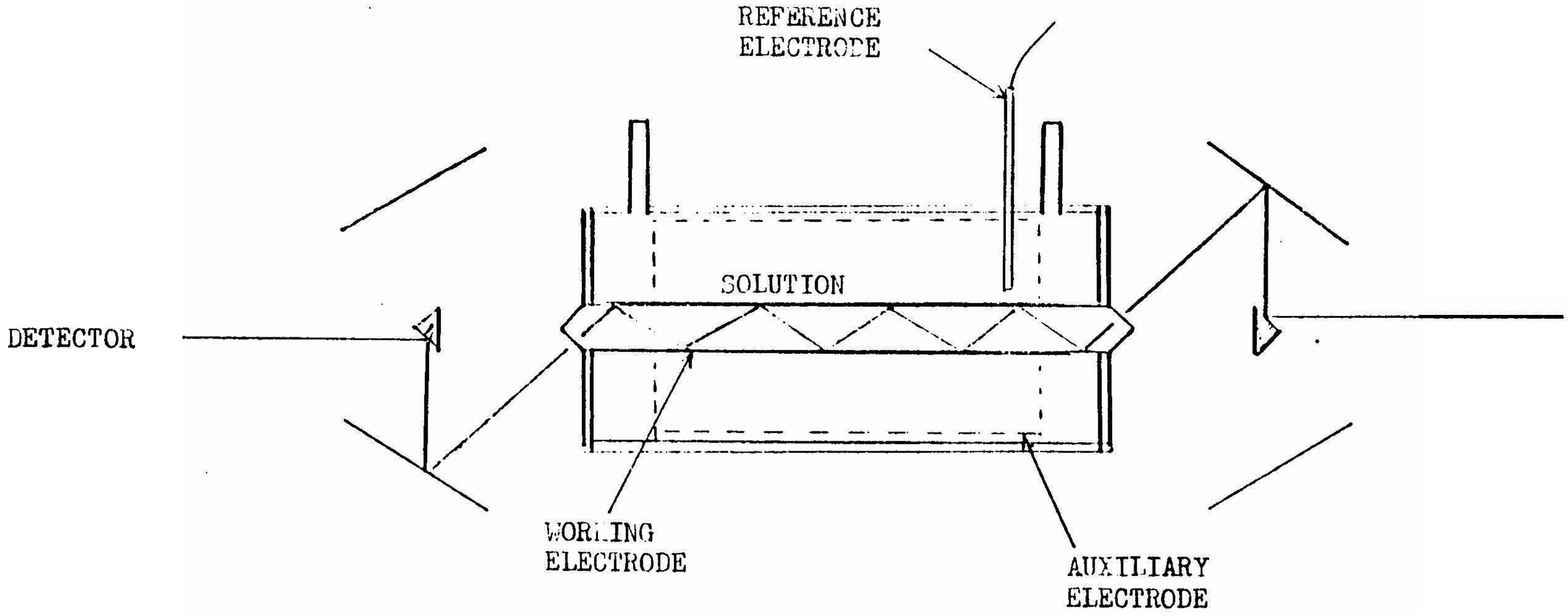

Figure 5. Modified Circle Cell.

The ATR crystal was placed in a vacuum chamber and coated with gold from a heated target. The gold thickness was not measured but was probably 500 to 1000 angstroms. This is based on the time of gold deposition and the subjectively observed transmission through the film. The second was a gold mini-grid wrapped around the crystal. A mini-grid is an electro-formed screen of gold. The grid had about 50 holes per inch with 10% gold area; i.e., the holes were 10 times wider than the gold wires between the holes. Electrical connection to the gold electrodes was made by attaching a thin copper wire with silver conductive epoxy. Two types of auxiliary electrodes were also tried. One was a silver foil tube on the inside of a plastic flow-through cell. The other was the stainless steel body of an open solution holder. The reference electrode was the same as used above: a silver/silver chloride electrode in a saturated (approximately 4 M) KC1 solution. A voltage was applied to the electrodes until a noticeable current was seen on the current meter: i.e., the meter needle moved at least one minor division.

The modified ATR attachment was installed in the FTIR and adjusted according to the manufacturer's procedure.[24] The spectra were obtained at a resolution of 4 cm^{-1} with 64 scans from 800 cm^{-1} to 4000 cm^{-1}. The area of interest extended from 1000 cm^{-1} to 3200 cm^{-1}.

SOLUTIONS

The solutions used consisted of 2-propanol in water with an acid catalyst and supporting electrolyte. The electrochemical solutions consisited of 2.5, 5, 7.5, and 10 percent by volume of 2-propanol. Sodium or potassium chloride was added in about 1 M concentrations as a supporting electrolyte. The spectroscopic solutions consisted of a 40 percent by volume of 2-propanol solution. To this was added 1 percent by volume nitric acid as a catalyst and the solution was made 1 M in KCl. A spectroscopy standard of 5 percent 2-propanol was also used to test the ATR setup.

RESULTS

ELECTROCHEMISTRY

Figure 6 shows the voltage versus current plot for the potential step experiment. This was for 5% 2-propanol in water at steps from 0V to -0.5 V and 0 V to -1.0V. Figure 7 shows a typical output for a CV experiment. This is a voltage versus current plot for a 10% 2-propanol in water solution. Figure 8 is the output similar to Figure 7 except only water was tested, A comparison of these two plots shows a peak at -0.5 V on the 10% 2-propanol solution that is not there on the

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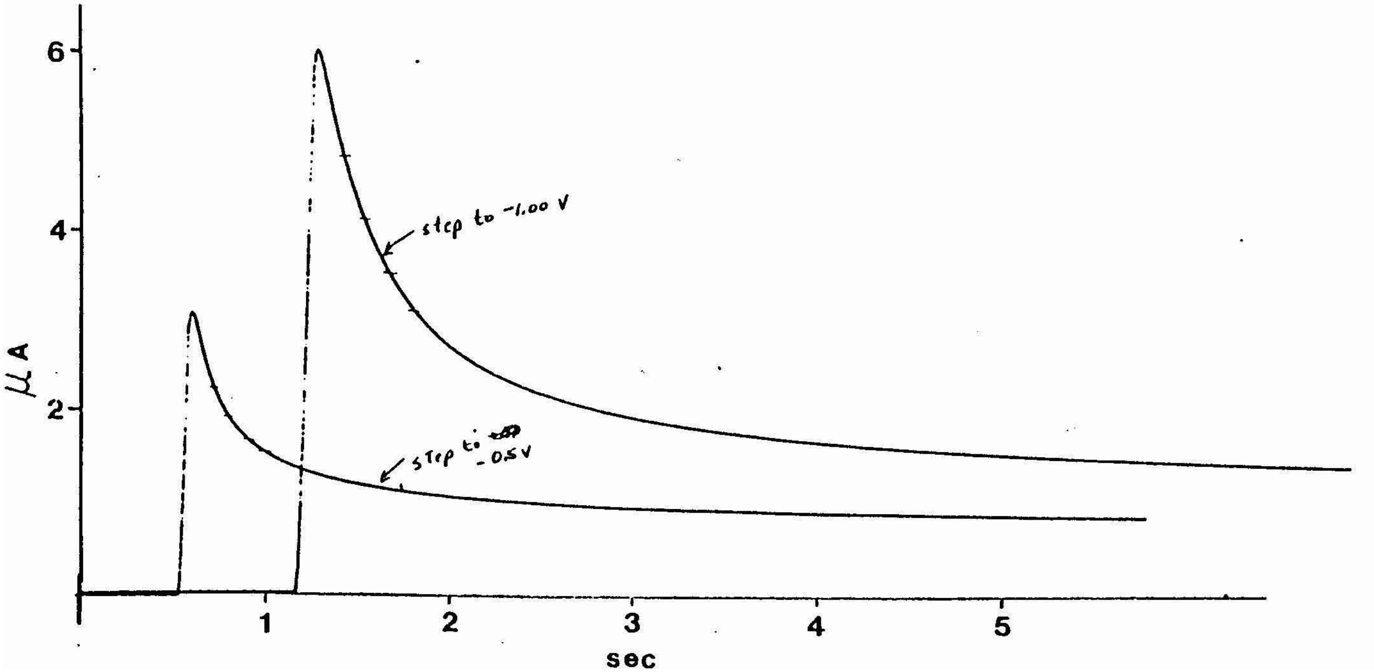

Figure 6. Output from Potential Step Experiment

5% I-propanol in water
gold electrode
1 Reference
Gain on BAS .02 mA/V
x axis 1 sec/inch
Y axis 100mv/inch

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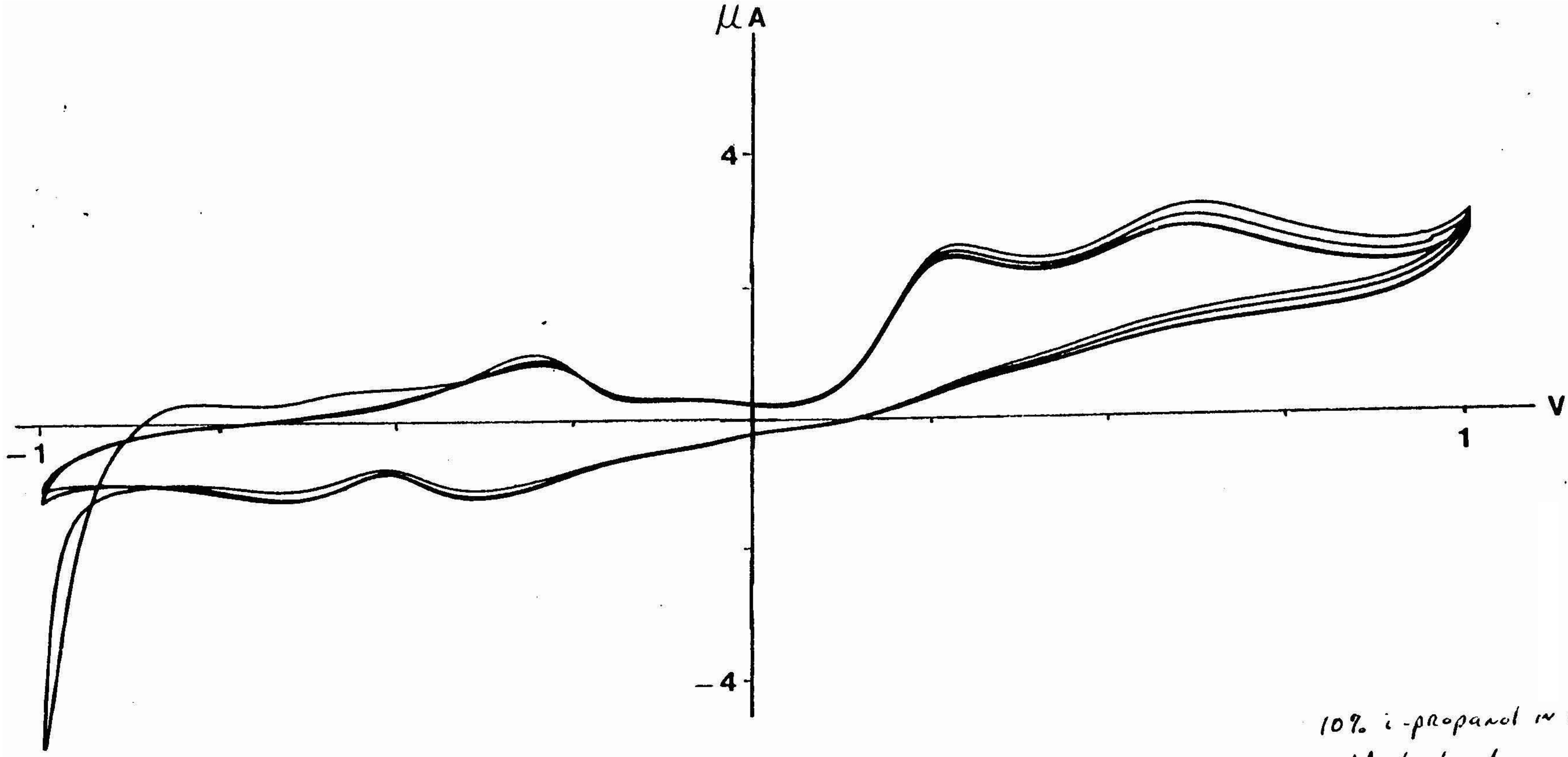

Figure 7. Typical Output from CV Experiment.

10% i-propanol in Water + NaCl
gold electrode
1 reference
Gain on BAS 0.02 mA/v
X Axis 200mv/in
Y Axis 100 mv/in

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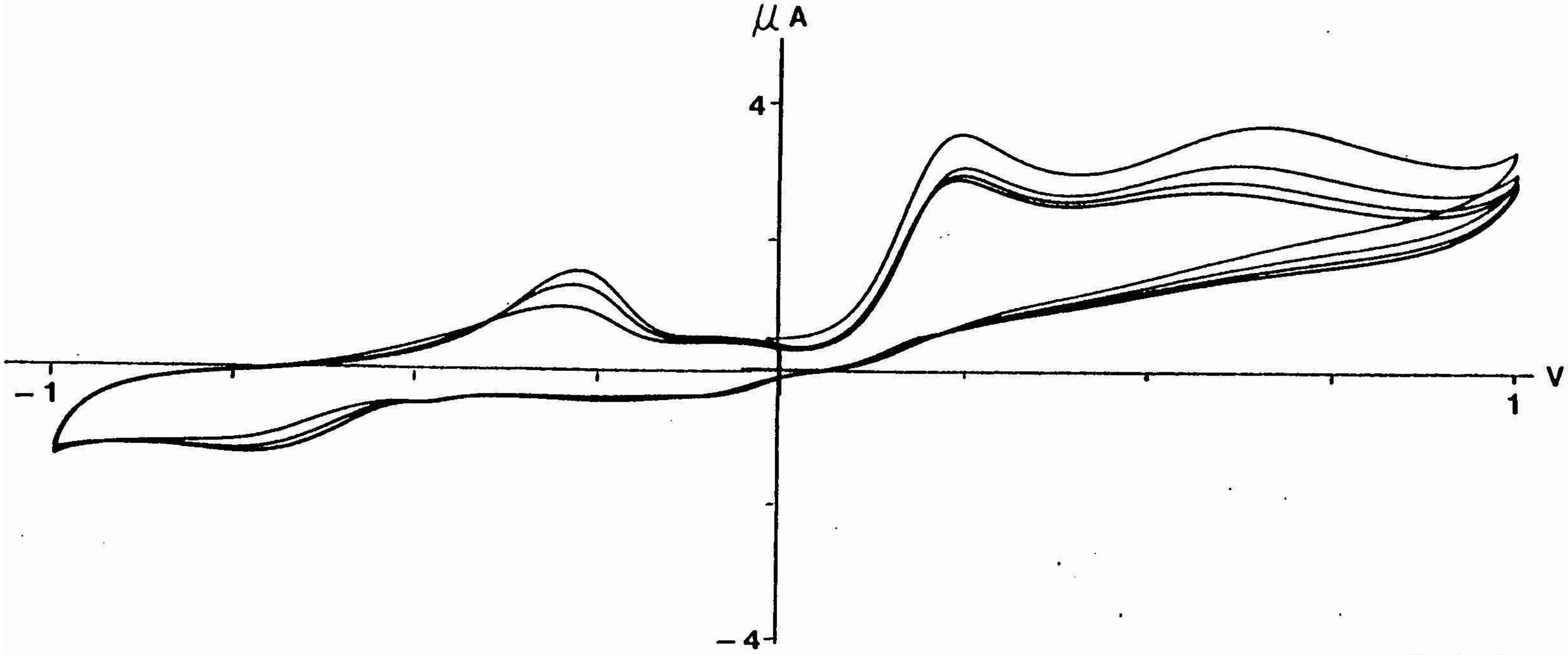


Figure 8. Output from CV Experiment; Water Only.

0% i-propanol in water No
gold electrode
1 reference
Gain on BAS 0.02 mA/v
X Axis 200 mv/in
Y Axis 100 mv/in

water plot. This is then due to some oxidation reaction of the 2-propanol. The current (i_p) at the voltage peak is measured' from the plot to be 0.63 x 10^{-6} A. Since this peak corresponds to a 2-propanol reaction and is at -0.5 V, we can use the results from the potential step experiment, at -0.5 V, to calculate the number of electrons used in this reaction. Combining the Cottrell equation with the Randles and Sovcik equation and solving for n gives

$$n = \left(\frac{F\, i_p}{\pi^{1/2}\left(2.69 \times 10^5\right) v^{1/2}\left(it^{1/2}\right)} \right)^2$$

where F is the Faraday constant, v is the sweep voltage used in the CV experiment (0.1 V/s). Current times the square root of time, $it^{1/2}$, is a calculated constant from the potential step experiment. From the current versus time plot the current is measured at various times. The measured data are as follows:

TIME (s)	CURRENT (10^{-6} A)	$it^{1/2}$ (10^{6} $As^{1/2}$)
0.20	2.95	1.31
0.32	2.52	1.41
0.47	2.20	1.54
0.59	2.01	1.52

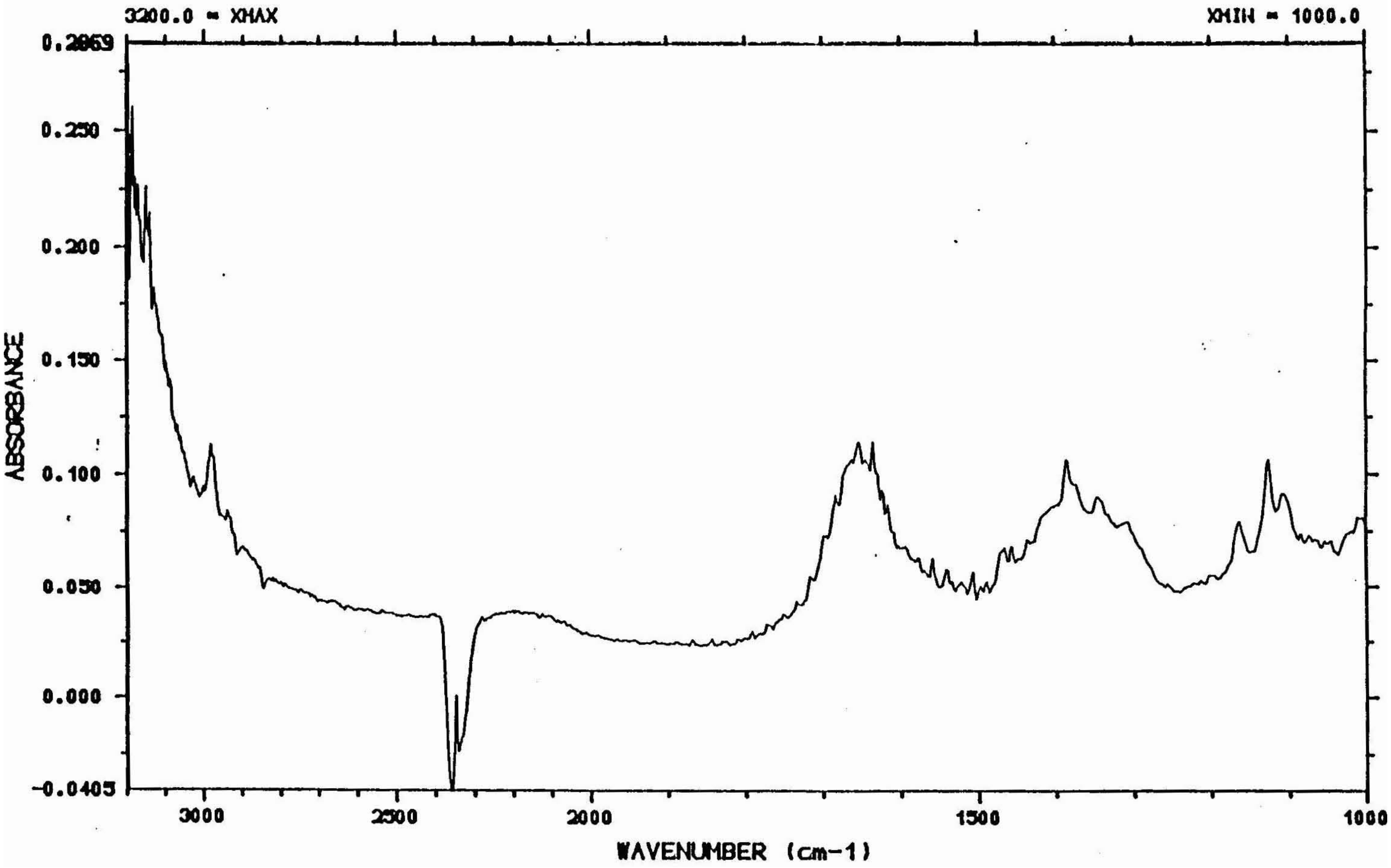
The average value for $it^{1/2}$ is 1.45×10^{-6} As1/2. Substituting the values into the Cottrell equation and solving gives a value of n of 0.77. Because electrons cannot be divided the reaction takes one electron.

This is an unexpected finding since the oxidation of 2-propanol to acetone is thought to be a two-electron process. Another reaction must be occurring under these conditions. The reaction might be the adsorption of the 2-propanol to the surface with the loss of a proton. This process would use only one electron. The hydrogen would come off in an oxidative addition step where the metal would take on a +2 charqe while the intermediate and the hydrogen would have a formal charqe of -1. The hydrogen could easily lose an electron to become a neutral adsorbed atom. Adsorbed hydrogen atoms are known to exist on metal surfaces.[6,18,26] The oxidation of this intermediate may occur at a voltage more negative than -0.5 V and would be lost in the large water oxidation peak.

SPECTRO-ELECTROCHEMISTRY

The ATR setup was first tested for the ability to observe 2-propanol in water. Following the manufacturer's procedure the spectrum in Figure 9 was obtained for *5%* 2-propanol in water which agrees with published spectra.[24] Obtaining this spectrum was very difficult due to the nature of the solution. Because water absorbs IR radiation strongly, nearly 90% of the input IR radiation was absorbed by the solution. The next experiment was designed to determine if acetone can be observed as a minor ingredient in a 5% 2-propanol solution. Figure 10 is the spectrum obtained for a 5% 2-propanol solution with 0.5% acetone added. A comparison between Figures 9 and 10 shows that acetone can be seen by the appearance of peaks at 1200 cm^{-1}, 1400 cm^{-1}, and 1700 cm^{-1}. The ATR cell can be used to determine acetone as a minor ingredient in a 2-propanol solution.

The next step was to actually do the electrochemistry. The vapor deposited gold crystal was tried first. The ATR cell electrodes were connected to the electronics and a 5% solution of 2-propanol was added to the cell. A baseline reading was taken and the potential was stepped to about -0.9 V. A series of spectra showed no difference. Examination of the crystal showed some reasons why this occurred. The deposited gold was burned off of the crystal at the point the wire was attached. This gold coating was not very transparent so, even though light was absorbed by the solution, not enough light was output to show anything but noise. A closer inspection of the spectra showed no peaks, just noise. Because of the low transparency of the vapor deposited gold films it was decided to use a gold mini-grid. The transparency of the crystal did not increase greatly but more IR was passing into the solution. Again the electrode was



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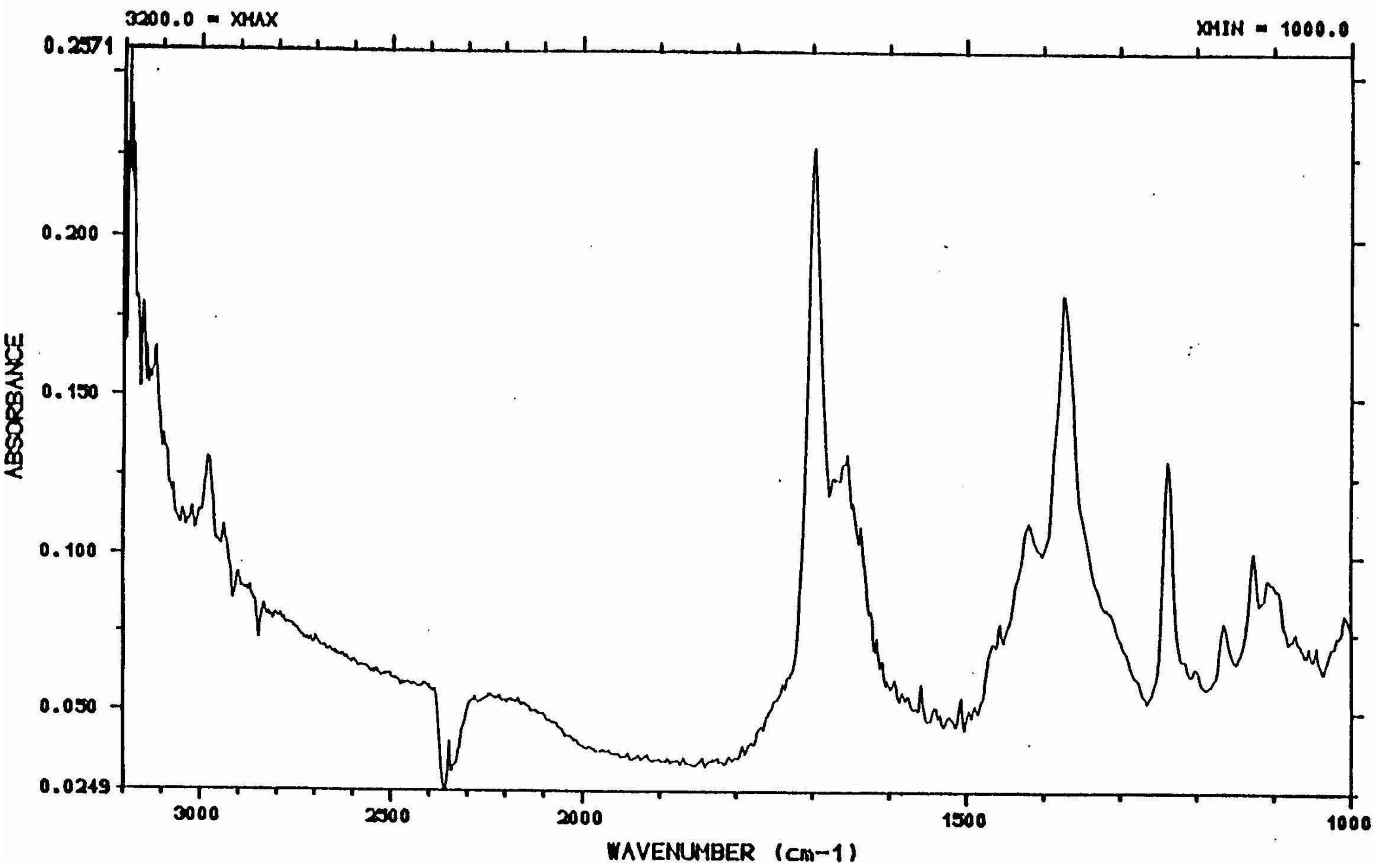
INSTRUMENTS LAB

SAMPLE NAME : 5X I-PROP; CIRCLE CELL; .89 WATER SUBTRACTED
SAHPLE FORM : LIQUID
OPERATOR : PAUL SHILLER
APODIZATION : NONE
RESOLUTION : 4 CM -1
SCANS : 0

Figure 9. FTIR Spectrum of 5% 2-Propanol.

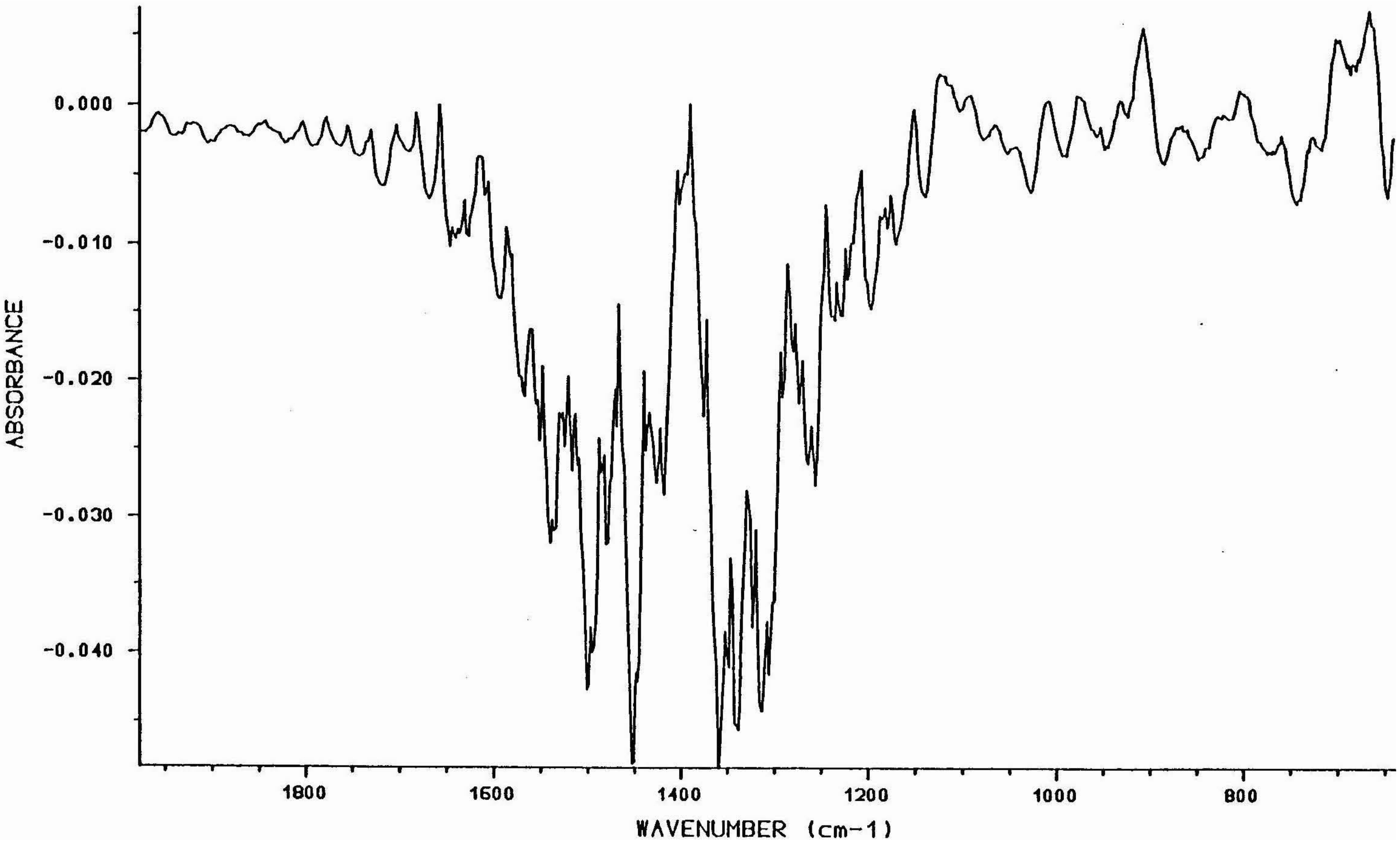


YOUNGSTOWN STATE
CHEMISTRY DEPT.
INSTRUMENTS LAB

SAMPLE NAME : 5% I-PROP + ACE; CIRCLE CELL; .89 WATER SUBT.
SAMPLE FORM : LIQUID
OPERATOR : PAUL SHILLER
APODIZATION : NONE
RESOLUTION : 4 CM -1
SCANS : 0

Figure 10 FTIR Spectrum of 5% 2-Propanol plus Acetone.

attached to the electronics and a 5% 2-propanol solution was added. The potential was stepped to about -0.9 V. Again the spectra showed no difference from the baseline. There were no acetone adsorption bands. The current meter on the power supply indicated that an electrochemical reaction was taking place. It was decided that perhaps the generation of acetone is not great enough to be detected by the spectrometer. The remedy would be to increase the concentration of 2-propanol to 40%. The same procedure was followed as above but using a 40% 2-propanol solution. Some peaks in the IR spectrum increased in intensity or appeared over the baseline spectrum after performing an electrochemical oxidation. Figure 11 shows the baseline spectrum for the 40% 2-propanol solution. Figure 12 shows a typical spectrum for a potential step of -0.9 V. The peaks were verified as being caused by the electrochemical process because the intensity of the peaks would grow when the potential was on and the intensity would decrease when the potential was turned off. This is as expected because the electrochemistry increases the concentration of products near the electrode and in this case near the ATR crystal. This increase in concentration is because the products do not diffuse away from the electrode faster than they are produced. When the potential is turned off the products have a chance to diffuse away from the electrode and the



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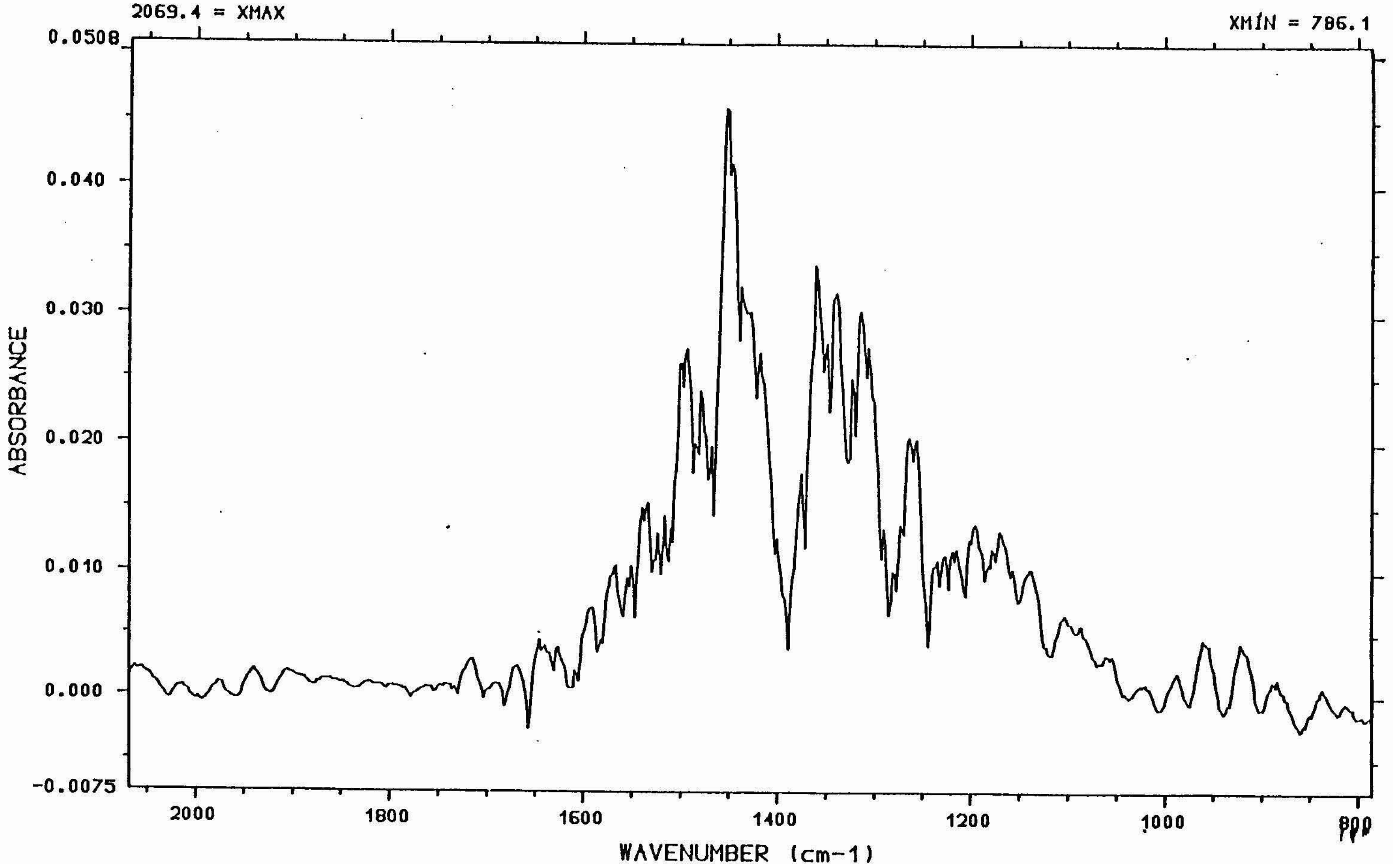
CHEMISTRY DEPT.
INSTRUMENTS LAB

SAMPLE NAME : PS010601
SAMPLE FORM : BACKGROUND I-PROP
OPERATOR : PAUL SHILLER
APODIZATION : BOXCAR

RESOLUTION : 4 CM -1
SCANS : 64

Figure 11. FTIR Baseline Spectrum of 40% 2-Propanol.



YOUNGSTOWN STATE
CHEMISTRY DEPT.
INSTRUMENTS LAB

SAMPLE NAME : P80106P9
SAMPLE FORM : AFTER ELECTROCHEM
OPERATOR : PAUL SMILO
APODIZATION : BOXCAR

RESOLUTION : 4 CM -1
SCANS : 64

Figure 12. Typical FTIR Spectrum of 40% 2-Propanol after Electrochemistry.

ATR crystal so the local concentration is lowered.

The only question remaining is whether the peaks do correspond to acetone or another intermediate. The peak that gains intensity in the spectra from the electrochemical experiments was centered at about 1400 cm^{-1}. This peak was also seen as an acetone peak in the IR spectra of 5% 2-propanol with 0.5% acetone and is also seen in published spectra for acetone. This peak can be due to the deformation vibrations of the methyl groups.[22]

CONCLUSIONS

The ability to detect electrochemical products near the electrode surface by IR spectroscopy in aqueous solutions has been shown. We have shown the presence of acetone from the electrochemical oxidation of propanol. CV experiments indicated that 2-propanol may be adsorbed onto the surface through a one-electron process. Obtaining a useable IR spectra through an ATR device coated with gold is very difficult. Vapor deposited gold on the electrode does not seem to provide a sufficiently transparent surface for the IR radiation to pass through. The mini-grid solved this problem but the electrochemically active surface is no longer actually at the surface of the ATR crystal. This was acceptable to detect products but adsorbed intermediates probably cannot be observed using a mini-grid technique. The reaction might, in the future, be carried out on a conductive ATR crystal. Doped silicon crystals are available that are conductive. However, the surface of silicon would be vastly different from that of a metal. Other equipment might allow more sensitive results. There are spectrometers that have nearly 1000 times the light throughput of the one used in this study. This amount of light throughput would allow an increase in resolution from the 4 cm^{-1} used here. The time of spectrum acquisition would also be shortened, greatly, with an increase of signal to noise. An increase in light throughput of this magnitude would also increase the sensitivity of the system. Low concentration intermediates might then be observed. With these refinements to the technique a greater understanding of the electrochemical oxidation of alcohols may be realized. This understanding may lead to more efficient and more economical fuel cells that can take advantage of alcohols as fuels,

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