Influence of Solvent on the Infrared Spectrum of Carbon Monoxide Adsorbed on Platinum Electrodes

by

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(ABSTRACT)

The behavior of adsorbed carbon monoxide on platinum was studied using potential difference infrared spectroscopy. Three solvents and three electrolytes were chosen, and data gathered at both high and low adsorbate coverages. The rate of change of IR peak position with applied potential, the Stark tuning rate, was used as an indicator of the local electric field strength at the interface. It was determined that neither solvated cation size nor bulk dielectric constant accounts for the changes in Stark tuning rate with different solvents.

Acknowledgments

I probably would never have attempted graduate work without the encouragement of Professor Mark R. Anderson, an outstanding teacher and scientist. I am thankful that I had the opportunity to work with him and proud to say that he was my advisor.

The unwavering support of my family has been a great comfort to me in my years here. The love and patience of my husband Nick made a difficult situation bearable. I am indebted to my parents, who have emphasized the intrinsic value of education and learning all my life. My brother Matt has helped me to keep my perspective these past two years.

Finally, thanks to all the fellow students, graduate and undergraduate, whose friendship will always make Virginia Tech a special place in my memory.

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List of Abbreviations

CO	Carbon Monoxide
PDIRS	Potential Difference InfraRed Spectroscopy
DMF	n,n-DiMethylFormamide
FTIR	Fourier Transform Infrared
IHP	Inner Helmholtz Plane
OHP	Outer Helmholtz Plane
PZC	Potential of Zero Charge
SCE	Saturated Calomel Electrode
SERS	Surface Enhanced Raman Spectroscopy
SNIFTERS	Subtractively Normalized Interfacial FT-IR Spectroscopy

Chapter 1

Introduction

1.1 In Situ Infrared Spectroelectrochemistry

Electrochemists have long recognized that the adsorption of intermediates and products to electrodes during electrochemical reactions plays an integral role in the kinetics and mechanism of heterogeneous processes. Although the extent of strong and weak adsorption can be quantified using strictly electrochemical methods[1-3], electrochemistry alone provides no direct structural information about the composition or structure of either the products or adsorbed species.

In situ spectroelectrochemistry has been shown to be an effective way of obtaining this structural information. Because of the wealth of information available from an infrared spectrum, in situ infrared spectroscopy combined with electrochemical measurement has become a popular technique [4]. Reflection spectroscopy is especially applicable to studying surface structure and interactions. Reflection in situ infrared spectroscopy has been very useful in studying two problems. The first application is in the study of the structure and bonding of adsorbed species on the surface. Because of the interactions of electromagnetic radiation upon reflection from a metal surface, only bonds with a vector component perpendicular to the surface can be detected in the spectrum. From this information, one may draw conclusions about the orientation of an adsorbed molecule by the presence and absence of characteristic infrared absorptions. Scientists have determined orientations of

molecules in self-assembled monolayers by this method [5,6]. The second application is the identification of reactants, products, and adsorbed intermediates of electrode reactions. "Pure" electrochemical data provide no direct structural information, while infrared spectra taken before and after the reaction can provide evidence of structural change without subsequent analysis.

The identification of adsorbed intermediates can yield information about the mechanism of the reaction. IR Spectroelectrochemistry has been used to study the oxidation of simple alcohols, particularly methanol at platinum electrodes. Although methanol could be an important electrochemical fuel because of its high efficiency (six electrons per molecule), it cannot be continually oxidized at a catalytic surface for long periods of time. While some of the methanol undergoes complete oxidation to carbon dioxide, some of the methanol partially oxidizes to form intermediates that are adsorbed to the catalytic surface. These "poisoning" intermediates block the electrode surface and prevent electron transfer, reducing the efficiency of this reaction. Both for its use as a convenient energy source, and the more academic interest in the mechanism of simple alcohol oxidations, the identity of adsorbed intermediates on platinum surfaces has been the subject of many studies.

Beden et. al. [7] has identified by infrared three intermediates when methanol is chemisorbed to a Pt (100) electrode in an acidic solution and partially oxidized. Two have been identified from infrared peaks as single and bridge bonded species of carbon monoxide. Carbon monoxide is a well-known intermediate of the complete oxidation of methanol in aqueous solution, so this

is not surprising. The third species has an absorption band corresponding to a C=0 bond, which Beden suggests to be in a "formyl" structure (H-C=O). Beden also found that at low concentrations of methanol, the proportion of bridge bonded carbon monoxide increased.

Weaver [8] has used potential difference infrared to identify products of methanol oxidation in both anhydrous and concentrated acidic mediums. He has identified 1,1-dimethoxymethane and methyl formate as the products of the oxidation in anhydrous methanol. These results suggest that the cation HCHOH is a possible short-lived chemisorbed intermediate. This ion could combine with methanol to form methyl formate. Previous to the infrared spectroelectrochemical results, carbon monoxide was the only chemisorbed intermediate identified because it was stable enough to withstand subsequent treatment after partial oxidation.

In recent years, the unique characteristics of IR spectroelectrochemistry have been used to obtain information about the electrochemical double layer. By choosing adsorbates very sensitive to the environment of the interface, one can determine the change in the interface with changing experimental conditions.

1.2 Literature Review

The combining of electrochemical control and surface reflection vibrational spectroscopy was first conducted using Raman spectroscopy, and this combination instigated the development of SERS (surface-enhanced Raman spectroscopy). In situ SERS, while being a potentially useful technique, generates results that are difficult to interpret because (i) electrochemistry and SERS perform best using smooth and rough surfaces, respectively, and (ii) the fundamental mechanism of SERS has not be established.

Reflectance infrared spectroscopy is effective with a smooth surface, making it a suitable technique to pair with electrochemistry. Bewick [9,10] demonstrated this method in 1980, using external reflectance. External reflectance in situ IR has been shown to be useful for studying adsorbed intermediates of oxidation reactions [7,8,11-13]. It is also useful for studies of the electrochemical double layer. A diagram of the double layer is shown in Figure 1 [14]. Adsorbed to the negatively charged electrode are various molecules; anions, cations, and solvent molecules are all possible. The geometric centers of these molecules forms the "Inner Helmholtz Plane" (IHP). Because of the negative charge on the electrode, cations (with their solvation spheres) are attracted to the electrode. The "Outer Helmholtz Plane" (OHP) is the average of the geometric centers of these cations. By adsorbing a molecule to serve as a probe to the surface of the electrode, and studying the changes in the vibrational frequency of the bond or bonds of the probe with changes in conditions, one can

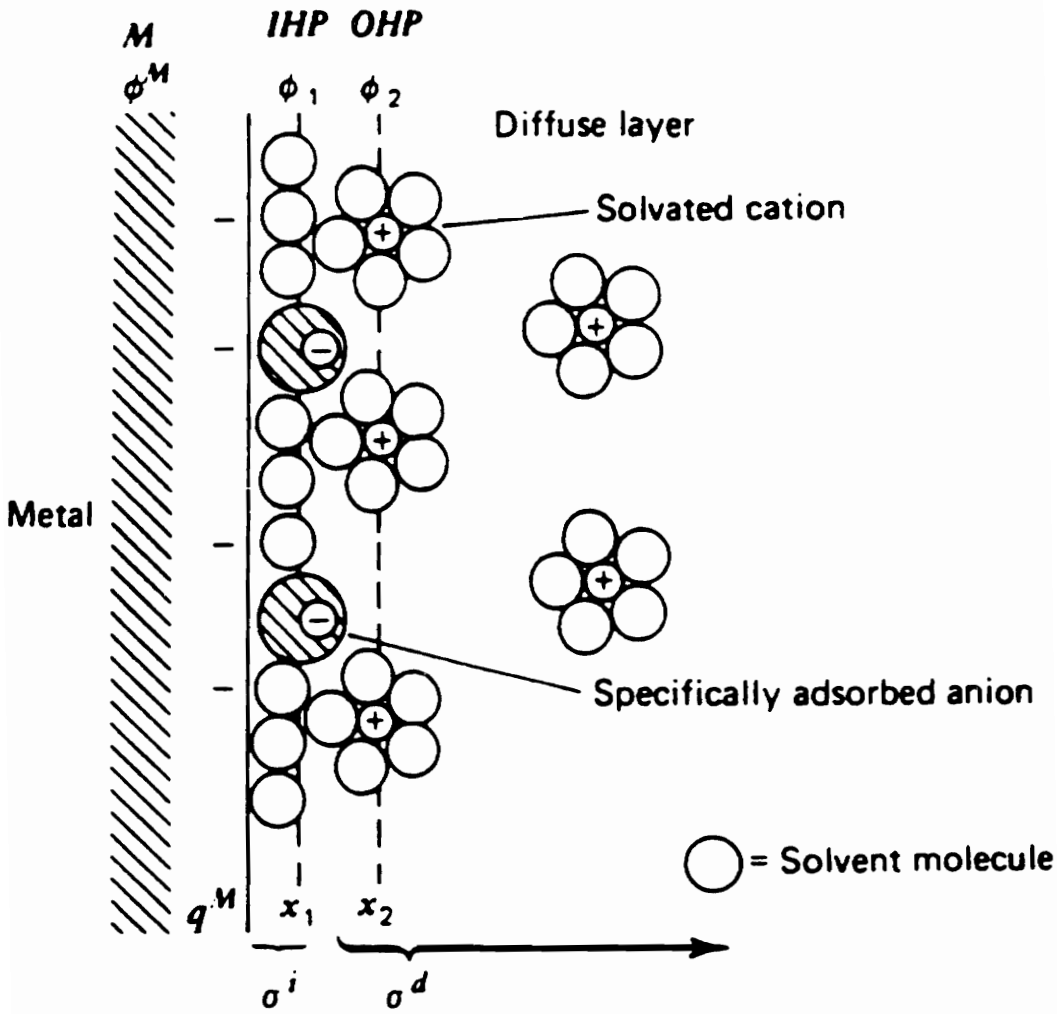


Figure 1 Electrochemical Double Layer [14]

gather information about the character of the double layer. Studies have been made on the effect of different electrolytes and different solvents [15-18].

IR spectroelectrochemical investigations of the double layer began when Russell [19] found that the vibrational frequency of adsorbed carbon monoxide on platinum shifted with applied potential. He also found that the magnitude of this shift changed with different coverages of carbon monoxide. The change of peak potential with respect to applied potential is called the Stark tuning rate. This phenomena was given its first exhaustive theoretical treatment when Lambert [20-23] developed a theory explaining the behavior of carbon monoxide on platinum surfaces. Lambert developed the theory that this shift was due to changes in the electric field at the surface. A second theory, attributing the frequency shift with applied potential to the donating and withdrawing properties of the electrons in the platinum electrode, has been treated theoretically by A.B. Anderson [24].

With the discovery of this phenomena and the development of tentative theories to explain it, research was conducted to determine if changes in the interface (i.e., different cations, solvents and coverages) would result in a change in the rate of shift with applied potential. Of particular interest was the influence of solvent on the interface, because of the lack of knowledge of solvent influence in the double layer. Solvent effects have been attributed to (i) the dielectric strength of the solvent, (ii) solvent dipole reorganization when under applied potential, or (iii) lack of opportunity for the solvent to exert influence on the system when the IHP is saturated [17].

Pons et al. [16] found a Stark tuning rate of circa 30 cm^{-1}/V in aqueous systems, in agreement with the predictions made by Lambert [20]. The tuning rate for three aprotic solvents (1,2-dichloroethane, N-methylformamide, and acetonitrile) was circa 20 cm^{-1}/V. Previous to this work, few studies had been made in nonaqueous systems, probably due to the difficulty in surface preparation when electrochemical hydrogen adsorption and desorption is unavailable as a cleaning method. The aprotic solvents were chosen to represent a wide range of bulk dielectric strength, so that an influence of dielectric strength on the tuning rate (and the interface) could be observed. Because of the lack of correlation between dielectric strength and tuning rate, it was surmised that the difference between the aprotic and aqueous systems was likely due to the difference in adsorption of aprotic and protic solvents to platinum.

Using four nonaqueous solvents with a range of solvation properties and bulk dielectric constants, Weaver [15] found no significant change in tuning rate with solvent when a given cation was used. Weaver suggested that the solvent molecules were excluded at high adsorbate coverages from the IHP, and that the presence of solvent in the double layer was limited to the solvation spheres of the electrolyte in the OHP. This result could then be interpreted as verifying Lambert's theory, since the electric field would change very little with solvent if the solvent were indeed confined to the cation solvation spheres.

Pons et al. [25] also studied the Stark tuning rate as a function of the composition of the methanol/water mixture that served as solvent. The tuning rate was circa 22 cm^{-1}/V ("aprotic" behavior) in pure methanol. The rate

remained constant with increasing proportion of water until about 75% methanol/25% water, when the tuning rate changed sharply to 30 cm^{-1}/V and remained constant for mixtures with higher than 25% water. This behavior was explained in terms of the "reorganization" or redistribution of solvent at the interface. These results indicate that the interface cannot be approximated by bulk properties. Rather, the molecular content must be considered. A similar phenomena was observed by Pons [25] in ethanol/water and acetonitrile/water solutions. No such change was observed in an ethylene glycol/water mixture up to 60% water; the tuning rate remained "aprotic".

When methanol is chosen as the solvent, Pons et al. [16] found the behavior of the interface over a wide potential range cannot be classified as "protic" or "aprotic". Rather, the tuning rate has three distinct regions. The tuning rate is 25 cm^{-1}/V with applied potential negative of +0.2V vs. SCE. Between +0.2 and +0.4 V, the tuning rate is zero (or independent of potential). At potentials positive of +0.4 V, the tuning rate is 20 cm^{-1}/V. The potential of zero charge, or PZC, probably occurs in the region in which the peak position is independent of potential. The different tuning rates on either side of the proposed PZC have been suggested to be the result of solvent reorientation.

Although no correlation between dielectric constant and tuning rate could be identified when aprotic and protic solvents were compared, an inverse relationship between the tuning rate and bulk dielectric constant at low coverage was found when several straight-chain alcohols were studied [17]. It was suggested that this relationship was evident only under these conditions because

of the higher contribution to the capacitance of the double layer and because of the similarity in patterning and adsorption properties of the alcohols.

1.3 Research Objectives

The objectives of this research were (i) to study solvent effect on the Stark tuning rate of adsorbed carbon monoxide, (ii) to determine if this solvent effect could be explained by differences in solvation spheres and dielectric constants, (iii) to compare Stark tuning rates of similar systems where adsorbate coverage is varied and (iv) determine if this data supports the theory that solvent effect is not observed unless the solvent has the opportunity to enter the inner Helmholtz layer [17].

Chapter 2
Experimental

2.1 Instrumentation

IR spectroelectrochemistry has two major problems, which are responsible for the slow development behind other types of in situ spectroelectrochemistry. The first problem is absorption of infrared radiation by the solvent. This problem is exacerbated by the limited choices of solvent available for electrochemistry. Typical solvents are strong infrared absorbers; water, the most popular electrochemical solvent, is rarely used in traditional infrared spectroscopy. Conversely, infrared solvents such as carbon tetrachloride are unsuitable for electrochemistry, since they generally do not dissolve electrolytes.

Solvent absorption cannot be totally eliminated; however, it can be minimized by using a spectroelectrochemical cell that is designed so that the path length of the infrared beam through the bulk solution is as small as possible. The cell used for this work is shown in Figure 2 [26]. Developed by Pons, the cell is formed from a modified syringe barrel. The working electrode is fashioned from the syringe plunger with a flat disc of platinum at the front, sealed to glass. A platinum wire is sealed through the outer cell to serve as the secondary electrode. An optical window, mounted on a ground glass fitting, is placed on the end of the cell and secured with teflon tape. The cell is filled from a hole in the top of the cell; because the cell is made from a syringe, leakage is minimal at

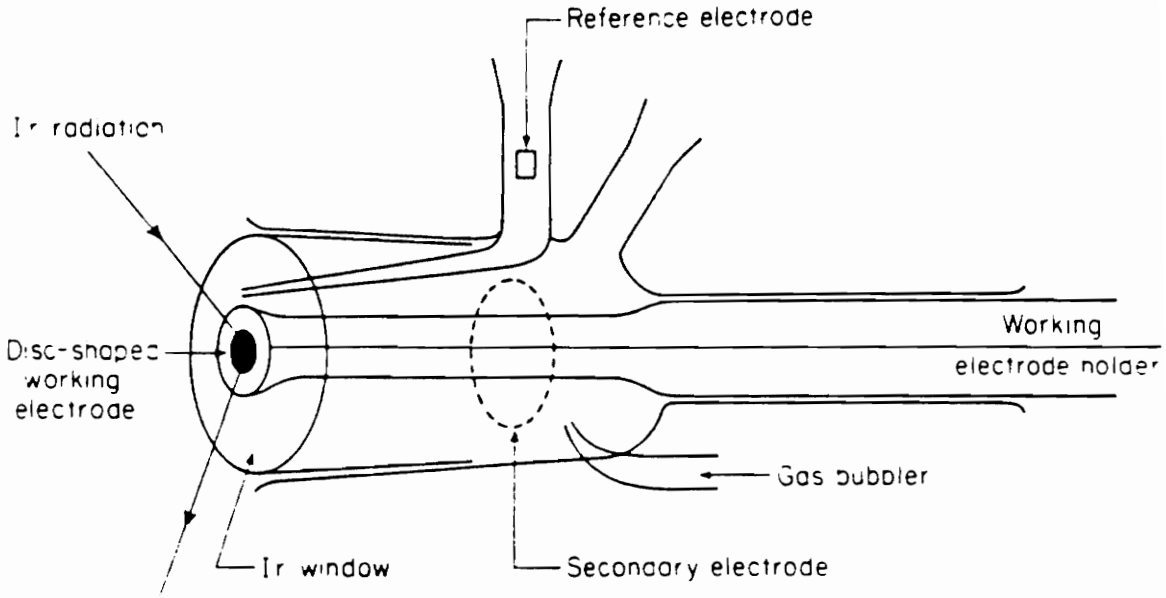


Figure 2 Spectroelectrochemical Cell [26]

the back of the cell. During an experiment, the working electrode is forced against the infrared transparent optical window to form a solution thin layer. The thin layer minimizes the bulk solvent in the optical path to an estimated 10 μm [27]. The thin layer is especially useful for experiments where only adsorbate molecules are of interest, since the contribution of signal from the bulk solution is reduced without reduction of signal from adsorbed molecules. This distance of 10 μm is estimated to be thousands of times larger than the electrochemical double layer; therefore, the thin layer does not affect the electrochemical response. When desired, the electrode can be pulled back to allow free movement of the bulk solution across the electrode (i.e., for bubbling a gas to adsorb on the working electrode, or to electrochemically clean the electrode by rapidly scanning between two extreme potentials.)

2.2 Signal to Noise Enhancement

The other problem, and one more troublesome for detection of adsorbate molecules, is that of signal to noise. In dispersive infrared, high concentrations of analyte are used so that the peaks are easily discernible from the baseline. When a monolayer is studied, the change in percentage transmittance varies from 0.1% to 0.5%, depending on the coverage of the monolayer and the strength of absorption of the adsorbed molecule. To distinguish monolayer peaks from noise, the random noise must be reduced by averaging the data from many spectra. Fourier transform infrared spectroscopy greatly increases the speed with which spectra can be taken. By using this technology, one can record many spectra in a fraction of the time it would take with traditional dispersive infrared. Hence, for this research, more than one hundred interferometer scans were taken for each spectrum.

However, caution must be used when deciding on the number of interferograms. If the compound or adsorbate is somewhat unstable over long periods of time, as is sometimes the case with adsorbates under an applied potential, there may be some degradation with the extended time periods. The degradation may involve an oxidation or reduction of the adsorbate, or the adsorbate may desorb without changing composition. In addition, the signal-to-noise ratio is proportional to the square root of the number of spectra [28]. Hence, to double the signal-to-noise ratio the number of scans must be quadrupled. It is clear that there is a trade-off to be made between signal-to-noise and time required to collect data.

Even when using a cell designed to minimize absorption from the bulk solution, the contribution to the signal from the bulk dominates the spectrum, while the contribution from the adsorbate molecules is unable to be detected (Figure 3). After enlarging the spectrum to show only the area of interest, the peak from adsorbed carbon monoxide (at approximately 2070 cm^{-1}) is still barely visible (Figure 4). In order to see the adsorbate peak, the solvent contribution must be eliminated. To do this, two spectra at different applied potentials are recorded. The absorption frequency of the carbon-oxygen bond changes with applied potential, while the absorption frequencies of molecules in the bulk solution do not experience this change. By subtracting one spectrum from the other, the absorption from the bulk is canceled out, while the shift in wavenumber of the adsorbate peak is clearly evident (Figure 5).

This method of identifying adsorbate peaks is called SNIFTIRS (Subtractively Normalized Interfacial FT-IR Spectroscopy) or PDIRS (Potential Difference IR Spectroscopy). While special experimental and signal processing techniques can be used on a dispersive instrument to obtain such information, it is much more convenient to use a FTIR spectrometer.

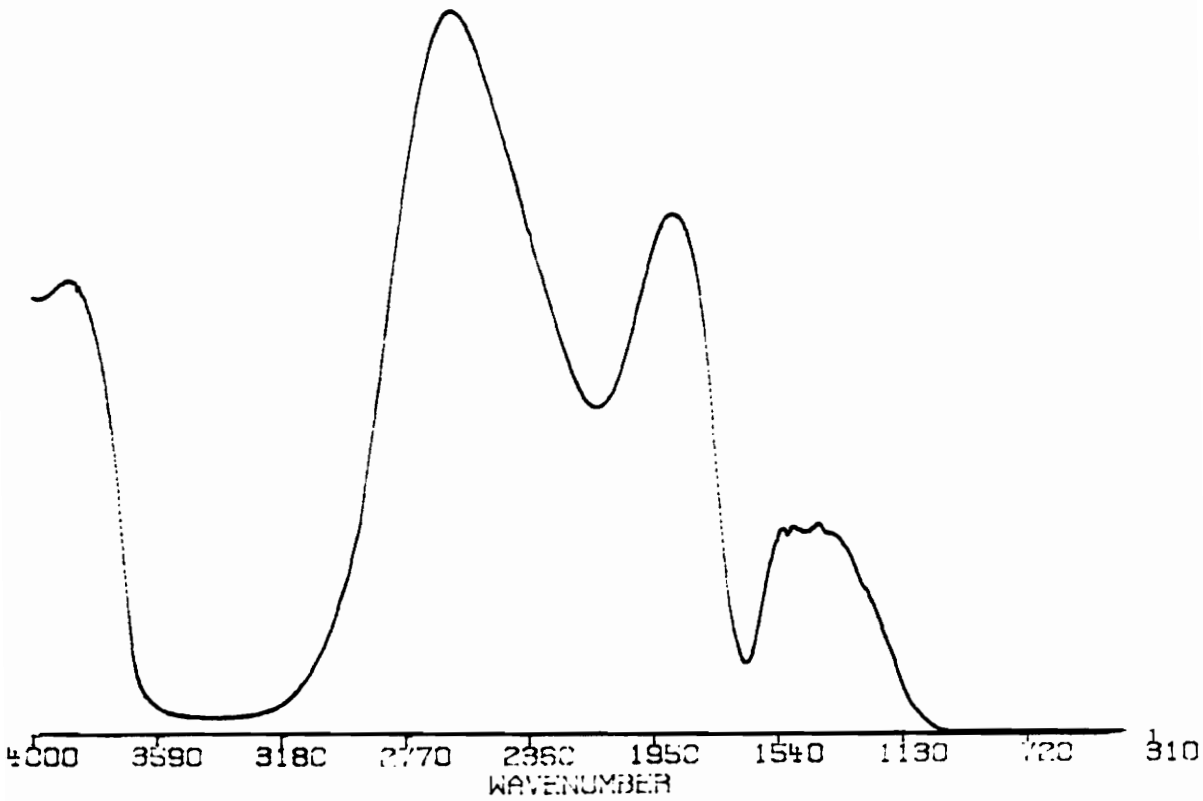


Figure 3 Single Beam Spectrum of Adsorbed CO
(+0.2 V vs. SCE in 0.1M Sodium Perchlorate in Water)

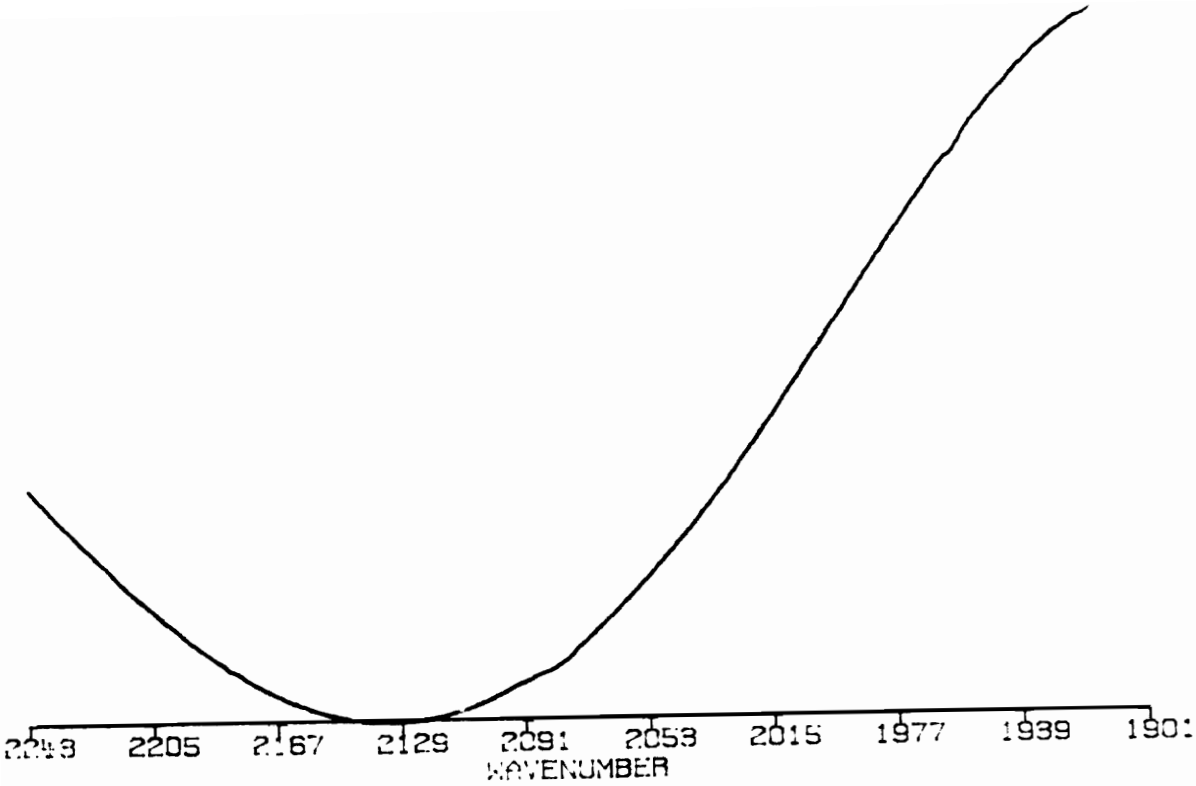


Figure 4 Single Beam Spectrum of Adsorbed CO, Expanded
(+0.2 V vs. SCE in 0.1M Sodium Perchlorate in Water)

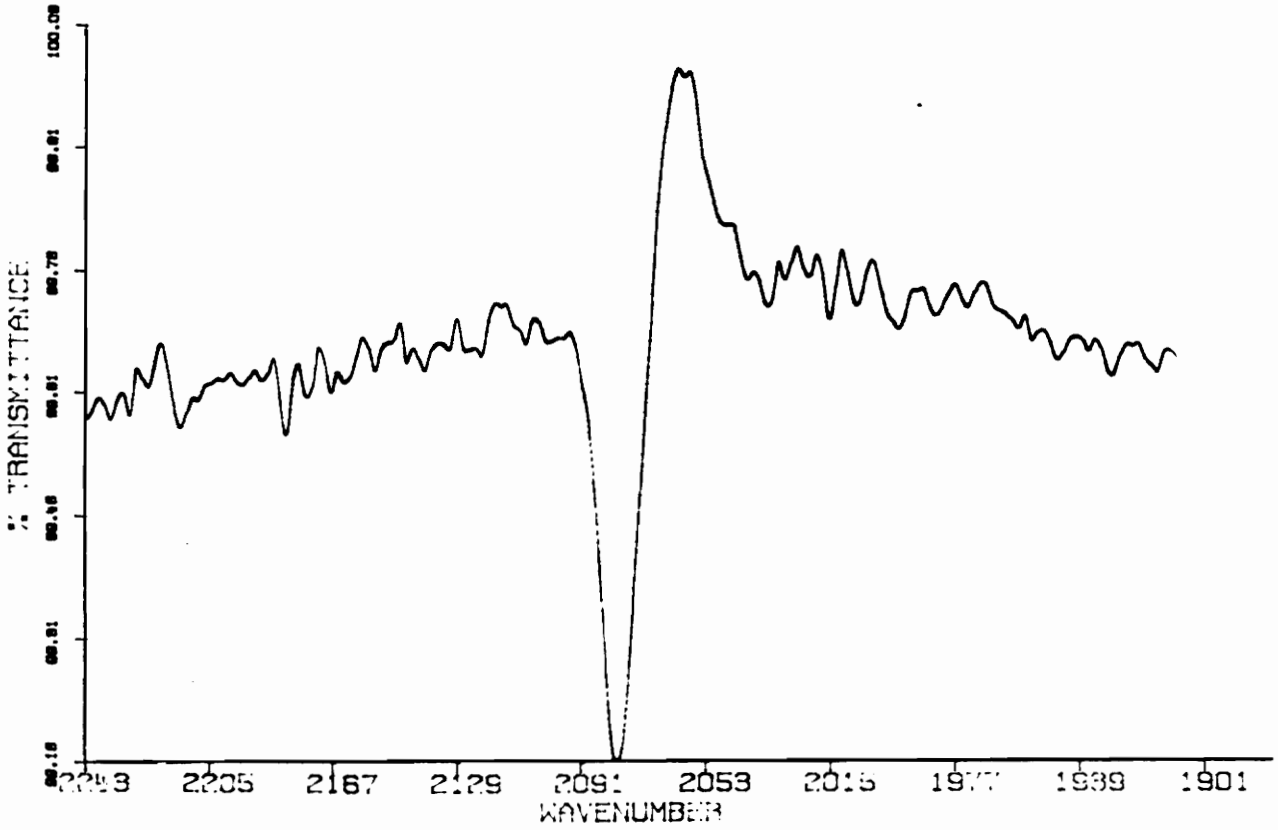


Figure 5 PDIR Spectrum of Adsorbed CO
(0.1M Sodium Perchlorate in Water: Background = -0.5, Sample = +0.2)

2.3 P and S Polarized Light

In addition to the signal processing techniques discussed above, signal-to-noise is increased by filtering out orientations of light that do not interact with the adsorbed molecules. A beam of light is made up of light waves at different orientations. The orientation of any light wave can be expressed with two vector components, referred to as p and s polarized light. When light is reflected from a surface, the plane of incidence is perpendicular to the plane of the surface. The electric wave of p-polarized light is parallel with this plane; the electric wave is perpendicular with the surface. The electric wave of s-polarized light is perpendicular to the plane of incidence. Figure 6 [29] illustrates this concept.

When either polarization of light hits the surface, it experiences a phase shift. The degree of phase shift depends upon the angle of incidence and the polarization of light. At any angle of incidence, s-polarized light has a 180 degree phase shift at the surface. This phase shift causes complete destructive interference at the surface. It is important to understand that while s-polarized light has some intensity before it hits the surface and after it is bounced from the surface, at the surface (for an estimated one-quarter wavelength) it has no intensity [4]. Because of this, s-polarized light will not be absorbed by any adsorbates. It will, however, contribute to the noise. For this reason, the s-polarized light is removed before processing by the detector, since it will contribute to noise but not the signal.

P-polarized light also undergoes some phase shift, but the magnitude of the shift is dependent upon the angle of incidence. If the angle of incidence is

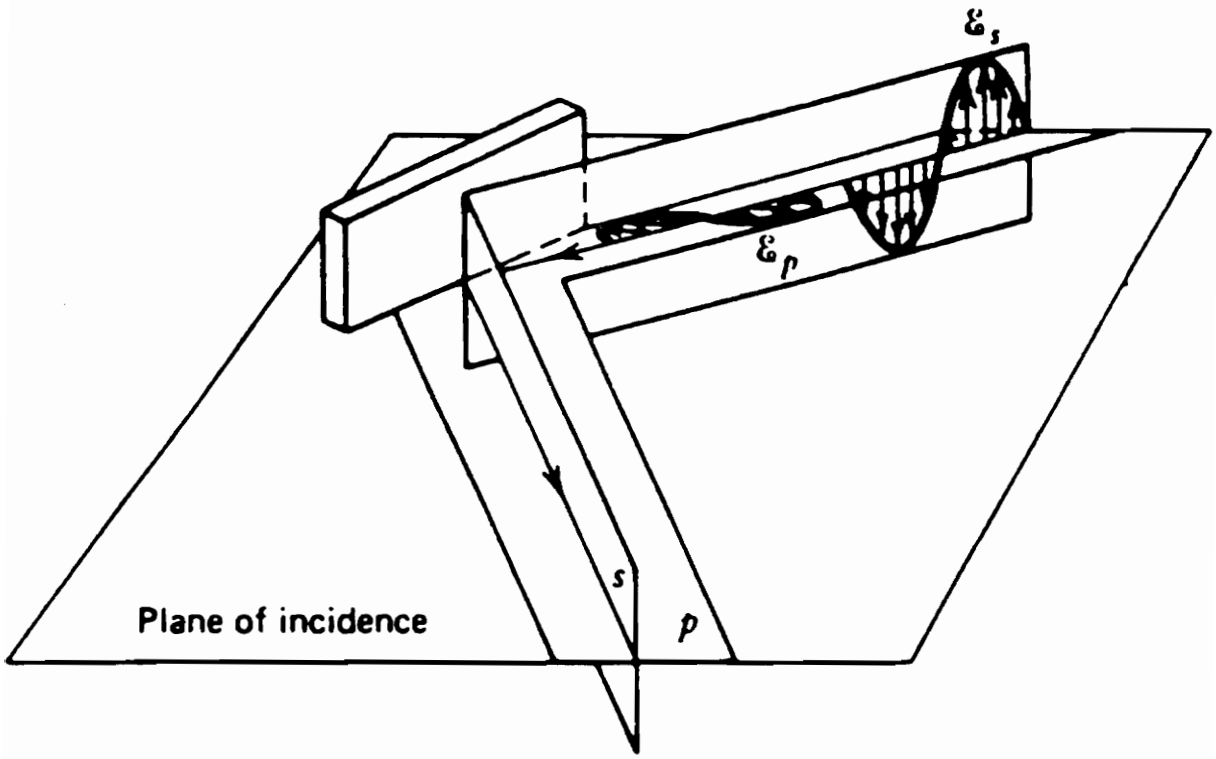


Figure 6 P and S Polarized Light [29]

normal to the surface, then p-polarized light also undergoes complete destructive interference; at this angle it is indistinguishable from s-polarized light. However, at a more glancing angle, the phase shift is reduced (Figure 7) [30]. For optimal efficiency, the light should be nearly parallel to the surface. Since it is difficult to focus a beam at such an angle on a small surface, a compromise must be made between signal-to-noise and experimental ease.

In order for any bond to absorb light, it must have a vibrational moment in the same plane as the electric field of that light wave. Therefore, any bond of an adsorbed molecule must have a vector component perpendicular to the surface to be detected by infrared spectroscopy. A bond perpendicular to the surface will show the strongest absorption, while a bond parallel to the surface will not be evident from the spectrum. A bond, for example, angled at 30 degrees relative to the surface would show half the absorption of an identical bond that is perpendicular to the surface, since the sin (30°) = 0.5. This has been shown [5,6] to be useful for identifying orientations of adsorbates.

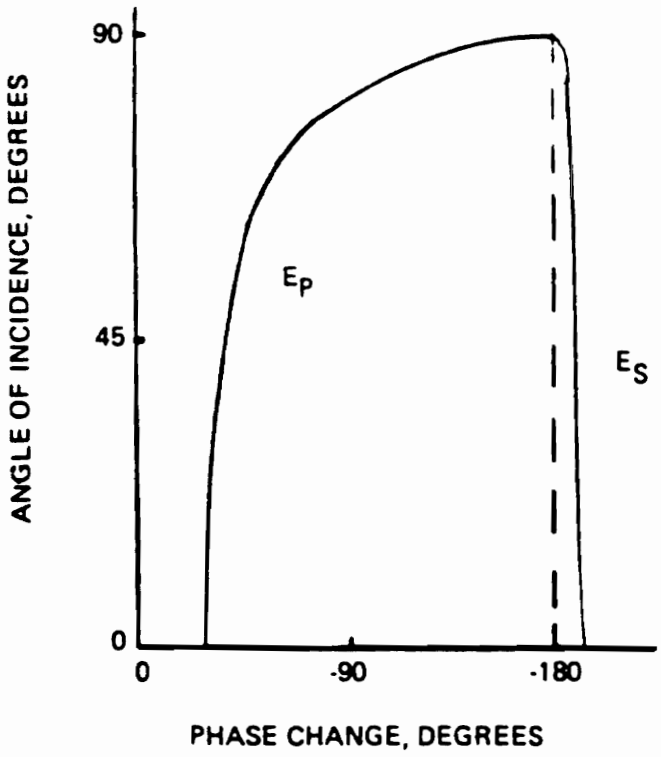


Figure 7 Phase Shift of P and S Polarized Light [30]

2.4 Double Layer Probe Molecules

As mentioned, adsorbed molecules can serve as probes to gather information about the double layer. The ideal double layer probe molecule would have several characteristics. First, it would adsorb strongly to the working electrode in the solvents of choice. It would have a strong infrared absorption, preferably in a region free of other bands, such as solvent absorption or carbon dioxide absorption. Thirdly, it would be very sensitive to its environment, so that one could detect changes in the frequency of the bond with changing electrolytes, solvents, and applied potential.

Several molecules have been used as probe molecules [31, 32], such as thiocyanate ion, cyanide ion, and carbon monoxide. All three of these molecules satisfy the above requirements. Carbon monoxide has the advantage of adsorbing only with the carbon adjacent to the platinum, while thiocyanate has other possible conformations [32]. Carbon monoxide has been extensively used as a probe molecule and can be adsorbed to platinum by a number of different methods [16,33,34]. In this research, carbon monoxide was adsorbed to the surface by saturating the adjacent solution.

2.5 Experimental Equipment and Chemical Purification

The Nicolet 710 FTIR from Nicolet Instruments with an MCT detector (liquid nitrogen cooled) and Nicolet silver front surface mirrors were used. The polarizer used to filter out s-polarized light was from Cambridge Physical Science. The air purifier, used to keep the experiment and detector in a dry, carbon dioxide free environment, was a Balston 75-60 from Balston Filter Products. The potentiostat was a JAS model JDP 1600 from JAS Instruments, and the waveform generator (for pulsing and electrochemical scanning) was an EG&G model 273 from EG&G Instruments. Saturated calomel electrodes were made locally. Calcium fluoride windows (32x3 mm) were obtained from Spectral Systems Incorporated.

Water was purified with the Corning NANOpure system and used immediately. Acetonitrile and DMF, obtained from Fisher Chemical, were both distilled under nitrogen over calcium hydride as a drying agent. The solvents were freshly distilled the day of the experiment and used immediately after removal from the still. The first 5-10 ml of distilled solvent was removed and discarded before collection. Dried alumina was added to the cell when DMF was used to further guard against contamination by atmospheric moisture. During the experiment, the cell was sealed from the atmosphere to prevent moisture from entering the solution.

Both lithium perchlorate and sodium perchlorate were used as received from Aldrich and stored in a dessicator to prevent hydration. TEAP was synthesized from tetraethylammonium bromide and perchloric acid in water

and recrystallized from water until no bromide was detected by the silver nitrate test. All compressed gases were obtained from AirCo.

2.6 Surface Preparations

Several methods are available for adsorbing carbon monoxide to a platinum electrode. As mentioned, oxidation of methanol produces adsorbed carbon monoxide as a poisoning intermediate. Anderson et al. [15, 16, 25, 38] successfully used the oxidation and successive decomposition of vanadium hexacarbonyl to produce adsorbed carbon monoxide. Both of these methods are not suitable for all solvents chosen for this project. The oxidation of methanol requires an oxygen source, not available in acetonitrile, and the decomposition of the vanadium complex requires an appropriate competing ligand (water or acetonitrile have proved useful). Since the purpose of this project was to study solvent effects, a method that worked in pure water, acetonitrile, and DMF was desired. For this reason, the method of bubbling carbon monoxide into the cell and forcing the carbon monoxide to adsorb using various electrochemical techniques was used. This method has been used successfully by others [18,33,34].

The electrochemical technique used to adsorb the carbon monoxide varied from solvent to solvent. Methods were found for each solvent by trial and error, with the peak intensity used as a measure of high or low coverage, since peak intensity is proportional to concentration by Beer's law. Coverage may be quantitated by comparison to aqueous results, where quantitation by electrochemistry is possible. The specific methods for each solvent and coverage are listed below. Regardless of the solvent used, the electrode was pretreated by

polishing with an aqueous suspension of 0.05 μm alumina (Buehler Micropolish) and soaking in hot nitric acid for two minutes. The electrode was then electrochemically cleaned by scanning between +1.3 and -0.3 V (vs. SCE) in aqueous acidic solution for twenty minutes. The electrode was then dried and placed in the cell with the appropriate solution. The solution was then purged in the cell with nitrogen to remove oxygen.

To obtain high coverage in water, the solution was saturated with carbon monoxide while holding the potential at +0.2V vs. SCE. The solution was purged with nitrogen to remove excess carbon monoxide. In acetonitrile, high coverage was obtained by first saturating the solution with carbon monoxide, while scanning the potential from +0.5V to -1.5V at 0.1 V/s. The applied potential was then pulsed between +2 and -2 V at five second intervals. The solution was then purged with nitrogen. The procedure for high coverage in DMF was identical to that for acetonitrile, except the pulses were +1 and -1 V.

For low coverage in water, the solution was saturated with carbon monoxide at no applied potential, then purged with nitrogen to remove excess carbon monoxide. Low coverage in acetonitrile in acetonitrile was obtained by saturating the solution with carbon monoxide while scanning as for high coverage. (The pulsing was omitted.) The solution was purged with nitrogen.

2.7 Data Collection

Single-beam infrared spectra were collected at each potential. Either 128 (acetonitrile and DMF) or 256 (water) interferometer scans were collected and coadded for each spectrum. The larger number of interferograms was required for water because of the larger noise contribution when water was used.

After collection of spectra at each desired potential, the interfacial spectrum was determined by ratioing each single beam spectrum versus a spectrum where the carbon monoxide had desorbed or at a potential 0.5-1 V from the sample spectrum. In this manner, there was no interference from the overlap of sample and background peaks. The peak frequencies were then plotted versus applied potential and the Stark tuning rate (the slope of this plot) determined using linear regression (Cricketgraph). A sample plot is shown in Figure 8. Each experiment was repeated a minimum of three times. The standard deviations and confidence intervals for the slope were calculated using the data from each trial.

Water has a fairly narrow potential window for this experiment, due to the reduction of water at -0.5 V (vs. SCE) and the oxidation of carbon monoxide at +0.7 V.[32] The adsorbed carbon monoxide will oxidize when held at a potential more positive than +0.3 V, because of the relatively long time required to collect data (ca. three minutes). In order to keep experimental conditions as similar as possible from solvent to solvent, this potential window was chosen for other solvents. (Acetonitrile has a much wider range than the other solvents.) The carbon monoxide desorbed in DMF at potentials more negative than 0 V.

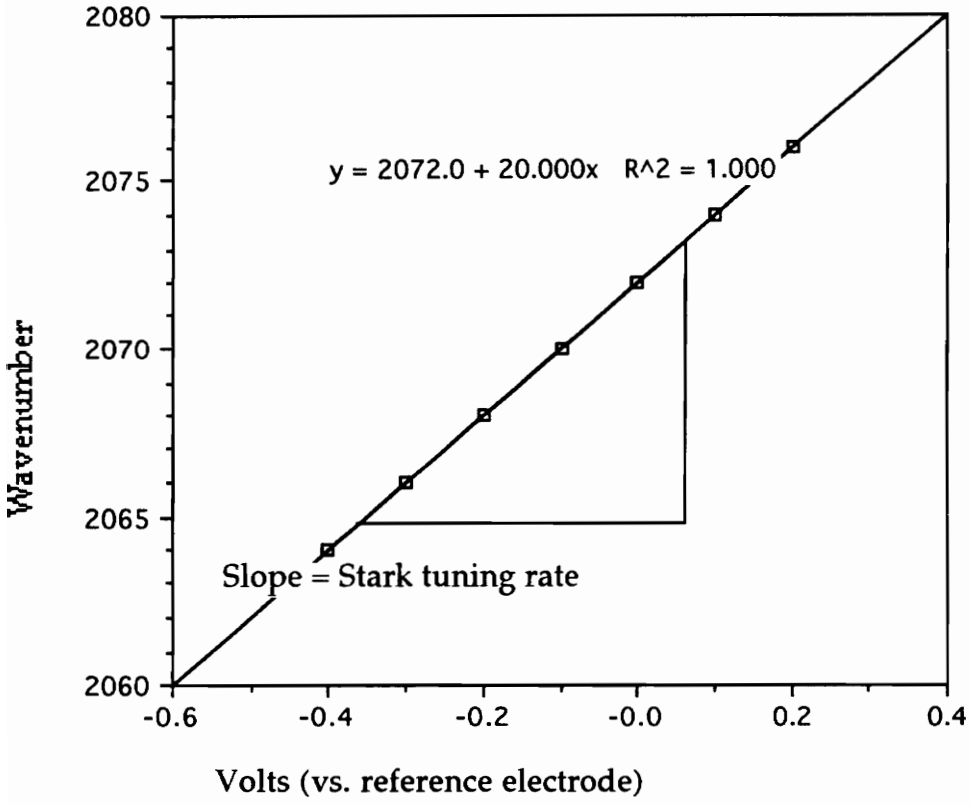


Figure 8 Sample Plot of Peak Position vs. Electrode Potential

For this reason, the potential window chosen for DMF was 0.1 to +1.0 V. Spectra were taken at 0.1 V intervals.

Chapter 3

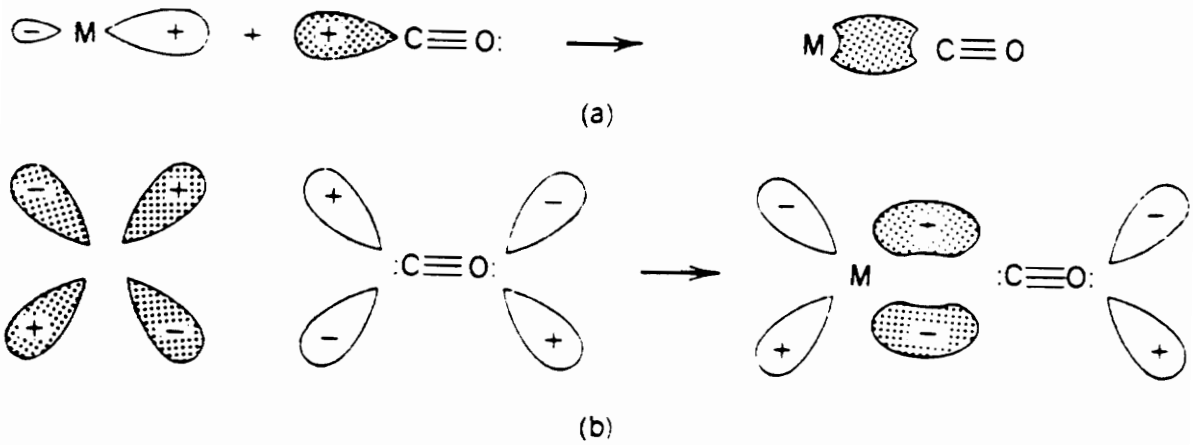
Theory

3.1 Linear and Bridged Adsorption of CO

Carbon monoxide has shown several types of adsorption to platinum, only two of which predominate. In linear adsorption, the carbon is bonded to one platinum atom, while the carbon is bonded to two different atoms in bridged adsorption. The carbon-oxygen bond in linear adsorption is a triple bond, while the carbon-oxygen bond in bridged adsorption is a double bond. Linear and bridged adsorbed carbon monoxide therefore absorb infrared light at different frequencies. Linear adsorption is the dominant of the two at all potentials; bridged adsorption is usually undetected and depends on the applied potential and the crystallographic orientation of platinum. A transition from linear to bridged adsorption has been found at extremely negative applied potentials in some systems by Weaver [34], in agreement with predictions made by A.B. Anderson [24,39] on the basis of molecular orbital calculations. In this research, it was desired to have entirely linear adsorption. Bridged adsorption would obviously change the interface and would render calculations made assuming only linear adsorption inaccurate. To avoid bridged adsorption, the window of applied potential was limited to that which had previously shown only linear adsorption.

Carbon is triply bonded to oxygen in adsorbed carbon monoxide, and each atom has a lone pair. The formal charge on carbon is then -1, while the

formal charge on oxygen is +1. Since carbon is not normally electronegative, it donates this lone pair to an empty orbital on platinum as shown (Figure 9) [41]. This triple carbon oxygen bond adsorbs at approximately 2070 cm and the peak position varies with applied potential; a more negative applied potential results in a lower frequency. Two explanations for this phenomenon are discussed below.



(a) Donation of carbon electrons to metal to form bond.

(b) Back donation of metal electrons into carbon monoxide antibonding orbital.

Figure 9 Bonding between Carbon and Platinum [41]

3.2 Donating and Withdrawing Properties of Platinum Electrons

An electrode under an applied potential may have a charge. In this research, the applied potential was kept negative of the potential of zero charge, so that presumably only cations would be attracted to the electrode. As the potential is made more negative, the electrons in the electrode become more donating in character, resulting in back donation to the platinum-carbon antibonding orbital. The carbon-oxygen bond strength then decreases slightly because the carbon-platinum bond strength is increased slightly. The vibrational frequency of the carbon-oxygen bond is therefore lowered. A schematic diagram of this back donation into the π^* orbital is shown in Figure 9 [34, 40, 41].

This model is plausible and probably is partially responsible for the behavior of the carbon-oxygen bond. However, this model alone does not account for the difference in the magnitude of the carbon-oxygen frequency shift with difference in potential (i.e., if the frequency shift were solely due to the withdrawing/donating character of the carbon-platinum, the Stark tuning rate would remain the same in different solutions.)

3.3 Electrochemical Double Layer

The second model, and the one on which the hypothesis of this research was based, concerns the theory that the double layer behaves like a parallel-plate capacitor. A diagram of the double layer is shown in Figure 1 [14]. In this research, this layer of adsorbed molecules was replaced with carbon monoxide, both to serve as a probe and to provide a consistent layer across different solvent-electrolyte systems. (Figure 10). Because of the resemblance of this model to a parallel-plate capacitor, the behavior of the double layer is often explained in terms of the laws governing a capacitor [42].

A parallel-plate capacitor is made up of two plates of opposite but equal charge at a given distance from each other. Capacitance is defined as [43]

$$C = \frac{eA}{4\pi d}$$

where e is the dielectric constant of the medium (including adsorbed material), A is the plate surface area, and d is the distance between the two plates. In the electrochemical double layer, the electrode and the OHP form the two plates [44]. The strength of the electric field between the plates is dependent on three factors; the charge on the plates, the distance between the plates, and the dielectric constant of the substance(s) between the plates. The vibrational frequency of the carbon-oxygen bond in adsorbed carbon monoxide is very sensitive to changes in the electric field strength and has been used to study the changes in the electric field when changes are made in these factors.

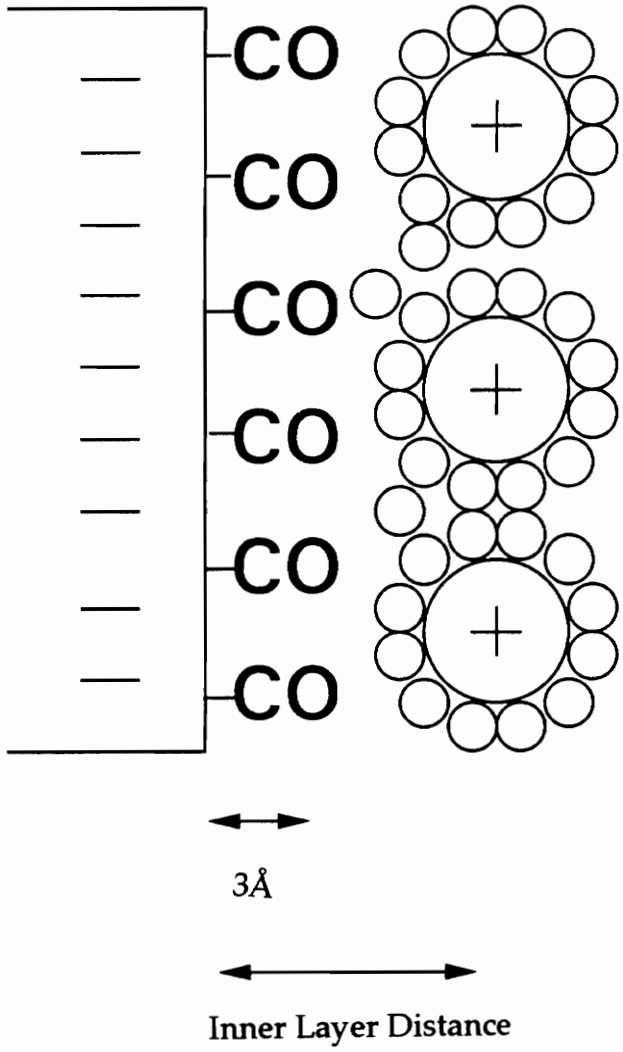


Figure 10 Diagram of Electrode with Adsorbed CO

3.4 Electrochemical Stark Effect

For a given adsorbate, the Stark tuning rate varies as a function of the electric field and the applied potential

$$\text{Stark tuning rate} = \partial = \frac{dv}{dE}$$

Since by the definition of capacitance there is also a linear relationship between the applied potential and electric field,

$$\frac{dE}{dV} = \frac{C}{e}$$

one can combine these equations to give

$$\partial = \frac{dv}{dE}\frac{C}{e}$$

If the composition of the double layer can be kept constant (that is, the adsorbate coverage and solvation of the double layer throughout both the IHP and OHP are kept constant) then the measurable tuning rate (∂) should be constant throughout [20].

3.5 Predictions based on Capacitor Model

When the solvent is changed, two of the three factors that determine the electric field in a capacitor are changed, the dielectric constant and the distance between the plates (because the size of the solvated cations are changed.) A correlation between bulk dielectric constant and tuning rate has been found when n-alcohols were utilized as solvent [17]. Because the carbon monoxide itself contributes to the capacitance (or dielectric constant), it is difficult to make a quantitative prediction; however, one could identify trends.

As shown in Table 1 [45], the bulk dielectric constant of acetonitrile and DMF are approximately equal, while water is circa twice this value. Because capacitance is inversely proportional to the dielectric constant between the plates, one would expect, based on this information, that the tuning rate for water would be much less than that for acetonitrile and DMF.

If the solvated cation size is considered, the opposite effect is predicted. The size of solvated cations was predicted based on the Stokes radii [46,47]. This calculation is based on the limiting conductivity for the ions as a measure of ionic transport. The values determined for each of these ions are shown in Table 2. When the Stokes radius is added to the distance from the oxygen to the platinum atom (about 3Å), one has an estimate of the distance d between the positive and negative plates. It should be noted that the Stokes radii are, at best, estimates of the actual cation size, and that this calculation does not allow for the possibility of additional solvent ions (not in a particular solvation sphere) that may be

Table 1

Solvent Dielectric Constants [45]

Water	78.54
Acetonitrile	37.5
DMF	36.7

Table 2

Solvated Radii

(Stokes radius calculation)

Cation	Solvated radius (in Å)		
	Water	Acetonitrile	DMF
Lithium	2.38	3.43	4.12
Sodium	1.84	3.09	3.45
Tetraethyl ammonium	1.61	2.80	2.89

sandwiched between the plates. In addition, if any solvent is adsorbed to the electrode distance, this could affect the platinum-oxygen distance.

In every electrolyte the distance d is much less in aqueous solution than in the other two solvents. As mentioned, the reduction of d results in an increased change in electric field with changing charge on the plates; water would then have a greater Stark tuning rate than the other two solvents. Predictions based on these two factors are then inconclusive, except that in the case of both the dielectric constant and the cation size, there is no appreciable difference between the two organic solvents.

3.6 Gouy-Chapman-Stern Model [48]

The double layer is not a perfect capacitor, in that the plate defined by the OHP is not a distinct plane as in a capacitor. Due to the finite volume available for solvated ions to crowd next to the inner plane, the plane defined as the OHP immediately next to the electrode does not completely balance the charge on the electrode. Because of this, there is an excess of cations outside the outer plane. The charge of these cations is referred to as the diffuse charge.

The Guoy-Chapman-Stern model states that the total capacitance of the double layer is the combined capacitance of two capacitors in series. The first is the capacitor made up of the outer Helmholtz plane and the electrode (as in the simple capacitance model) and the second is the capacitor with the positive plate made up of the diffuse charge.

The effect of this model is that the outer plane does not account for the entire balancing charge of the cationic plate, and a portion of this charge is distributed beyond the outer Helmholtz plane. However, because of the strong forces attracting the cations, the differences between the two models are very small. The simple capacitance model has been very successful when predicting the behavior of the Stark tuning rate when electrolytes of various sizes are used in the same solvent [18]. The largest flaw in both of these models is the lack of accounting for the increased organization of solvent molecules when under the influence of a local electric field and in a solvation sphere.

Chapter 4

Results and Discussion

4.1 High Coverage Data

The data for the high coverage of carbon monoxide is shown in Table 3. Representative plots for each solvent are shown in Figures 11-13. To first examine the tetraethylammonium ion (as the cation experiencing the least solvation), there is no difference between the tuning rate in water and acetonitrile. However, there is a large difference (tested at the 95% level) between the tuning rate in DMF and the other two solvents. This discrepancy between DMF and the other solvents occurs with all three electrolytes.

One possible explanation for this behavior is that the bulk dielectric constant is not reduced proportionally in the presence of an electric field. For instance, the dielectric constants of water and acetonitrile could change drastically while the dielectric constant of DMF was more stable in an electric field.

The DMF data raises another point. It has been suggested in the literature that the Stark tuning rate has two possible values, the "aqueous" value and the "organic" value (respectively 22 and 30 cm^{-1}/V) [24,25]. Perhaps because the organic solvents used happened to have similar Stark tuning rates, the impression has been made that Stark tuning rates must be in this range. As shown in Table 4, the Stark tuning rate for DMF does go below 17 cm^{-1}/V with one ion. It is suggested by the data shown that this idea of two "basic" tuning rates be reexamined.

Table 3

High Coverage Data

(in $cm^{-1}/V \pm$ standard deviation)

	Solvent		
Cation	Water	Acetonitrile	DMF
Sodium	23.7 ± 0.8	26.1 ± 0.2	18.1 ± 0.8
Lithium	22.3 ± 0.5	25.8 ± 0.2	16.2 ± 0.8
Tetraethyl ammonium	24.3 ± 0.5	23.5 ± 0.8	19.8 ± 0.2

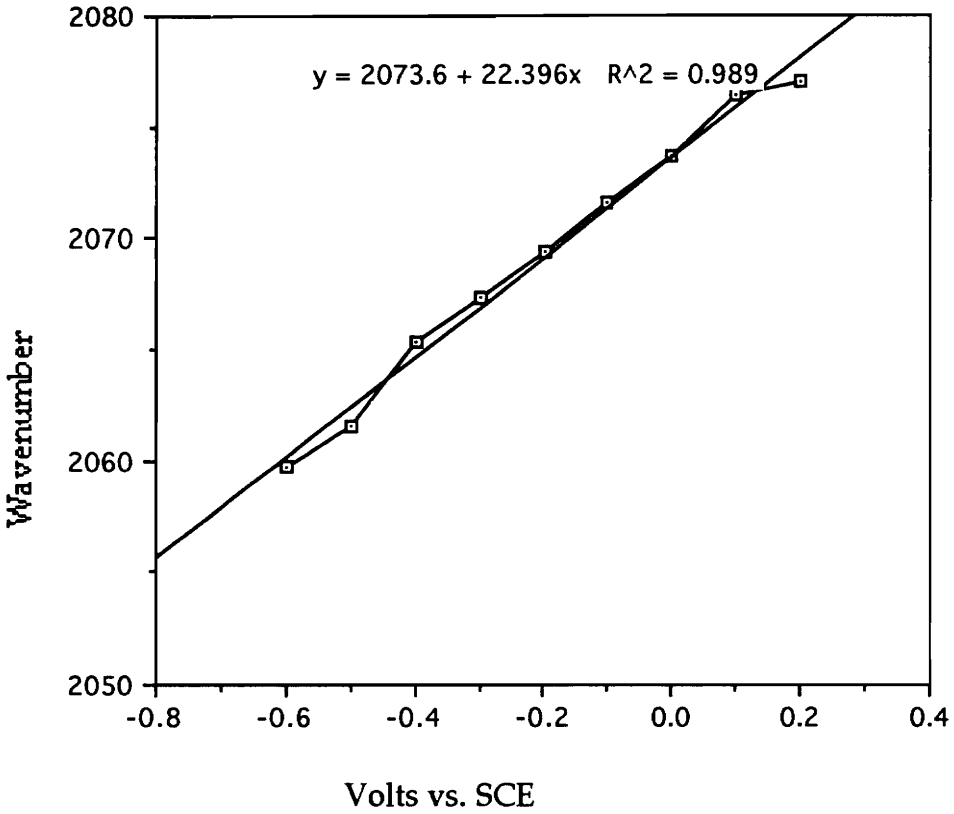


Figure 11 Plot of Peak Position vs. Electrode Potential in 0.1M Lithium Perchlorate in Water (High Coverage)

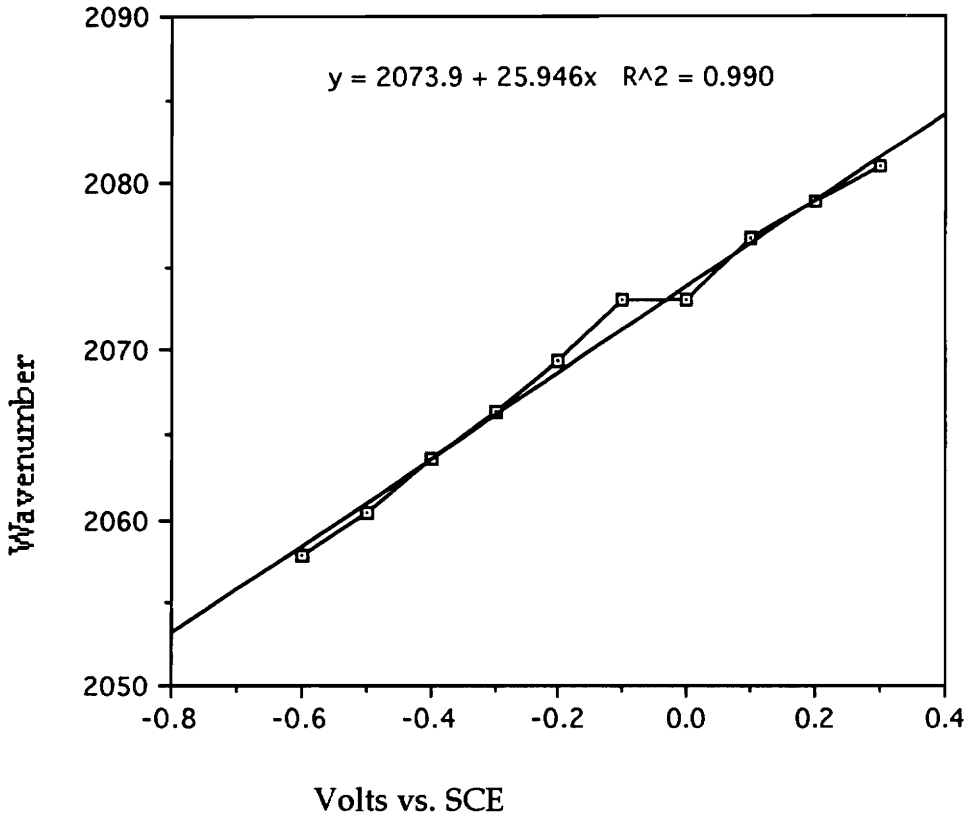


Figure 12 Plot of Peak Position vs. Electrode Potential in 0.1M Lithium Perchlorate in Acetonitrile (High Coverage)

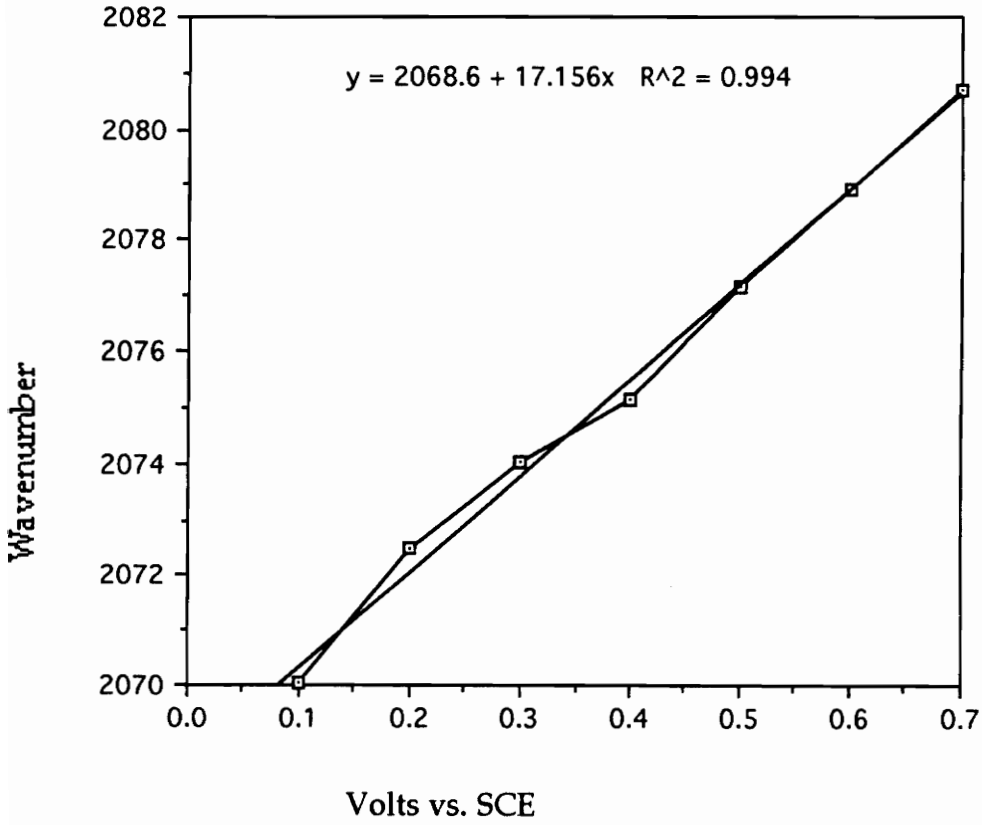


Figure 13 Plot of Peak Position vs. Electrode Potential in 0.1M Lithium Perchlorate in DMF (High Coverage)

As discussed in the introduction, there is a sharp change in the Stark tuning rate with a gradual change in solvent composition. This suggests that when mixtures of solvents are used, the bulk solvent composition is not wholly indicative of the solvent composition at the interface. For example, in Pons' [24] papers on the behavior in methanol/water mixtures, the Stark tuning rate shifts at a composition of about 25% water/75% methanol from 22 to 30 cm^{-1}/V. It was suggested that this result corresponds to a reorganization of the solvation spheres at this composition. It is also interesting that with only 25% water, the tuning rate is virtually identical to that found for pure water. Many of these studies were done using the decomposition of vanadium hexacarbonyl. The method of partial oxidation of methanol also requires trace amounts of water to serve as the oxygen source for the reaction to occur. With these two methods, the solvent is likely not completely dry.

To clarify the role solvent plays at the interface, more extensive studies should be done with rigorous attention to the purity of solvent. The carbon monoxide should be adsorbed using a method (such as bubbling carbon monoxide gas into the solution) that does not require contamination by methanol or water. It is evident from past research and the work discussed in this thesis that the role of solvent at the interface is more complex than originally thought. In addition, the change in the dielectric constant while under the influence of an electric field should be studied. At present, it is not known whether the dielectric reduces by some factor constant for all solvents. It is suggested by this research that 1) the bulk dielectric constant can no longer be

considered a measure of the dielectric constant when in an electric field and 2) the dielectric constant of a solvent may not be a good approximation of the properties of the interface.

Although the Stark tuning rates for the tetraethylammonium ion in water and acetonitrile are the same, there is a difference between the two solvents with both the sodium and lithium ion. One would expect solvent to have a greater effect with these ions because they are much more highly solvated, due to their small size and high charge density. The tuning rate for both the ions in water is lower than in acetonitrile.

4.2 Partial Coverage

In past research on solvent effect, often the solvent effect has been minimal. This has been attributed to the lack of ability for the solvent to penetrate the IHP when a high coverage of adsorbate was present. However, a correlation between bulk dielectric strength and Stark tuning rate has been found [16] when n-alcohols were utilized as solvent at low coverages. To determine if a similar correlation could be made between the dielectric constants of solvents used in this research, experiments were conducted at low adsorbate coverages. The partial coverage data is shown in Table 4. Representative plots for both solvents used are shown in Figures 14 and 15. No partial coverage data was taken for DMF because of the difficulty of keeping a partial monolayer of carbon monoxide on the electrode in DMF.

For every electrolyte, the tuning rate went down when the solvent was changed from water to acetonitrile. This may attributed to the changing size of the solvated cation, but it is unclear why this effect would be observable only with a partial coverage of adsorbate. This data supports the hypothesis that the dielectric constant of solvent in a double layer cannot be determined using the bulk dielectric constant. Although there would be much more solvent in a partial monolayer, the Stark tuning rates cannot be explained by using the bulk dielectric constant. Because the dielectric constant is higher for water than for acetonitrile, the Stark tuning rate would be expected to decrease in water. The opposite effect is observed.

Table 4

Partial Coverage Data

(in $cm^{-1}/V \pm$ standard deviation)

	Solvent	
Cation	Water	Acetonitrile
Sodium	30 ± 1	26 ± 1
Lithium	26.2 ± 0.2	22.0 ± 0.5
Tetraethyl ammonium	27 ± 1	22 ± 1

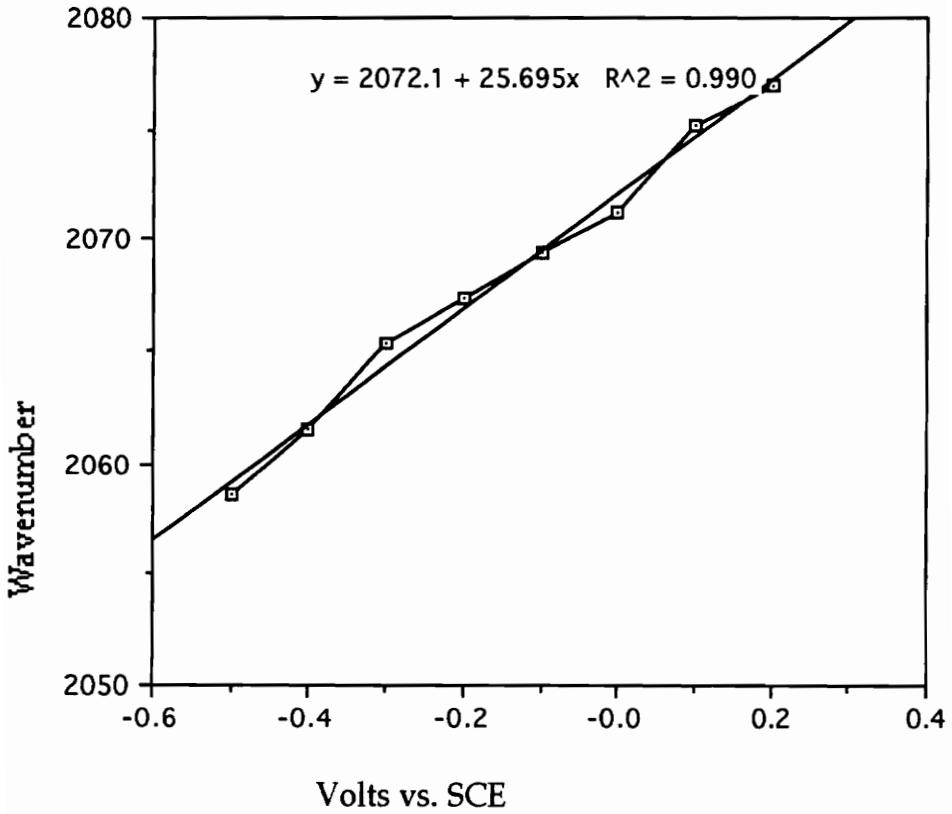


Figure 14 Plot of Peak Position vs. Electrode Potential in 0.1M Lithium Perchlorate in Water (Low Coverage)

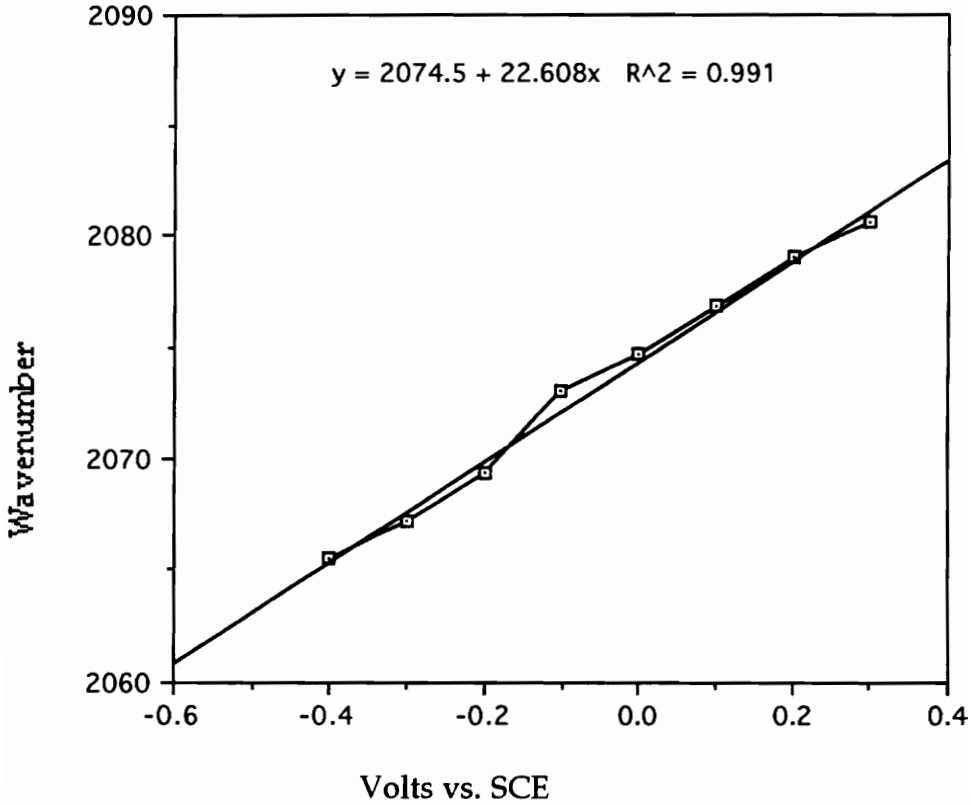


Figure 15 Plot of Peak Position vs. Electrode Potential in 0.1M Lithium Perchlorate in Acetonitrile (Low Coverage)

There are two possible explanations for these results. The first is the previously mentioned theory that the change in dielectric constant of a solvent when an electric field is applied is unique for each solvent and is dependent on the reorganization of the solvent molecules. The second explanation for the lower tuning rate in acetonitrile involves the adsorption at the electrode. When only a partial coverage of carbon monoxide is on the electrode, the free sites at the electrode are filled with other molecules and ions. The most common adsorbates are solvent molecules, simply because they are the most numerous. The acetonitrile molecule is larger than the water molecule. This could change the position of the inner Helmholtz plane and effectively "push" the solvated cations further from the electrode and increasing the distance d between the two charged plates.

4.3 Comparison of High and Low Coverage

There is no consistent pattern in the Stark tuning rates of high and low coverages, when the cation and solvent is kept constant. The precise reasons behind these differences are not understood, and further research is needed in this area.

A large portion of the total capacitance in the double layer is from the adsorbed carbon monoxide itself. When some of the carbon monoxide is replaced with solvent molecules (or ions), the capacitance and inner Helmholtz plane of the double layer may change. One area that needs further study is the effect carbon monoxide has on the double layer, so that the effect of the other factors can be studied more thoroughly.

The capacitance of a double layer can be determined by the Faradaic current. This is a fairly simple electrochemical measurement to make. If the capacitance of the double layer with the adsorbed carbon monoxide in the different environments were found and compared to the capacitance of the double layer with no adsorbate, this would yield two things. The first would be the amount of dielectric strength (or capacitance) that the adsorbate itself has. In this way, the experiments with adsorbed carbon monoxide would yield more information about the double layer itself, since the effect of the adsorbate would be known. The second reason for doing this experiment would be a confirmation of the validity of the Stark tuning rate as a measure of the capacitance of the double layer. It is assumed that a low tuning rate means that either the dielectric strength is very high or that the distance between the electrode surface and the

outer Helmholtz plane is relatively great. The measure of the capacitance electrochemically would confirm these assumptions. Also, more would be known about the differences between partial and full monolayers. These studies were attempted by the author numerous times, and the capacitance does increase when carbon monoxide is adsorbed to the surface (Figure 16). However, reproducibility of these experiments was difficult so quantitative values are not available.

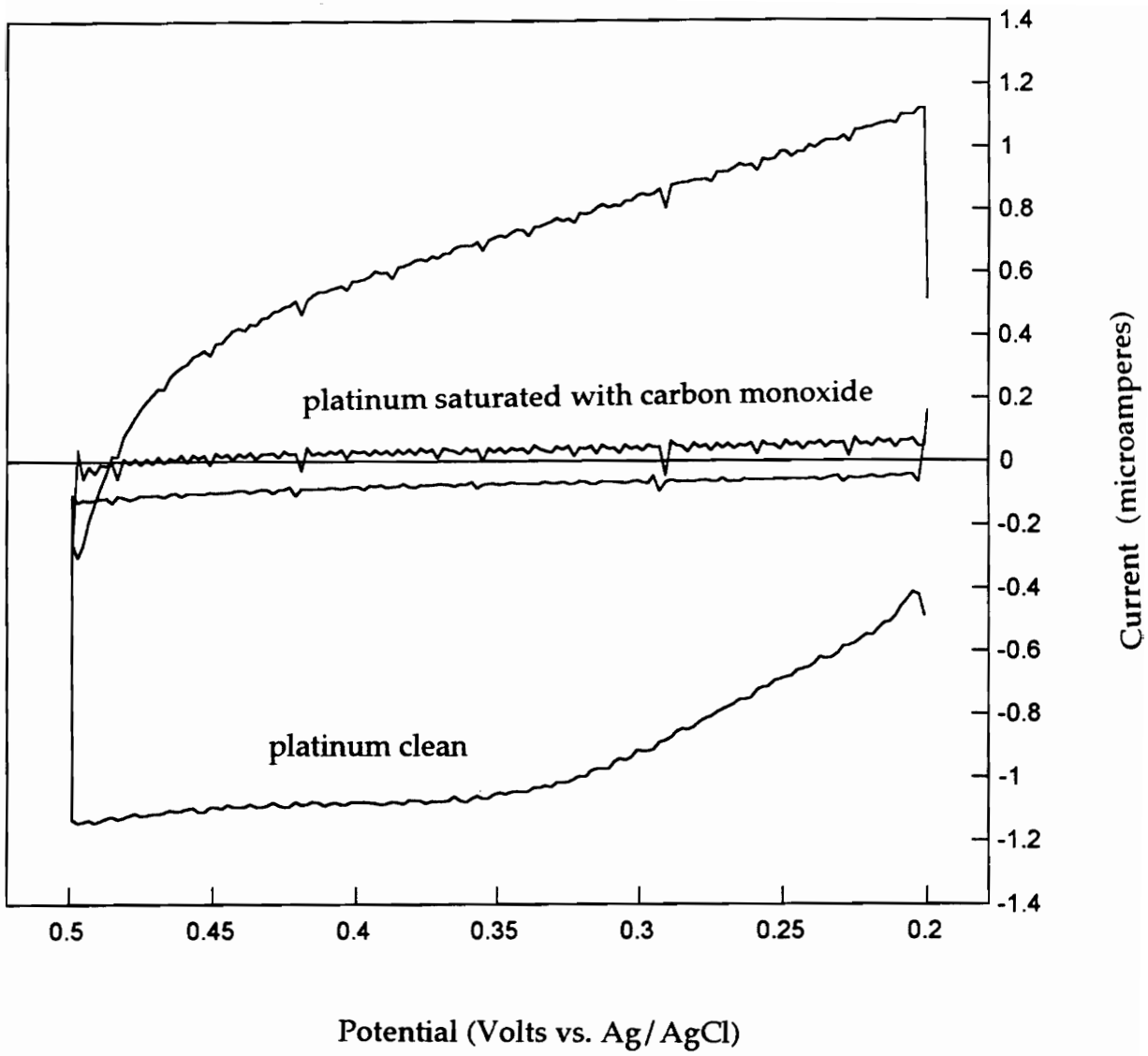


Figure 16 Cyclic Voltammetry of Clean and Saturated Platinum Electrode

Chapter 5

Summary

This research was undertaken for two major reasons; to find out more about the behavior of adsorbed carbon monoxide in various environments, and to apply these findings to the double layer itself. The double layer has been modeled as a parallel-plate capacitor for some time. This concept is certainly useful and has helped to clarify the behavior of the interface. However, this model has several limitations. The dielectric constant of a solvent cannot be used as an indicator of its dielectric strength when in a local electric field. This change in dielectric strength does not appear to correlate to the dielectric constant. Previous to this work, the Stark tuning rates of carbon monoxide in various solvents were often referred to as "organic" or "aqueous". DMF, an organic solvent, does not exhibit a tuning rate that agrees with the "organic" value. It is suggested that this convention of two basic tuning rates for all solvents should not be used anymore.

As mentioned, this work should be continued by a study of the behavior of adsorbed carbon monoxide in various solvents, with rigorous attention to purity of solvent and electrolyte to prevent contamination of the solvation spheres by water. A method of adsorbing carbon monoxide that does not require addition of traces of water should be used. The determination of capacitance of the double layer with and without adsorbed carbon monoxide would also help find how carbon monoxide affects the double layer, and how different environments affect the capacitance of the double layer. This research

would also determine if the assumption that the tuning rate can be used as an indicator of the double layer's behavior as a parallel-plate capacitor is valid.

References

1. J. Giner, *Electrochim. Acta*, **9** (1964) 63.

2. A. Capon and R. Parsons, *Electroanal. Chem. Interfac. Electrochem.*, **45** (1973) 205.

3. S. M. Dana, M. E. Jablonski and M. R. Anderson, *Anal. Chem.*, **65** (1993) 1120.

4. J. K. Foley and S. Pons, *Analytical Chemistry*, **56** (1985) 945A.

5. D. L. Allara, S. V. Atre, C. A. Elliger and R. G. Snyder, *J. Am. Chem. Soc.*, **113** (1991) 1852.

6. D. L. Allara, Z. Wang and C. G. Pantano, *J. Non-Cryst. Solids*, **120** (1990) 93.

7. S. Juanto, B. Beden, F. Hahn, J.-M. Leger and C. Lamy, *J. Electroanal. Chem.*, **237** (1987) 119.

8. P. Gao, S.-C. Chang, Z. Zhou and M. J. Weaver, *J. Electroanal. Chem.*, **272** (1989) 161.

9. A. Bewick, K. Kunimatsu and S. Pons, *Electrochim. Acta.*, **25** (1980) 465.

10. A. Bewick and K. Kunimasu, *Surf. Sci.*, **101** (1980) 131.

11. D. C. Corrigan and M. J. Weaver, *J. Electroanal. Chem.*, **241** (1988) 143.

12. T. Iwasita and F. C. Nart, *J. Electroanal. Chem.*, **317** (1991) 291.

13. B. Beden, S. Juanto, J.M. Leger and C. Lamy, *J. Electroanal. Chem.*, **238** (1987) 323.

14. A. J. Bard and L. R. Faulkner, *Electroanalytical Methods*, Wiley, New York, 1980, p9.

15. S.-C. Chang, X. Jiang, J. D. Roth and M. J. Weaver, *J. Phys. Chem.*, **95** (1991) 5378.

16. M. R. Anderson, D. Blackwood, T. G. Richmond and S. Pons, *J. Electroanal. Chem.*, **256** (1988) 397.

17. A. E. Russell, D. Blackwood, M. R. Anderson and S. Pons, *J. Electroanal. Chem.*, **304** (1991) 219.

18. M. R. Anderson and J. Huang, *J. Electroanal. Chem.*, **318** (1991) 335.

19. J. W. Russell, M. Severnson, K. Scanlon, J. Overend and A. Bewick, *J. Phys. Chem.*, **87** (1983) 293.

20. D. K. Lambert, *J.Chem.Phys.*, **89** (1988) 3847.

21. D. K. Lambert, *Solid State Commun.*, **51** (1984) 297.

22. D. K. Lambert, *Phys. Rev. Lett.*, **50** (1983) 2106.

23. D. K. Lambert, *J. Vac. Sci. Technol. B*, **3** (1985) 1479.

24. A. B. Anderson, *J. Electroanal. Chem.*, **280** (1990) 37.

25. A. E. Russell, S. Pons and M. R. Anderson, *Chem. Phys.* **141** (1990) 41.

26. A. Bewick and S. Pons in R. E. Hester and R. Clark (Eds.), *Advances in Infrared and Raman Spectroscopy*, Vol. 12, Heyden, London, 1984, p5.

27. M. R. Anderson, *Personal Communication.*

28. P. R. Griffiths and J. A. deHaseth, *Fourier Transform Infrared Spectrometry*, Wiley, New York, 1986, p255.

29. A. J. Bard and L. R. Faulkner, *Electroanalytical Methods*, Wiley, New York, 1980, p585.

30. J. K. Foley, C. Korzeniewski, J. Daschbach, and S. Pons in A. J. Bard (Ed.), *Electroanalytical Chemistry*, Vol. 14, Wiley, New York, 1986, p316.

31. H. Kawashima, Y. Ikezawa and T. Takamura, *J. Electroanal. Chem.*, **317** (1991) 257.

32. K. Ashley, M. G. Samant, H. Seki and M. R. Philpott, *J. Electroanal. Chem.*, **270** (1989) 349.

33. J. W. Russell, M. Severson, K. Scanlon, J. Overend and A. Bewick, *J. Phys. Chem.*, **87** (1983) 293.

34. J. D. Roth, S. Chang and M. J. Weaver, *J. Electroanal. Chem.*, **288** (1990) 285.

35. A. M. Bond and R. Colton, *Inorg. Chem.*, **15** (1976) 2036.

36. Q. Shi, T. G. Richmond, W. C. Trogler and F. Basalo, *J. Am. Chem. Soc.*, **106** (1984) 71.

37. T. G. Richmond, Q. Shi, W. C. Trogler and F. Basalo, *J. Am. Chem. Soc.*, **106** (1984) 76.

38. M. R. Anderson, D. Blackwood and S. Pons, *J. Electroanal. Chem.*, **256** (1988) 387.

39. S. P. Mehandru and A. B. Anderson, *J. Phys. Chem.*, **93** (1989) 2044.

40. J. G. Love and A. J. McQuillan, *J. Electroanal. Chem.*, **274** (1989) 263.

41. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Ed., Wiley, New York, 1988, p59.

42. A. J. Bard and L. R. Faulkner, *Electroanalytical Methods*, Wiley, New York, 1980, p500.

43. *CRC Handbook of Chemistry and Physics*, 1st Student Ed. CRC Press, Boca Raton, 1988, F-44.

44. A. J. Bard and L. R. Faulkner, *Electroanalytical Methods*, Wiley, New York, 1980, Ch. 1.

45. *CRC Handbook of Chemistry and Physics*, 67th Ed. CRC Press, Boca Raton, 1986, E-50-52.

46. N. Matsuura, K. Unemoto and Y. Takeda, *Bull. Chem. Soc. Jpn.*, **48** (1975) 2253.

47. B. Kratochvil and H. L. Yeager, *Fortschr. Chem. Forsch.*, **27** (1972) 1.

48. A. J. Bard and L. R. Faulkner, *Electroanalytical Methods*, Wiley, New York, 1980, Ch. 12.

Vita

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