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Publication Date
1985-12-01

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(*M.S. Thesis)

December 1985

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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LBL-20680

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This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098 with the Lawrence Berkeley Laboratory.

Analysis of Trace Water Contamination in Propylene Carbonate Electrolytes

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Abstract

The measurement and removal of trace water contamination in organic electrolytes are of great importance in nonaqueous electrochemistry. This work was aimed at evaluating an electrochemical method for determining ppm levels of water in propylene carbonate electrolytes. Solutions of 0.5M KPF_6 in PC were prepared using solvent which had been vacuum distilled and dried with Na/K alloy or molecular sieves. Solution preparation and limiting current measurements were performed in a helium atmosphere from which water and oxygen were excluded.

The rate of mass transfer controlled reduction of water was measured on a rotating disk electrode, at a potential of +0.4V vs. K/K^+. From the limiting currents obtained at various rotation speeds a diffusion coefficient of 0.85×10^{-5} cm^2/sec was calculated. A gradual decrease in water concentration with time was detected under open-circuit conditions. The water content of solutions dried following the addition of KPF_6 using Na/K alloy or molecular sieves was in the range of 1-2 ppm. The water content of a solution in which the salt was added to the solvent without careful drying was above 15 ppm, indicating that the salt may be a significant source of moisture.

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Acknowledgements

First and foremost among those who deserve thanks for their help during the course of this work is my research advisor, Professor Charles Tobias. Professor Tobias has been a constant source of advice and encouragement, not to mention forbearance through the course of my research. The members of my committee were most helpful in reading and suggesting improvements in this thesis.

I owe a special debt of gratitude to Rudi Nunlist and Rich Mazzarisi of the NMR lab, for their help and advice.

Finally, I must thank my co-workers from the third floor of Gilman Hall. Without their help and support, this research would perhaps have never gotten started, and would have certainly been a lot less fun.

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098 with the Lawrence Berkeley Laboratory.

I. Introduction and Literature Review

Propylene carbonate (PC) is one of several aprotic organic solvents which have been evaluated for use in electrochemical processes involving alkali metals. PC has been proposed as a solvent for secondary lithium batteries, either alone or mixed with another dipolar aprotic solvent, and is currently used in primary lithium batteries . The properties of PC which are of importance for electrochemical applications include stability, a wide liquid range (m.p. −49°C, b.p. 241°C), a high dielectric constant, and the ability to ionize many inorganic salts. A process for electrodeposition of potassium in PC has been proposed in this laboratory [1]. The behavior of halogen couples in PC for use as the anodic reaction in a potassium electrodeposition process has been studied [2].

For several reasons it is necessary to produce PC electrolytes which are as free of water as possible. Water reacts vigorously with alkali metals and may contribute to the decomposition of PC. Studies of the stability of PC electrolytes could be affected by the presence of water even at the ppm level. The detection and removal of water at the ppm level is, however, a difficult problem. Water is partially miscible with PC (8% by weight), making removal of the last traces of water difficult. More importantly, few analytical methods have been shown to be suitable for the accurate determination of water water at concentrations below 20 ppm.[*]

It was the purpose of this work to investigate various methods for determining water at concentrations below 1 ppm in PC and PC-based electrolytes, and to evaluate techniques for the removal of water to below 1 ppm.

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[*] 1ppm water in PC = 6.7×10^{-5} M. All ppm are w/w.

1.2. Electrochemical Studies of Water in PC Electrolytes

The electrochemical behavior of water in nonaqueous electrolytes has been studied by others both as a means for determining water contamination and for understanding the effect of water on the other components of the system. Electrochemical reduction of water in nonaqueous systems would seem to offer a direct method of determining water content, since the standard reduction potential for water is much lower than that of potassium or lithium. Dey [3] studied the reduction of water at high concentrations (0.1-2M) in $LiClO_4$/PC electrolytes using voltammetry and chronopotentiometry. The reduction of water was found to take place at a potential of -1.5 to -2.5V vs. an aqueous calomel reference. Dey concluded also that the water molecules interacted strongly with the lithium cation, reducing the activity of water at lower concentrations.

Burrows and Kirkland [4] studied the reduction of water in the same system at lower concentrations (20-500 ppm, ~0.01-0.1M). In voltammetric experiments the anodic and cathodic peaks for water appeared at +1.3 and +2V vs. Li/Li^+, which is in the same potential range vs. SCE as found by Dey et. al. Chronopotentiometric results indicated that a porous, insoluble layer of LiOH formed on the electrode surface, which had the effect of partially blocking the electrode.

Jansta, Dousek, and Riha [5,6,7] studied the reduction of water in 0.5M KPF_6 electrolyte which had been dried in a vacuum line system using liquid Na/K alloy. This technique allowed them to start with an electrolyte which was completely free of protonated impurities, and to study the effect of added water by mixing an electrolyte of known water content with the driest solution. Using single cathodic sweeps at a vibrating platinum wire, they observed a peak at 0.5 V vs K/K^+ (-2.8V vs. SCE), the height of which responded to water concentration. At the lowest levels of water, from 0 to 20 ppm, the current increased with increasing water concentration. At higher levels of water the current leveled off, apparently due to blockage of the electrode surface by insoluble reaction products. The blocking layer included both KOH and potassium glycolate, a product of the decomposition of PC. Unlike the reaction studied by Dey et. al. and Burrows and Kirkland, this reaction was found to be irreversible. The height of this cathodic peak was used to estimate the water content of the solution. Water levels as low as 0.1 ppm could be detected. The reproducibility was poor below 20 ppm, however, and because the surface of the electrode was not planar, quantitative results could not be compared with theoretical expectations.

Similar techniques were used by Law [1] to study water in 0.5M KPF_6 in PC and 0.5M $KAlCl_4$ in PC. Law studied the response of a cathodic current peak at +0.5 V vs. K/K^+ in the KPF_6 electrolyte. By cycling the voltage at a platinum screen electrode from +0.1 to +2V vs. a potassium reference and measuring the change in peak current upon the addition of water, Law found that the peak current was proportional to the amount of water added in the range of 0-3 ppm water. The current peak disappeared slowly with time, indicating that water was being removed faster than was possible electrochemically. No clear reason was given for this behavior. The reduction of water was not observed in the $KAlCl_4$ system. The anodic dissolution of a stainless steel electrode, related to the formation of HCl in the system due to the presence of water, was noticed. As in the Jansta work, the quantitative results could not be compared with theory.

Direct comparison of these studies is difficult due to the different experimental approaches. Comparing the potentials given for water reduction is especially difficult where different reference electrodes are used. For example, potentials stated as vs. the aqueous calomel reference may be affected by an unknown junction potential. Still, several comments can be made about the studies reviewed here. The reduction potentials for water were more negative than would be expected. In the potassium electrolyte studies water reduction was found to take place at a potential of +0.5 to +1.0V vs. potassium reduction. For comparison, in aqueous solution the standard potentials for the two reactions (water reduction and alcohol deposition), are -0.41 and -2.924V respectively. In the Burrows & Kirkland study, the potential for water reduction was in the range of +1.5V vs. Li/Li^+. The standard potential for lithium reduction in aqueous solution is -3.045V. Thus the potential for water reduction in PC electrolytes is much closer to the alkali metal reduction potentials than in aqueous solution, especially in the KPF_6 solution studied by Jansta et. al and Law.

The interactions of trace water with both the solvent and the ions in the electolyte could affect its reduction potential. This effect has not been studied. Cogley et. al. [8] did report on the selective solvation of ions by water in PC. Molal association constants for water and the more commonly studied ions were determined using proton magnetic resonance measurements. Among the cations studied water was found to have a far stronger affinity for Li+ than for K+. In potassium electrolytes, water has no preference for the cation over the solvent. although water did not associate with most anions considered, an unusually strong affinity for the chloride anion was found.

In each of the above studies it was found that water, even in trace concentrations, could have a drastic effect on alkali metal deposition. Jansta found, for example, that 10 ppm levels of water could block the deposition of potassium at a stationary electrode. Reaction mechanisms proposed by Jansta in the same study indicate that water plays a role in the decomposition of propylene carbonate at a potassium cathode.

Water also seems to be involved in the decomposition of PC in the presence of halogens. Studies of the stability of PC in the presence of chlorine by Yu et. al. [9] and Hanson [2] showed that levels of water as low as 15 ppm increase the rate of decomposition of the solvent. Increases in the amounts of decomposition products such as propylene glycol, formaldehyde, and allyl alcohol were found using gas chromatography after contacting PC with chlorine gas. The decomposition was more extensive in PC containing higher concentrations of water.

1.3. Trace detection using the Karl-Fischer Method

The most important technique for determining water in organic solvents is the Karl Fischer titration [10]. The method dates from 1936 and is used for determining water concentrations from tens of ppm to large percentages. The reagent consists of iodine and sulfur dioxide, both complexed with pyridine, usually in methanol as the solvent. Typically sulfur dioxide and pyridine are present in excess, so that iodine is the limiting reactant. The reaction involves two steps with only the first step involving water:

$$C_5H_5N{:}I_2 + C_5H_5{:}SO_2 + C_5H_5N + H_2O = 2C_5H_5N{:}HI + C_5H_5N{:}SO_3$$

The second step completes the reaction:

$$C_5H_5N{:}SO_3 + CH_3OH = C_5H_5N(H)SO_4CH_3$$

In trace determination the iodine is generated coulometrically from the iodide-pyridine complex in spent reagent. The endpoint of the titration is determined either coulometrically or potentiometrically. In the coulometric endpoint method, current is measured across a pair of electrodes in a separate circuit from that used to generate iodine. When all of the water in the system has been titrated, free iodine depolarizes the electrodes and a current flows across the circuit. This is the method on which most commercial titrators for trace determination are based. A coulometric titrator available from Fisher Scientific, which uses coulometric generation of iodine and coulometric endpoint detection, is listed as having a detection limit of 10 ±5μg[*]. In PC, a sample size of at least 10 ml would be needed to determine 1 ppm water in a system such as the Fisher Scientific titrator.

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[*] Fisher Scientific 1986 catalog, Allied Corp.

Potentiometric determination of the endpoint was found by Cedergren [11] to give a more precise measurement for very small amounts of water. The potential increase resulting from the presence of iodine at the end of the titration was measured vs. a reference electrode in spent reagent, separated from the main compartment by a glass wool plug. The potential measured is that of the iodine- iodide complex couple.

Using this method Cedergren was able to determine amounts of water as small as .07 μg in a 0.4 μl sample containing 180 ppm water. However, for very low concentrations, the sample would have to be large enough to significantly alter the concentrations of the reactants and thus the endpoint potential. A correction in the titrated value of .001 mg of water per ml of solution was required for potentiometric titrations. The equivalent value for coulometric titrations was .004mg/ml. These values correspond to approximately 1 and 4 ppm water. The effect of this correction on the accuracy of determinations of water at low ppm levels was not reported.

The Karl Fischer titration is an absolute method for determining water. It is often assumed in trace determination studies such as that of Cedergren that the minimum detectable amount of water could be determined in much larger samples. This assumption has not been tested. The ability of the method to determine low ppm concentrations of water is doubtful. Probably the method is not suitable for analysis of water below 10 pppm.

1.4. Trace Determination Methods for Water in PC

In most electrochemical research with propylene carbonate, including studies previously reported in this lab [1,2], the analytical procedure for determination of water and organic contaminants in the solvent follows the gas chromatographic method described by Jasinski and Kirkland [12] and summarized below. This method is still the standard for analyzing PC; no major improvements have been reported since. A two-foot Poropak Q column was used by Jasinski et. al. to separate the contaminants in PC with dry helium as the carrier gas. Water was detected using a thermal conductivity cell and organic components were detected with a flame ionization detector. The detection limit for water in a 40 μl sample was 1.5 ppm; the detection limits for propylene oxide and propylene glycol, the two most common impurities, were .05 and .5 ppm, respectively. Determination of the 1,3 and 1,2 propylene glycols was made more difficult by the decomposition of the solvent in the injector port. To avoid decomposition, which gives spuriously high readings in propylene oxide and glycol content, the temperature of the injector port was lowered to 130°C. This resulted in lower peak heights and a loss of sensitivity for detection of organic contaminants.

While gas chromatography is the most sensitive method for determining water in PC there are several important limitations to its use. GC cannot be used to analyze salt solutions because the salts are not volatile and plug up the injector port. In addition, PC in the presence of salts decomposes in the injector port, giving spurious peaks. Since most salts, including such commonly used supporting electrolytes as $LiClO_4$ and KPF_6 are known to contribute tens of ppm of water to solutions even after drying the salts under vacuum, a means of evaluating the water content of PC electrolytes would be more relevant than the measurement of water in PC alone. Furthermore, GC results tend to be erratic. If the injector port is not enclosed in a drybox water contamination from the atmosphere causes significant contamination of the sample during handling and injection.

Several studies of the feasibility of using infrared spectroscopy for trace water determination have been published. Jasinski and Carroll [13] were able to determine water at levels above 20 ppm in pure PC by measuring the absorbance band of water at 1.9 μm. PC has a weak overlapping absorbance at 1.87 μm, so it was necessary to measure a differential spectrum against pure PC. This method of analysis gave satisfactory results for determining 20-100 ppm levels of water in pure PC. The analysis of $LiClO_4$ solutions was more complicated. A shift in the absorption maximum for water and a decrease in its extinction coefficient were noted in the presence of 0.5M $LiClO_4$. These effects were more pronounced in the presence of larger salt concentrations. The interaction between water and lithium cations apparently caused this effect.

Since the Jasinski and Carroll study (1968), Fourier transform infrared spectrophotometers have become available, offering greater signal-to-noise ratio and thus greater sensetivity for quantitative determination. FTIR analysis for water in PC was studied in this laboratory by Hanson [2]. As in the Jasinski study, the absorption band at 1.9 μm was measured; the instrument automatically subtracted the spectrum of pure PC. The lower limit of detection was found to be 10 ppm in pure PC and somewhat higher in salt solutions. The limitation on trace determination appears to be the overlap of the PC absorbance.

A method for determining trace water in organic electrolytes using UV-visible spectroscopy was studied by Thompson et. al. [14]. A solution of lead tetraacetate in benzene was added to the sample. Lead tetraacetate reacts with the water, producing lead dioxide and acetic acid:

$$Pb(OAc)_4 + 2H_2O = 4HOAc + PbO_2$$

Lead dioxide is brown in color and small quantities will remain well dispersed in solution. An absorbance at 405 nm was measured. The method was calibrated by standard additions of water in methanol. The absorbance was linear in the 10-50 ppm range and a detection limit of 5ppm was estimated. However, lead tetraacetate is a powerful oxidizing agent which reacts quantitatively with methanol [15]. The absorbance measured by Thompson et. al. could have been that of the methanol reaction product, which is yellow. This problem was not addressed in the Thompson study.

1.5. Drying of Propylene Carbonate and Propylene Carbonate Electrolytes

The most widely used technique for purifying PC is vacuum distillation, usually preceded by drying over molecular sieves. The process described by Jasinski and Kirkland [12] has been followed in most propylene carbonate studies: distillation at a vacuum of 0.5-1 mm Hg, in a stream of dry helium, with a kettle temperature of 110° C and a head temperature of 72° C. Distillation, followed by bubbling with dry helium for several days, was effective for removing water and several organic impurities found in commercial grade PC: 1,2 and 1,3 propylene glycol, propionaldehyde, propylene oxide, allyl alcohol, and formaldehyde. The removal of the 1,2 and 1,3 glycols was found to be the most problematic. Even after redistilling, the glycol concentration leveled off at 11 ppm. Two possible explanations were given: either propylene glycol forms an azeotrope with PC during distillation, or decomposition of PC takes place at the distillation column head. Explaining the presence of glycols as being due to decomposition of PC raises a problem. Stoichiometrically one molecule of water is necessary to produce one molecule of propylene glycol from PC; the product of anhydrous decomposition is not propylene glycol but propylene oxide.

Law [1] used vacuum distillation preceded by drying over molecular sieves and alumina to reduce the water content of PC to below 2 ppm. Hanson, using the same equipment and procedures, reported purity levels of <5-15 ppm in the final product over several runs [2].

While distillation can remove most impurities from PC, the introduction of impurities with the addition of salts presents another problem. Many such salts are crystallized from water; the removal of the last traces of water from crystalline solids is difficult due to the presence of water in inclusions within the crystal structure. Pistoia, for example, found that $LiClO_4$, a commonly used supporting electrolyte, contained 0.1% water (determined by Karl- Fischer titration) after fusion at 260°C under vacuum [16]. This is enough water to increase the water content of a 0.5M solution in PC by 40 ppm.

For water introduced by the addition of supporting electrolyte, a further drying step is necessary. The most widely used desiccants are molecular sieves. Alkali metal drying is also used, in the form of lithium amalgam or liquid Na/K alloy. Drying with alkali metals, however, causes detectable solvent decomposition [5]. There is little quantitative information about the drying of electrolytes. Jansta et. al [7] claim a water content of below .01 ppm in 0.5M KPF_6/PC dried using Na/K alloy. The same solution dried with molecular sieves was estimated to contain 0.3 ppm water using the potential sweep method described above. Other information is scarce, since gas chromatography cannot be used for analyzing salt solutions and the Karl Fischer method has not been extended to low ppm concentrations.

Burfield et. al [17] described a novel method of assessing desiccant efficiency using tritium-labeled water. Known amounts of tritiated water were added to various solvents which were then dried using several commonly used desiccants. By measuring the decrease in radioactivity after drying the fraction of water removed could be determined. The efficiency of desiccants was found to vary with the solvent; in general polar solvents were more difficult to dry. Molecular sieves were found to be at least as effective as chemical desiccants (such as P_2O_5, CaH_2, Na) The ultimate dryness achieved in acetonitrile using molecular sieves was 0.6 ppm; this is several orders of magnitude greater than the lowest residual water content recorded for benzene. While this method is useful for identifying the factors which affect the drying process, it cannot detect uncontrolled contamination from other sources, such as incompletely dried glassware, which could increase the water content of an electrolyte during handling.

1.6. Summary

In summary, the major obstacle to a better understanding of the role of trace water in electrochemical reactions in PC has been the inability to determine low ppm levels of water in PC electrolytes. Very little information exists about the sources of low level moisture contamination or the best method for its removal. Gas chromatography, which is used to determine low ppm levels of water in the solvent, is not applicable to salt solutions. No spectroscopic method is commonly used for trace determination of water. The Karl Fischer titration has not been demonstrated to be effective below 10 ppm. Direct electrochemical determination of water has been studied, but not in a well-defined mass transfer situation below 20 pmm.

Because of the detrimental role attributed to water with regard to the stability of the solvent, and that of reactive metals, the efficiency of techniques for dehydration requires scrutiny. Each laboratory in which electrochemical investigations involving PC were carried out developed their own method for removing impurities. Frequently the methods employed were not adequately described. Also, the limitations of the methods used for moisture determination in the solvent, with or without the ionic solute, were not characterized.

The purpose of this study was to compare several techniques for measuring trace water content, and to evaluate water contamination in PC solutions with potassium electrolytes. Several methods of trace water determination were studied which could be used for PC electrolytes, including NMR spectroscopy, stationary electrode voltammetry, and limiting current measurements at a rotating disk electrode. Finally, the extent to which trace water was removed by such commonly used techniques as molecular sieve and alkali metal drying was evaluated.

II. Experimental

2.1. Glove Box Operation

All electrolyte and solution preparation, as well as all electrochemical measurements, were performed in an inert atmosphere glove box. The glove box was designed by Lawrence Livermore labs and is the same one used by Law [1]. Helium was constantly recirculated through a column of molecular sieves and BTS catalyst to remove oxygen, water, and organic contaminants. The column was regenerated periodically by heating in a stream of hydrogen. The moisture content of the glovebox atmosphere was below 1 ppm as measured on a CEC humidity meter.

Most materials used in the glovebox were heated in a vacuum oven to 100° C overnight or longer before being used. Paper, plastic, and other heat-sensitive materials were vacuum-dried at 60°C. Heated materials were then placed in the glovebox antechamber which was evacuated to below .01 torr before refilling with dry helium and placing the objects in the glovebox.

2.2. Solvent Preparation

Propylene carbonate 'Distilled in Glass' grade was purchased from Burdick & Jackson. This grade of PC was vacuum-distilled by B&J for use in liquid chromatography; the major organic impurity is propylene oxide, (approx. 30 ppm). The water content for each lot was determined by the company using Karl-Fischer titration; all PC used in this study had a stated water content of 20 ppm. The water content as determined in this lab using gas chromatography was between 25-35 ppm. The process for redistilling PC described by Hanson [2] was also tested; however it was felt that the Burdick & Jackson PC was suitable for electrochemical use after one of the drying steps described below. The water content of the redistilled PC along with a brief description of the process, are given in the appendix.

Sodium-potassium alloy and molecular sieves are two commonly used desiccants for organic solvents. Both were used to dry PC solutions in this study. Initially sodium-potassium drying was used because this method is capable of removing glycols and other protonated impurities as well as water. Sodium pellets (Baker Analyzed) were added to molten potassium (Alfa) in a ratio of 70/30% by weight; some working of the mixture was needed to break up the sodium pellets. The alloy was then filtered through a small hole to remove oxides prior to use.

Filtered Na/K alloy, approximately 5g per 50 ml PC, was added directly to the solvent or electrolyte to be dried. The solution was shaken periodically to expose more surface area. No gas evolution from contacting PC with the alloy was observed. Globules of the alloy collected at the top of the solution but did not coalesce. The solvent or electrolyte was left to dry for at least several days. Filtration to remove the alloy was necessary; for this purpose qualitative filter paper (Whatman #1, W&R Balston) was used. PC thus filtered was clear; solutions of electrolytes were slightly yellowish.

Drying of PC and PC solutions with molecular sieves was also studied. Type 4A and 13x molecular sieves (Linde) were pretreated by heating to 500°C under argon. Pretreated sieves were stored either in the glove box or in an evacuated desiccator.

2.3. GC Analysis

A Varian 3760 gas chromatograph was used to determine water in PC at levels greater than 5 ppm. The columns were 24" (1/4" OD) stainless steel packed with Poropak Q. A thermal conductivity detector was used to measure water. The GC was also used with the flame ionization detector (FID) to measure propylene glycol contamination in dried PC. The conditions used in GC analysis are shown in table 2.1.

Table 2.1: GC Operating Conditions

	TCD Mode	FID Mode
Inj. Temp.	130° C	130° C
Column Temp.	100° C	170° C
Det. Temp.	200° C	200° C
He flow rate	60 cc/min	60 cc/min
H_2 flow rate		60 cc/min
Air flow rate		300 cc/min
Filament Temp.	240° C	
Sample Size	10μl	2μl

Calibration for water was by standard addition. Standards in the 2-20 ppm range were prepared from more concentrated (0.1%) water solutions in the glovebox so as to avoid contamination. Water gave irregularly shaped peaks, and drifting baselines made area measurement using the integrator unreliable. Peak area measurements were made by photocopying the output trace from the strip chart recorder, cutting out the peaks, and weighing.

It was found that the column history strongly affected the calibration for water. When the column had not been used for several months the retention time for water was 5 minutes; the peaks were irregular and the baselines drifted significantly around the water peak. After the GC had been used for several weeks the retention time for water under the same conditions grew shorter, to approximately 3 minutes. The peaks were more regular, there was less baseline drift, and the peak areas increased. Two GC calibration curves are shown in fig. 2.1. Because of this phenomenon the GC was recalibrated for each analysis.

A major problem with GC analysis is that the samples are subject to contamination during handling prior to injection into the GC. To assess the possibility of contamination of PC outside the glovebox, the effect of exposing PC to atmospheric moisture was tested. It was found that PC samples opened to the atmosphere prior to GC analysis for even a few seconds were contaminated with several hundred ppm of water. For a more controlled exposure to atmosphere, test tubes of redistilled PC (8 ppm water) were placed in a pyrex flask which was sealed while inside the glovebox. The sublimator was then attached to a vacuum manifold which was evacuated to 1 micron Hg. Another flask with a known volume of air was attached to the manifold; this flask was opened to the evacuated manifold. The air in the manifold then was let into the sublimator containing the vials of PC for 30 seconds, after which the manifold and sublimator were evacuated quickly to 50 microns Hg. In this way the PC was exposed to reduced pressures of air whose relative humidity was calculated, and the resulting water contamination was measured by gas chromatography. It was found that shorter exposure times became more difficult to control, as opening and closing of stopcocks took several seconds.

The results of these experiments are shown in table 2.2. In all samples tested the contamination was significant. Based on the relative humidity in the room at the time of the experiment (45%), the total amount of moisture present in the vacuum manifold and the vessel holding the vials of PC could be calculated. It was found that the amount of water taken up by the PC was nearly equal to the amount of water in the vessel adjacent to the PC vials. The amount of water absorbed was not proportional to the surface area exposed and it was not possible to predict what the contamination should have been. These results do, however, demonstrate the speed with which PC exposed to low levels of atmosphere can become contaminated.

Table 2.2a: Effect of 30 sec. exposure to 43 mm. air.

Surface area exp., cm^2:	6.3	2.4	1.6
H_2O contam., ppm:	10	7	4

Table 2.2b: Effect of 30 sec. exposure to 75 mm. air.

Surface area exp., cm^2:	6.3	2.4	1.6
H_2O contam., ppm:	13	10	7

2.4. Determination of Water using the Lead Tetraacetate Method

Because of the limitations of GC analysis for trace water, several other methods of analysis cited in the literature were investigated. The lead tetraacetate method, as described in reference 14, was tested to try to determine ppm levels of water using UV/visible spectroscopy. In [14], it was stated that the absorbance of lead dioxide could be measured to determine water content after adding lead tetraacetate to a sample. No specific absorbance for lead dioxide was given, however. The purpose of this brief study was to determine if the absorbance of lead dioxide could provide a means for determining ppm levels of water in PC.

Lead tetraacetate [Alfa] was used as received. Reagent grade benzene (Fisher Scientific) was dried over molecular sieves. A 3% solution of lead tetraacetate was made up in the glovebox and filtered over packed glass wool to remove enough lead dioxide to give a clear solution. The solution was transferred to glass-stoppered quartz cuvettes and known amounts of water in PC were added. The differential spectra were measured on a Perkin-Elmer spectrophotometer with the driest sample being used as a reference. The wavelength range studied was from 500 to 350 nm. The glass stoppers were sometimes, but not always, able to keep out moisture. When contamination

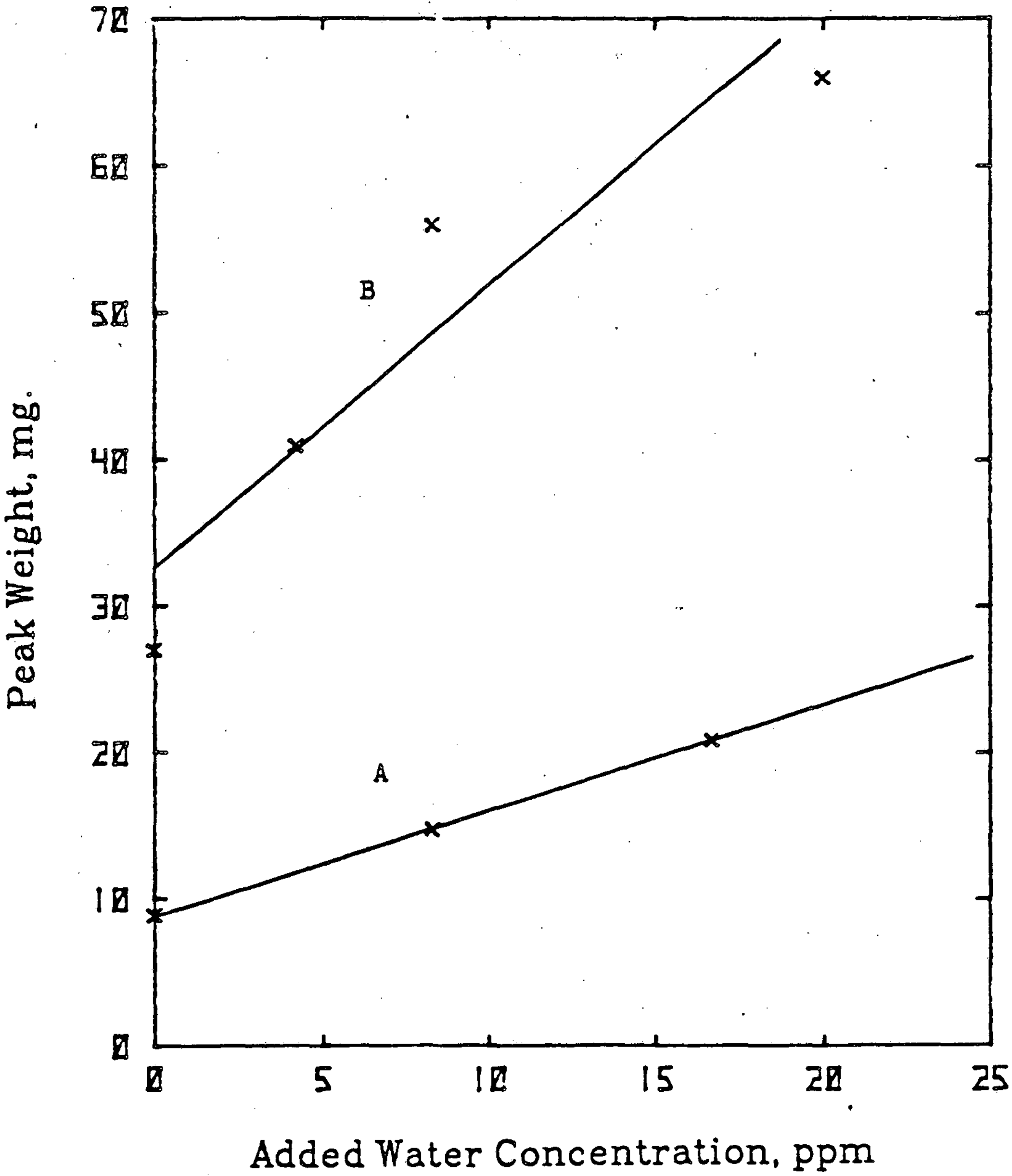

Figure 2.1: 2 GC calibrations for water in PC, showing the effect of continued use on the calibration slope. A) calibrated 6/13/84; B) Calibrated 7/16/84, after several weeks of intermittent use. The instrument, columns and experimental method are described in section 2.2.

took place it was apparent, as the solution quickly took on the brown color of lead dioxide.

In fig. 2.2 is shown the spectrum of a sample containing 3 ppm water. This spectrum was run against a cuvette of the same lead tetraacetate solution as a reference. No absorbance peak in the near UV was noted. The absorbance of lead tetraacetate became dominant below 360 nm and recording a spectrum became impossible because the reference was opaque in this region. When the solution was contaminated with water so that it became visibly brown in color, no new absorbanc peak was seen between 360 and 500 nm. The absorbance peak of the lead dioxide formed on reaction with water overlaps that of the lead tetraacetate. Since the lead tetraacetate must be present in excess the measurement of a small overlapping absorbance would not be practical. This method was not pursued further.

2.5. Trace Analysis Using NMR

The use of nuclear magnetic resonance spectroscopy (NMR) for determining water in PC was studied. A Bruker 500 Mhz FT-NMR, the most sensitive instrument available, was used to measure the proton spectrum of water in PC. For measuring the F^{19} spectrum of hexafluoroacetone (HFA) adducts with water and alcohols in PC a 180 Mhz FT-NMR was used. Both instruments are owned by the college of chemistry and the sample measurements were performed by Rudi Nunlist and Rich Mazzarisi of the NMR lab.

Standards of 0.1 and 0.5% water in PC were prepared in the glovebox for proton magnetic spectroscopy. HFA, which has been used as a fluoridating agent for NMR determination of alcohol mixtures, was purchased as a 5% solution from Tokyo Akai Chemicals. HFA was added to PC samples along with isopropyl alcohol as an internal standard. Several methods were tried to seal the NMR tubes to prevent moisture contamination outside the glovebox. Tubes with serum cap fittings were found to be easiest to handle and serum

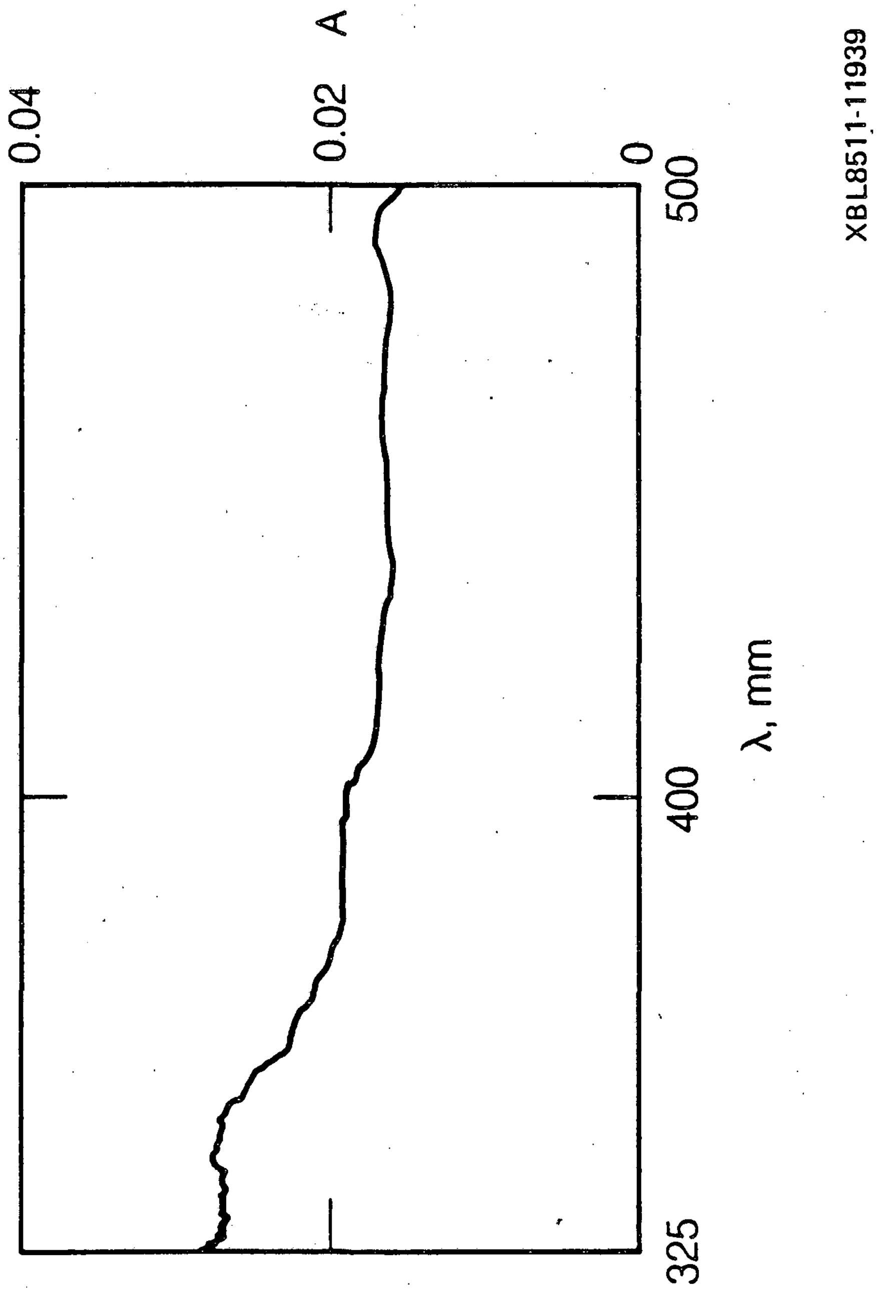

Figure 2.2: UV/Visible spectrum of lead tetraacetate to which 3ppm water was added, vs. the same solution with no water added in the referance beam.

caps worked reasonably well in preventing water contamination in GC sample vials.

2.6. Electrochemical Measurements

2.6.1. Electrolyte Preparation

Two supporting electrolytes were used in this work, KPF_6 and $KAlCl_4$. KPF_6 has been used extensively in studies of water content in PC electrolytes and was used to allow direct comparison with existing literature. KPF_6 (Alfa Inorganics) as received was found to give cloudy solutions in PC. For this reason it was recrystallized from reagent grade acetone; the insoluble components were removed by filtering the acetone solution and the salt gave clear colorless solutions after drying at a vacuum of 10 microns Hg at 250°C for 2 days.

$KAlCl_4$ has been studied for use in electrodeposition of potassium in PC [1]. The salt was prepared in this lab using a procedure outlined by Law. KCl and $AlCl_3$ were fused together under dry helium at 500°C in a quartz tube, then cooled and evacuated. $KAlCl_4$ solutions were cloudy as a result of excess KCl in the salt and were filtered prior to use.

2.6.2. Electrodes

The reference electrode used in this study was the potassium capillary electrode described by Law [1]. Molten potassium was drawn up into a glass capillary containing a tungsten lead. The capillary could be snipped back periodically during use to expose a fresh potassium surface.

Working Electrodes: For stationary cyclic voltammetry experiments a platinum disk electrode embedded in glass (Bioanalytical Systems, electrode area .03 cm^2) was used. For rotating disk experiments two electrode materials were used. Most data was obtained on stainless steel electrodes in teflon disks which had been constructed previously in this lab. The electrode area was .078 cm^2. Later a platinum electrode in an epoxy resin disk with the same area was used.

All working electrodes were polished with 1 micron alumina prior to use. The stainless steel electrodes were cleaned with reagent grade acetone and dried overnight in the vacuum oven at 100°C. The platinum electrodes were cleaned in 0.1M nitric acid, rinsed with deionized water, and dried in the vacuum oven.

2.6.3. Electrolysis Cells

The cell used in cyclic voltammetry experiments was the same as that used by Law [2] for water determination. The potassium reference-, platinum working- and counter-electrodes were held in place in a weighing beaker by a teflon cap. The cell held 12 ml. of solution.

The rotating disk cell was developed previously in this lab [1]. The counter electrode was a platinum sheet with an area of 1 cm^2. A sidearm held the potassium capillary reference electrode, placing it relatively close to the working electrode surface. The cell held 27 cm^2 of solution. It was held in place on the rotator by a teflon fitting with a rubber o-ring. The apparatus with the cell attached is shown in fig. 2.3. The rotator was capable of speeds up to 3600 rpm.

Current and Voltage measurements were obtained using a PAR model 173 potentiostat with a model 176 plug-in current follower. For scanning potentials, a PAR 175 universal programmer was used. Current/voltage scans were recorded using a Nicolet 4094 digital oscilloscope capable of transferring the data directly to an HP 9825 computer. Data collected in this manner was stored on flexible disks. Most limiting currents in the rotating disk electrodes were read from the current follower meter.

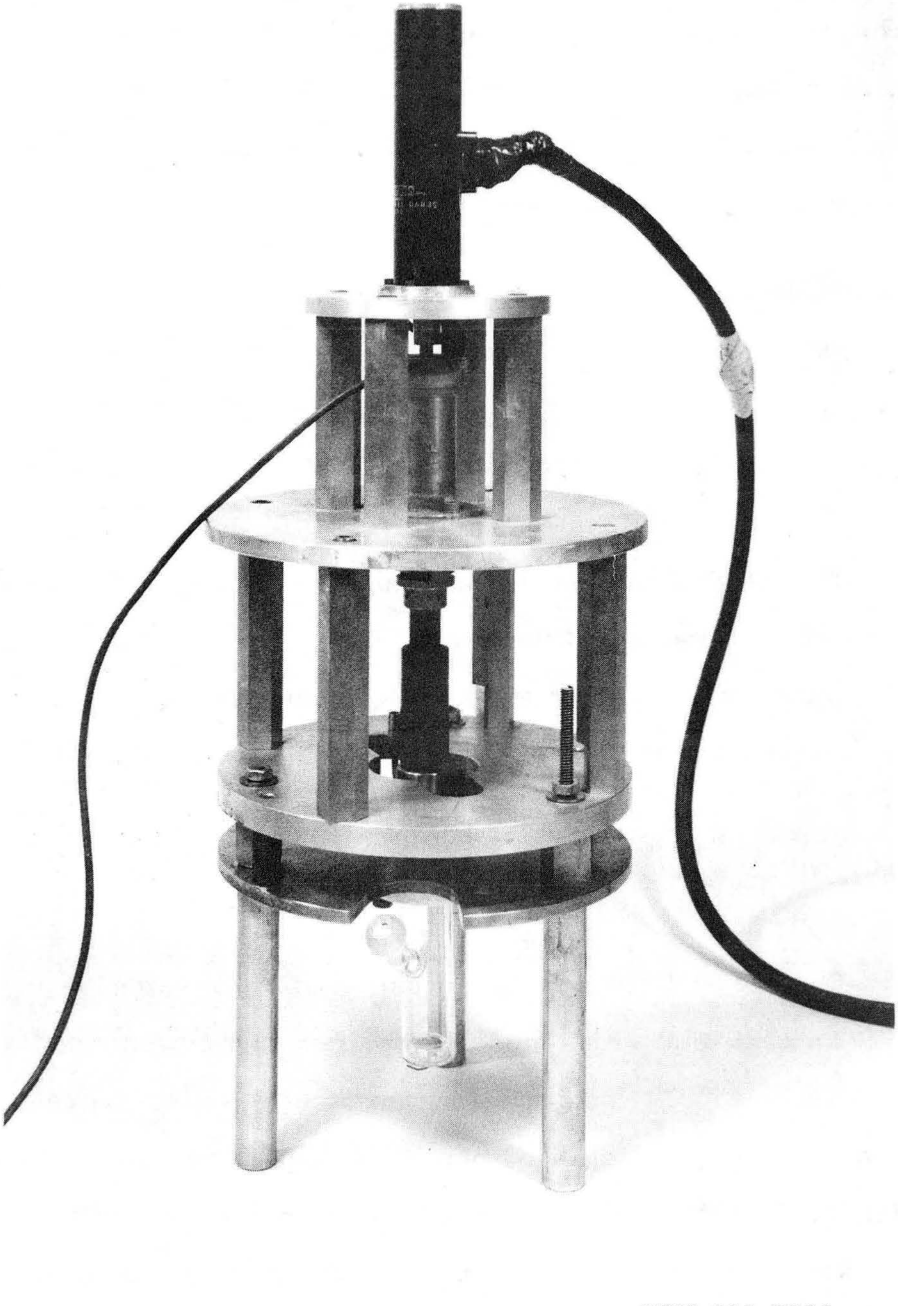

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Figure 2.3: Photograph of the rotating disk electrode apparatus used in this study, showing the cell with the sidearm for the reference electrode.

III. Results and Discussion

3.1. NMR Analysis

Nuclear Magnetic resonance spectroscopy (NMR) has been used previously to characterize the interactions of water at concentrations as low as 100 ppm with ions and solvent molecules in PC electrolytes [8]. In this work the feasibility of using NMR to determine lower levels of water in PC was investigated. The NMR spectra were run by Rudi Nunlist and Rich Mazzarissi in the UC Berkeley College of Chemistry NMR lab, both of whom are owed a great deal for their help and advice.

A proton magnetic resonance spectrum of PC containing 0.5% water is shown in fig. 3.1. The water peak can be clearly seen at 2.9 ppm. It was estimated that levels of water as low as 10 ppm could be detected using multiple scans to reduce baseline noise. The more difficult problem is that of calibration. Calibration for quantitative analysis in NMR spectroscopy requires the use of an internal standard of known concentration whose peak area can be compared to that of the signal being measured. The comparative integration of water vs. an internal standard would not be possible because of the small size of the water peak relative to the baseline variation. The baseline variation is due to the protons in the solvent molecules and cannot be eliminated. Thus the disparity in magnitude of the signals of PC and water makes direct trace determination of water impossible.

A more promising indirect method for using NMR spectroscopy to determine water was tried, which uses F^{19} NMR with hexafluoroacetone as a fluoridating reactant. Hexafluoroacetone (HFA) reacts with water to produce a gem-diol:

$$H_2O + F_3C{-}CO{-}CF_3 = C(CF_3)_2(OH)_2$$

Analogous reactions also take place with other compounds containing active protons, including alcohols. The method and its uses were

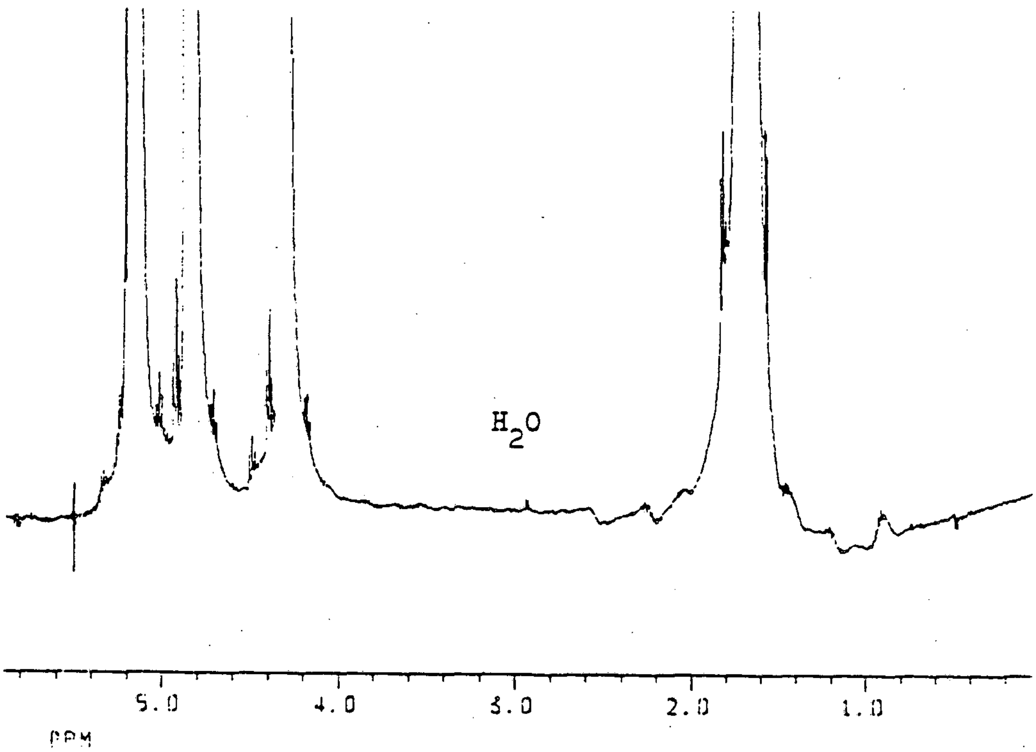

Figure 3.1: Proton magnetic resonance spectrum of PC to which 0.5% water has been added.

described by Leader [18]. This reaction is quantitative and rapid for water and the F^{19} shift for the diol has been determined. The signal from the water adduct can be integrated and compared to the signal from an internal standard of known concentration. Because the reaction involves six fluorine atoms per water molecule the signal obtained per water molecule is greatly enhanced. Since fluorine is not a major component of the solution, the baseline of the fluorine spectrum is level enough that standardization is possible. The internal standard can be a known amount of a compound such as a primary alcohol, which reacts quantitatively with HFA to produce an adduct whose F^{19} shift (relative to HFA or the diol) is known. In this work isopropyl alcohol was used.

In fig. 3.2 is shown the F^{19} spectrum of a 4 ml PC sample to which 0.4 ml HFA solution (5% w/w in ethyl acetate), and 120 ppm isopropyl alcohol had been added. In this sample, some of the HFA has evaporated (HFA is a gas at room temperature), leaving the water adduct as the major peak in the spectrum. Ethanol was apparently a contaminant in the HFA solution, as the ethanol adduct was detected in all of the spectra. The detection limit for IPA is approximately 10 ppm; in a sample containing 8 ppm IPA the peak for the adduct was barely larger than the baseline noise. Since the molar detection limit for water is the same as that of IPA the detection limit for water would be 3 ppm with the instrument used here. With a more powerful instrument such as the 500 Mhz FT-NMR at UC-Berkeley a greater sensitivity should be possible. However, a F^{19} probe was not available for the more powerful instrument.

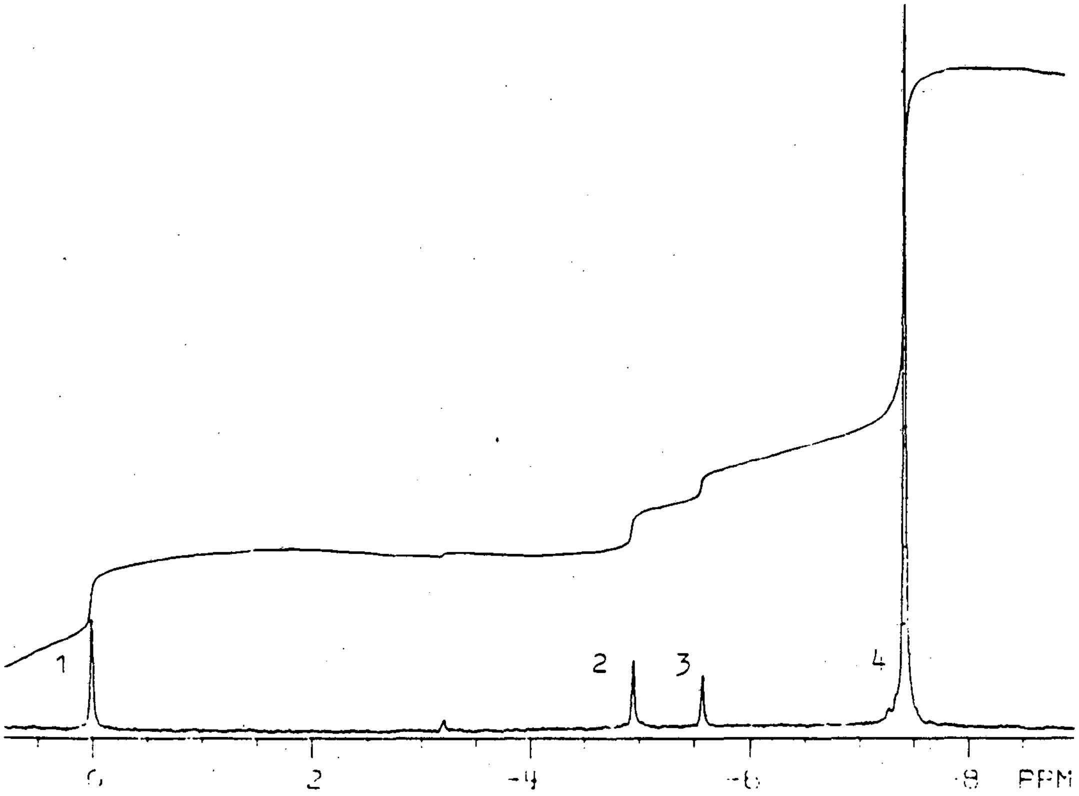

Figure 3.2: F^{19} spectrum of a PC sample containing 120 ppm isopropyl alcohol and 0.4% hexafluoroacetone. Peaks correspond to 1) HFA; 2) ethyl alcohol adduct; 3) isopropyl alcohol adduct; 4) water adduct.

The major problem with using this method is that the HFA solution was heavily contaminated with water during manufacture. Several precautions were taken to avoid water contamination of the samples after removal from the glovebox, including sealing the tubes under vacuum and using serum-capped tubes. Nonetheless, in all of the samples the water adduct proved to be the largest peak in the spectrum. Based on the amount of diol relative to the IPA adduct in the spectra it was estimated that 40% of the HFA in the ethyl acetate solution had been taken up by water during manufacture. Hanson[2] also estimated that a major fraction of the HFA in the Tokyo Akai solution had already reacted with water based on gas chromatography measurements.

The major use of HFA in NMR spectroscopy is not for trace determination of water but for characterization of alcohol and amine mixtures. For water determination this solution is unsuitable, because the contamination is so large relative to the amount of water to be detected. This method could prove to be feasible if a drier form of HFA were available. Other workers were able to use HFA gas directly by bubbling it through the sample. This technique, by which the problem of water contamination might be avoided, could not be tested because HFA gas is no longer available for sale.

3.2. Electrochemical Determination of Water in PC Electrolytes

3.2.1. Potential Sweep Methods

Several attempts were made to determine water in 0.5M KPF_6 solutions using potential sweep techniques. The current resulting from the reduction of water during a rapid potential scan at a platinum electrode has been studied by others as was mentioned in section I. In this work it was hoped that a more quantitative treatment of the reduction of water would be possible. This proved not to be the case.

Since the initial cathodic scan of a fresh platinum electrode tended to give voltammograms with irreproducible current peaks, the potential was cycled several times, allowing the irreproducible peaks to diminish. The limits of the potential scan were +4V, the limit of the potentiostat, and +0.1 V, above the potential for potassium reduction. The current/ voltage curves reached steady state after several cycles. A cyclic voltammogram in electrolyte dried with Na/K alloy is shown in fig. 3.3a. In fig 3.3b is shown a voltammogram in the same electrolyte immediately after adding 0.05 ppm water. The change in cathodic current at the lower end of the scan is striking; what this represents is not known, however, since no further change was seen after subsequent additions of water. The appearance of an anodic peak at 3.5V indicates that an oxidizable species is formed after the addition of water, but this peak likewise did not respond to further increases in water concentration. Vigorous stirring of the electrolyte was tried and did not appear to help. Likewise varying the potential sweep rate had no effect on the response of the I/V curve to additions of water.

The failure of stationary electrode voltammetry in detecting water could have been due to the decomposition of PC in the vicinity of the electrode surface and subsequent formation of polymeric films. Figures 3.3a and 3.3b do seem to show that the addition of water results in a rapid change in the condition of the platinum electrode surface. In other reported work where potential sweep methods were used, intense agitation of the working electrode was necessary to obtain reproducible results for detection of water. It is possible that agitation of the working electrode removes reduction products which contribute to the passivation of the electrode surface. In this work no film was visible on the electrode surface, and the components which contribute to passivation of the electrode surface were not identified in previous studies. However, under the assumption that chemical reactions leading to the deactivation of the electrode surface could be avoided at a moving electrode a rotating disk electrode was used in subsequent studies.

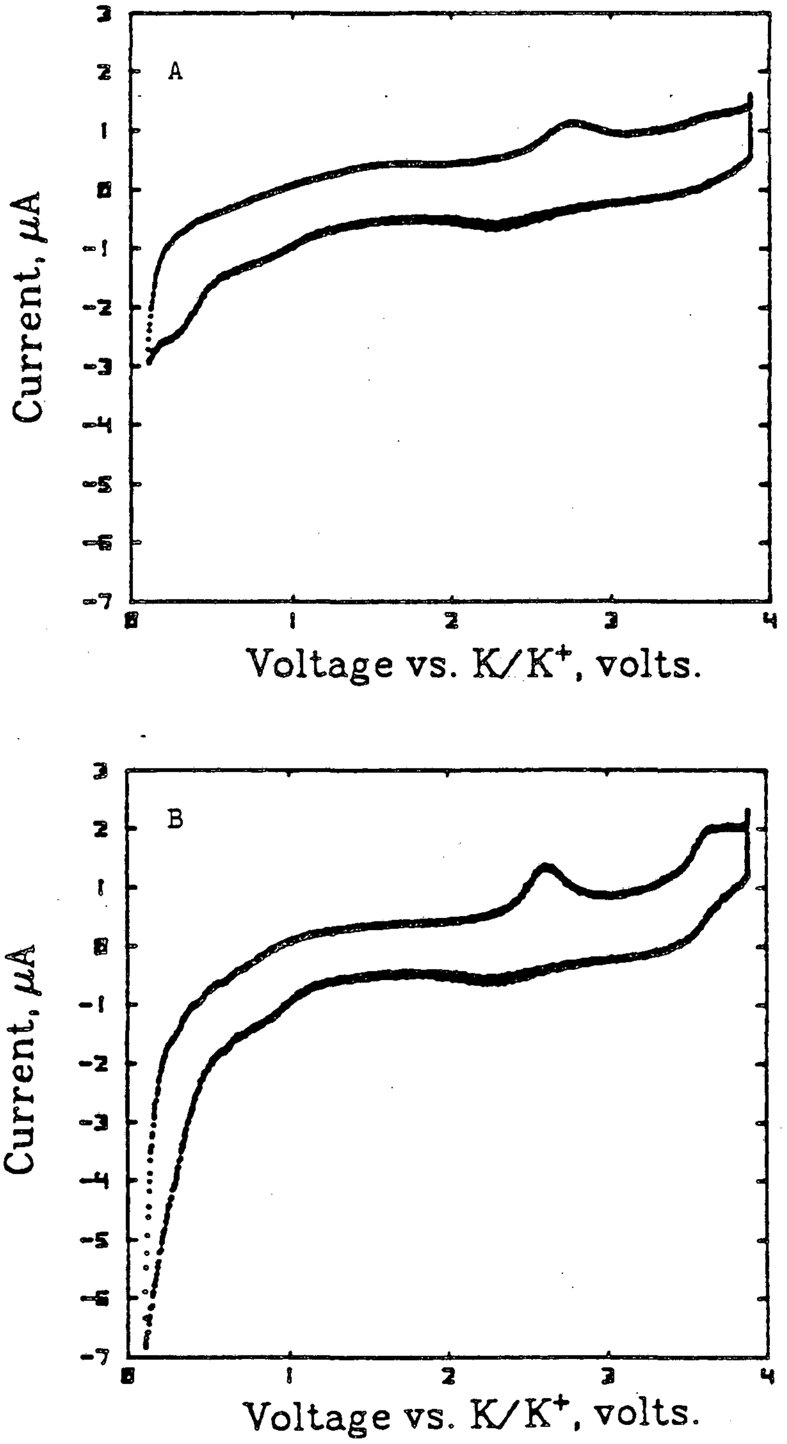

Figure 3.3: A) cyclic voltammogram at a platinum electrode in 0.5 M KPF_6 solution dried using Na/K alloy; B) Cyclic voltammogram in the same system after addition of .05 ppm water. Sweep rate = 200 mv/sec; electrode area =.03 cm^2.

3.2.2. Rotating Disk Electrode Experiments

It was found that water could be determined at the ppm level in solutions of KPF_6 and $KAlCl_4$ by using limiting current measurements at a rotating disk electrode. Reproducible calibrations were obtained for the response of limiting current to water addition in the 0.5-10 ppm range. However, intermittent electrode passivation was still a problem; no one electrode cleaning method was effective in producing an active electrode surface all of the time. This was true for both platinum and stainless steel electrodes. Most of the results reported here were obtained with a stainless steel electrode; the effect of the electrode material was checked using a platinum electrode at the end of this study. Platinum electrodes likewise became inactive some of the time.

When electrode deactivation took place it was complete. Limiting currents were observed to rapidly decay to zero, such that it was not possible to measure the response of current to changes in electrode rotation speed or water concentration.

Limiting current behavior at a rotating disk electrode is described by the Levich equation:

$$i_l = 0.62nFAD_o^{2/3}\omega^{1/2}\nu^{-1/6}C^*$$

where:

n = number of electrons
F = Faraday Constant
A = electrode area, cm^2
D_o = diffusivity, cm^2/sec
ω = angular velocity of the disk, sec^{-1}
ν = kinematic viscosity, cm^2/sec
C^* = bulk conc. of the reacting species, mol/cm^3

3.2.2.1. KPF_6 Solution Results

The I-V curves from slow (2mv/sec) potential scans at a stainless steel RDE is shown in fig. 3.4 for several rotation speeds. The sharp onset of a cathodic current can be seen at +0.7V vs. K/K^+. These I-V curves do not seem to show limiting current behavior; that is, the currents do not reach a constant value. It was found that at +0.4V the current did increase linearly with $\omega^{1/2}$ as is predicted for a limiting current by the Levich equation. Thus the I-V curves are somewhat anomalous. For a potential step at a rotating disk, the current is within 1% of its limiting value at a time τ when [23]:

$$\omega\tau(D/\nu)^{1/3}(0.51)^{2/3} \geq 1.3$$

For this system this equation predicts a τ of 0.3 sec at 1000 rpm. The slow current increase in the I-V curves is over several minutes.

In order to determine whether limiting current behavior was followed in the potential range of +0.1 to +0.4V, currents were measured at several rotation speeds at 0.1V, 0.3V, and 0.4V vs. K/K^+. This potential range was chosen based on observation of the I-V curves in figure 3.4. The initial steep increase in current in the I-V curves occurs between 0.8V and 0.5V; limiting current behavior would be expected at potentials below 0.5V. Currents were measured after allowing several minutes to reach a steady state. The results of these measurements are shown in figure 3.5, for a solution containing 6 ppm added water. Since the Levich slopes do not vary by more than 10% it appears that the current is not a function of the potential below 0.4V, and that true limiting current behavior is followed. Thus the absence of a plateau in the current vs. voltage curves of fig. 3.4 appears due to the mass transport not reaching steady state.

Voltage scans were not used to obtain the limiting current measurements shown in this work. Once it was established that limiting current behavior was followed at +0.4V, the limiting currents were measured by stepping the potential to 0.4V. Using this procedure several minutes had to be allowed for the currents to slowly increase to constant values which were recorded. Typically currents drifted upward by several microamps before reaching steady state.

The response of the current measured at +0.4V to additions of water in the range of 1-15 ppm at a single rotation speed is shown in fig. 3.6. The relationship is linear, as predicted by the Levich equation, with a slope of $53.6 \mathrm{Acm}^3\mathrm{mol}^{-1}$, equal to the product $0.62nFD_o^{2/3}\omega^{1/2}\nu^{-1/6}$. There is some scatter in the points at the lowest concentrations which could be related to the transient features seen in the I/V curves. Nonetheless it seems reasonable to assume that the reaction being observed is the reduction of water:

$$2H_2O + 2e^- = H_2 + 2OH^-$$

The standard potential for this reaction in aqueous solution is -0.41V vs. NHE, while that of potassium deposition is -2.9V. Thus the reduction potential for this reaction is much higher (more negative) than would be expected. At a platinum RDE the onset of cathodic current was seen at +1.0V vs. K/K^+, indicating that the electrode material was not the major factor in the potential being unexpectedly negative. The reduction of water has been observed in this potential range by others as well, as mentioned in chapter I; to date there is no satisfactory explanation.

A more complete and precise calibration for water is shown in figs. 3.7 and 3.8. The limiting currents were measured over a range of rotation speeds after a series of additions of water in the 1-20 ppm range. The measured currents are plotted vs. $\omega^{1/2}$ in figure 3.7. These curves are linear at rotation speeds up to 2800 rpm, indicating that a true limiting current is being measured. The lines showed relatively small positive intercepts (3-8 μA) at zero rotation speed, indicating a small contribution to the current by another reaction. The intercepts were not affected by additions of water. The $I/\omega^{1/2}$ slopes are plotted vs. added water concentration in fig. 3.8. The slope of fig. 3.8 gave the Levich constant, $i_l/C\omega^{1/2}$. This was calculated by least squares to be 3.6 μA $\sec^{1/2}$cm^{3}mol^{-1}. The same constant based on least squares fit of fig. 3.6 is 3.1 μAsec$^{1/2}$cm^{3}mol^{-1}. The difference in the two figures (15%) could be due to the greater uncertainty in fig. 3.6. Since the use of the slopes of i_l vs. $\omega^{1/2}$ eliminated the effects of nonlimiting currents from the calibration, the Levich constant from fig. 3.8 was used for calibration purposes. The 95% confidence limits of the slope of fig. 3.8 were ±11%, indicating an excellent linear fit.

From the Levich constant the diffusivity of water in the solution was calculated, based on a solution density assumed equal to that of PC and a solution viscosity of 3.8 cP[19]. D_o was found to be 0.85x10^{-5}cm^2/sec. The correlation of King et. al.[20] is often used to estimate molecular diffusivities in nonaqueous solvents:

$$D_{AB} = 4.4\text{x}10^{-12}\,\frac{T}{\mu_B}\left[\frac{V_B}{V_A}\right]^{1/6}\left[\frac{\Delta H_B}{\Delta H_A}\right]^{1/2}\ \text{m}^2/\text{sec}$$

where:

T = Temp., K

μ_B = solvent viscosity, cP.

V_A, V_B = solute and solvent molal volumes, cm^2

$\Delta H_{A,B}$ = solute and solvent molar heats of vaporization

This gives an estimate of 0.4x10^{-5} cm^2/sec if the solution viscosity is taken to be that of the electrolyte. If the viscosity of pure PC (2.5 cp.) is used the estimated value is 0.6x10^{-5} cm^2/sec. One possible reason why the King equation predicts a diffusivity so much lower than the experimental value is the appearance of the heat of vaporization in the correlation. The heat of vaporization of water is unusually high due to hydrogen bonding in liquid water and may not be a measure of the energy required to displace an isolated water molecule in PC solution.

None of the methods currently used for estimating diffusion coefficients take into account all of the factors which affect water in a PC electrolyte. For example, hydrogen bonding between the water molecule and the carbonyl group of the PC molecule would be expected to result in strong interactions and a decreased diffusivity. Hydrogen bonding of water molecules in PC was studied by Cogley et. al. [24] using NMR and IR spectroscopy at fairly high concentrations of water (0.1-3.5M). In the work of Cogley et. al. it was found that hydrogen bonding did take place; however, the formation of discrete chemical species was not observed. Thus while there are interactive forces which could hinder the diffusion of water molecules it is not seem that water molecules are strongly bonded in PC-water complexes.

The situation would be further complicated by the addition of an electrolyte. One major effect of adding electrolyte is the increase of the viscosity of the solution. Another factor which could be important is that a some of the hydrogen bonding sites on the PC molecules (i.e. carbonyl groups) are participating in solvation of cations. Since a liquid solution of PC is approximately 11M in PC, a significant fraction of the electron donor sites would participate in the solvation of cations in a 0.5M KPF_6 solution. The resultant decrease in the number of sites available for hydrogen bonding with water molecules could be the cause of the high diffusivity of water in the electrolyte. In the work of Cogley et. al. it was found that water does not preferentially solvate the potassium cation; therefore the diffusivity of water would be relatively unaffected by interactions of water molecules with cations in the solution.

In table 3.1 the literature values of diffusion coefficients of water in several polar solvents are listed, along with the calculated values of $D\eta/T$. It can be seen that $D\eta/T$ is much higher for 0.5M KPF_6 than for most of the solvents listed, with the exception of aniline. Aniline, an aromatic amine, is different from the other solvents listed in that the lone electron pair which would normally contribute to hydrogen bonding is delocalized on the benzene ring. Thus the value of $D\eta/T$ calculated in this work for water in 0.5M

KPF_6/PC is unusually high but not physically impossible in an organic solvent.

Table 3.1: Values of diffusivity for water in various solvents.

	D cm^2/sec x 10^5	T °C	η cp.	$D\eta/T$ dynes/degx10^{10}
Ethanol	1.1	25	1.1	4.1
Methanol	2.2	20	0.6	4.5
Pyridine	1.5	20	0.97	5.0
Acetone	5.5	25	.32	5.9
n-Propyl Alcohol	0.8	20	2.3	6.3
Aniline	0.7	25	4.4	10.3
0.5M KPF_6/PC	0.85	25	3.8	10.8

All single solvent D and η values are from [25]; the electrolyte value for D is from this work; Electrolyte η value is from [19].

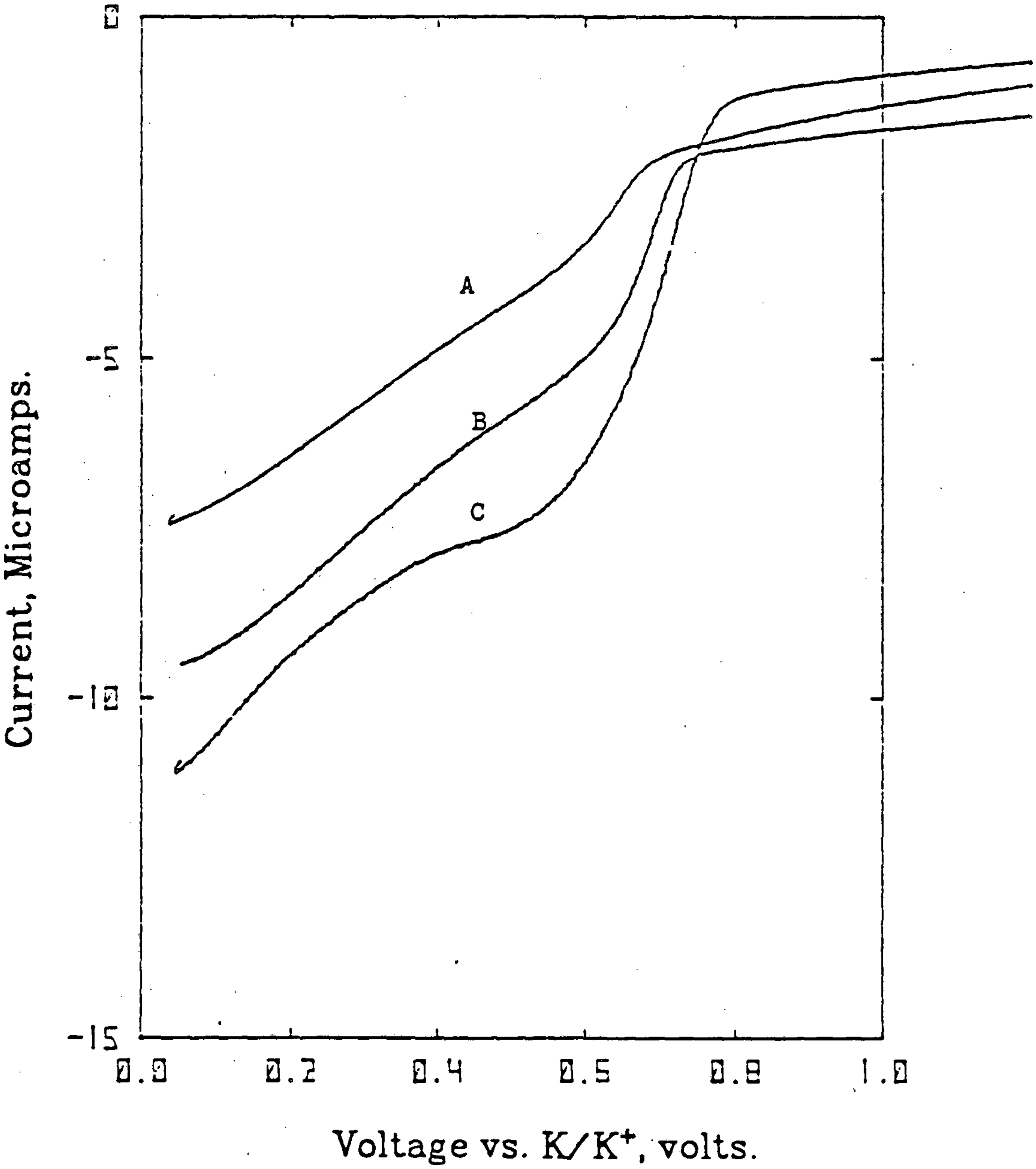

Figure 3.4: Current vs. voltage curves for slow (2 mv/sec) potential scans at a stainless steel rotating disk in 0.5M KPF_6 solution. Electrode area = .08 cm^2; A) 1000 RPM; B) 2000 RPM; C) 2880 RPM. Reference electrode K/K^+.

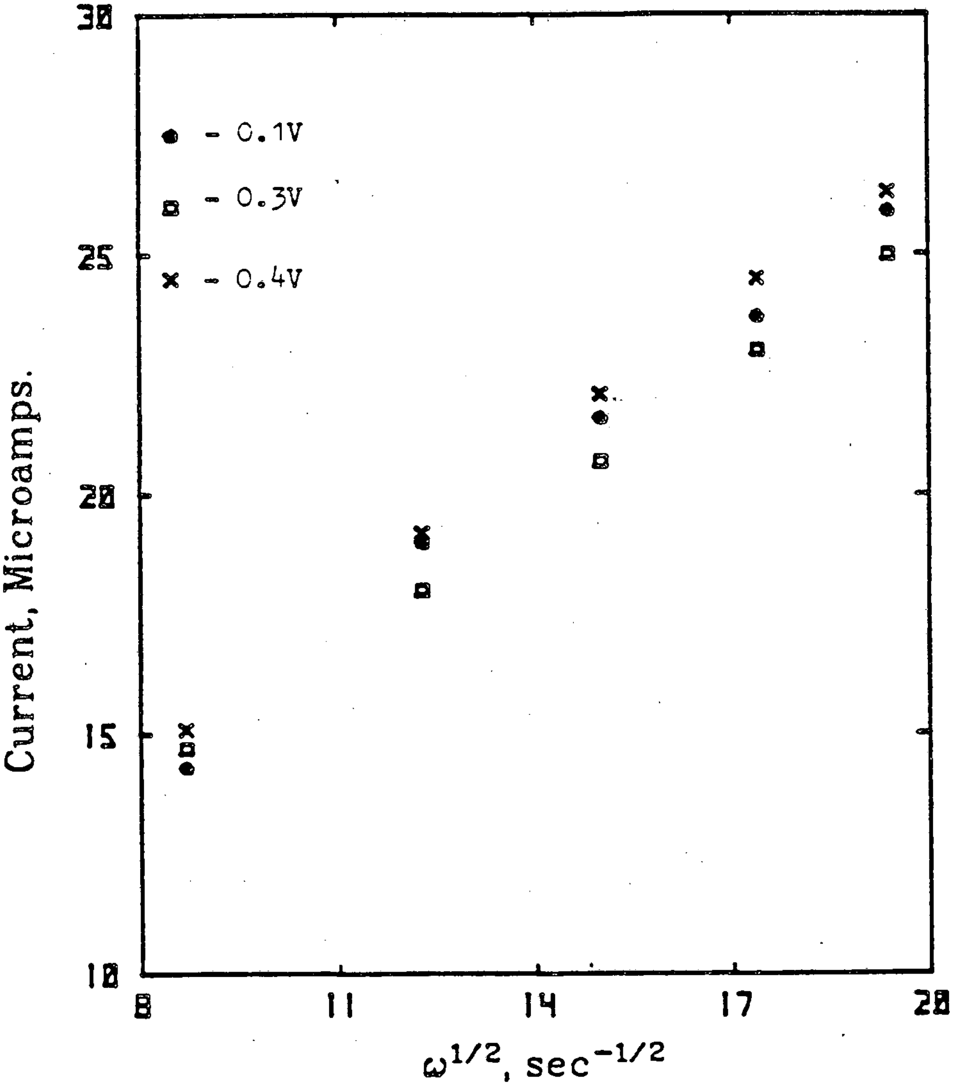

Figure 3.5: Current vs. $\omega^{1/2}$ measured at several potentials in 0.5M KPF_6 solution containing 6.05 ppm added water. Working electrode: stainless steel RDE, area =0.8cm^2; reference electode K/K$^+$.

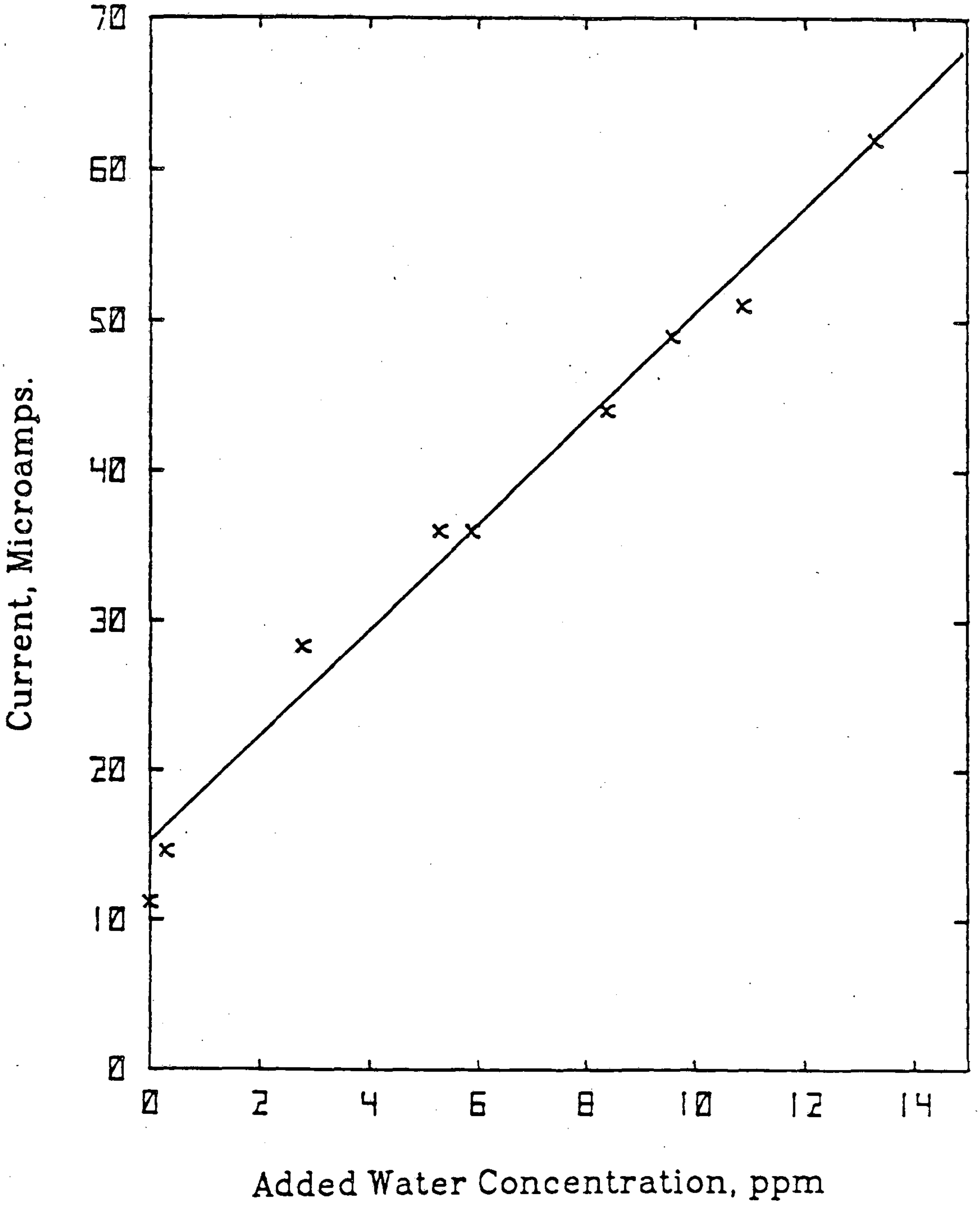

Figure 3.6: Current vs. added water concentration at a stainless steel rotating disk electrode (f=2880 rpm); 0.5M KPF_6; current measured at +0.4v vs. K/K^+.

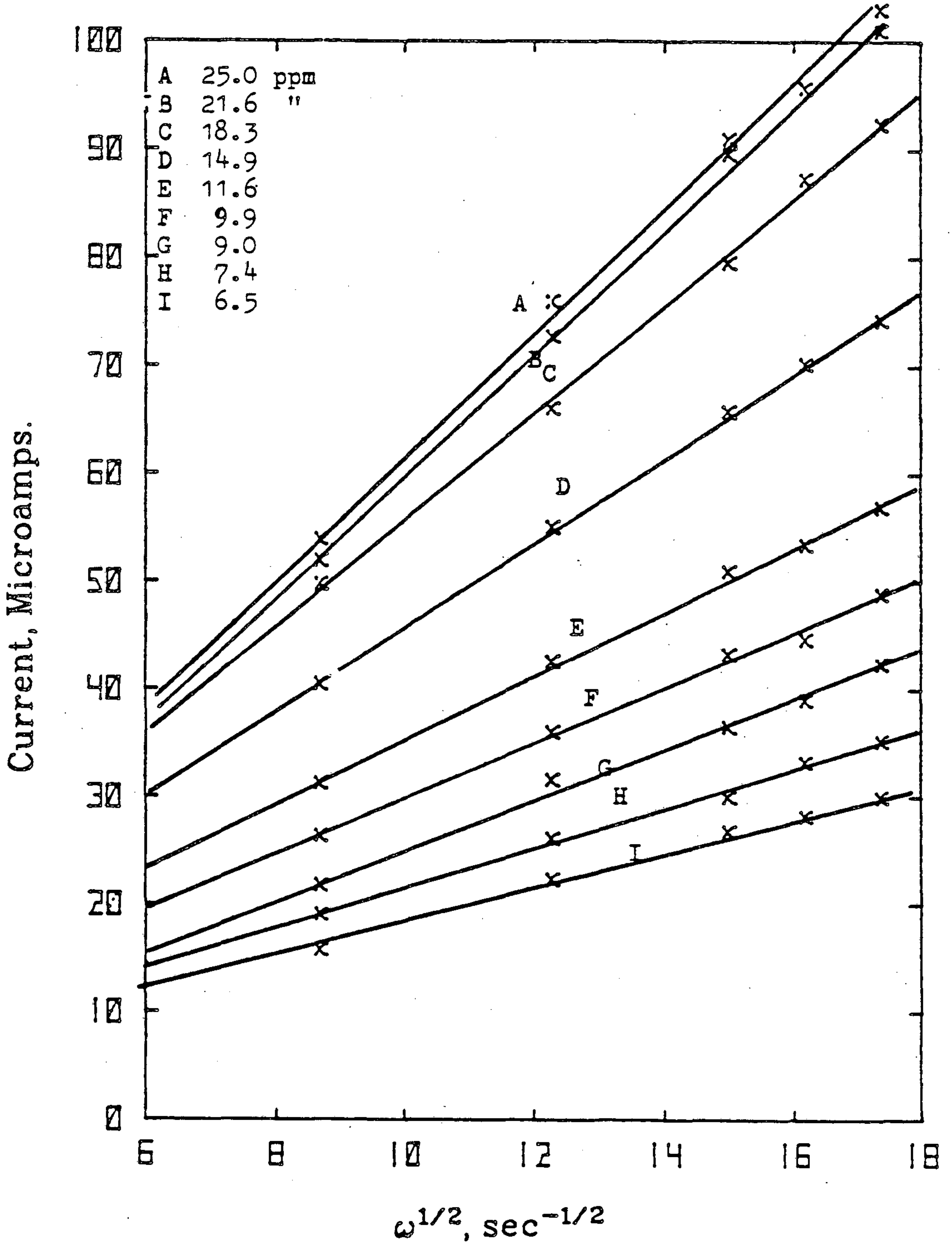

Figure 3.7: Current vs. $\omega^{1/2}$ plots for varying concentrations of water; 0.5M KPF_6 solution.; current measured at +0.4v vs. K/K^+. working electrode: stainless steel rotating disk, area=0.8 cm^2.

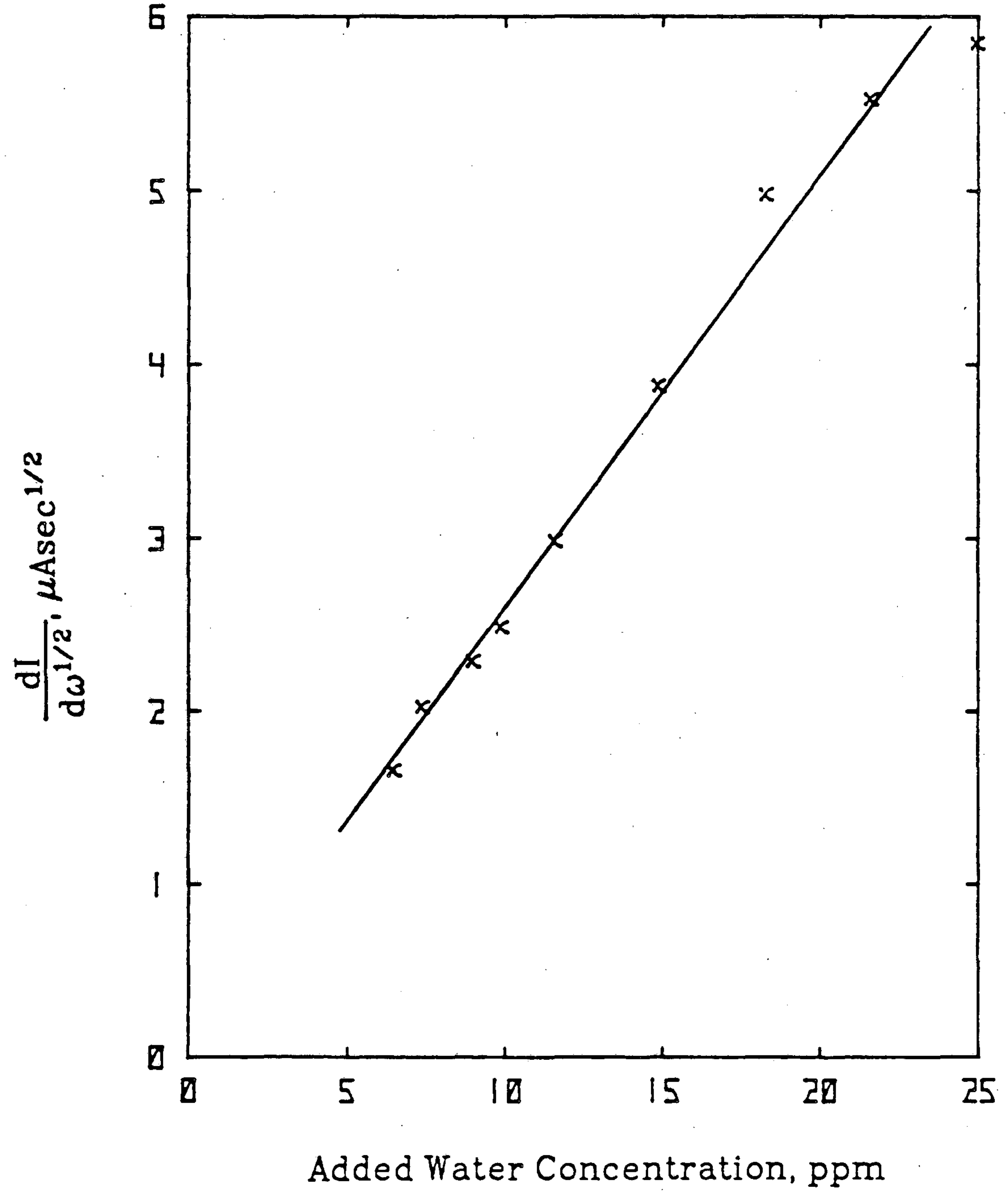

Figure 3.8: Slopes of the current vs. $\omega^{1/2}$ plots in fig. 3.7 vs. added water concentration.; current measured at +0.4v vs. K/K$^+$. 0.5M KPF$_6$ solution; Working electrode: stainless steel rotating disk.

3.2.2.2. Disappearance of Water

In several instances, when solutions were left in the measurement cell overnight or longer with no current flowing, the limiting current measurements indicated decreases in water content of KPF_6 solutions. These solutions had been dried using Na/K alloy, however the decreases in water content took place after the alloy had been removed by filtration. The Levich plots and calculated values of water content for several recorded instances are shown in figs. 3.9 and 3.10. The loss of 15 ppm was noted in one instance; in all cases the decline represented a significant fraction of the water in the solutions. The gradual disappearance of water as measured electrochemically was noted by Law over the course of several hours; Law concluded that water was being consumed by some component of the system.

In figure 3.11 Levich slopes vs. added water concentration are plotted for the system of figure 3.10, showing the effect of added water before and after the decrease in limiting current was measured. The intercept of the points for water additions on day 2 is negative, indicating a loss of 2.5 ppm water. This figure is the same as the amount of water loss calculated from the change in Levich constant from day 1. This shows that the decrease in limiting current measured was not due to the loss of active electrode area. Another possibility which was discounted was a reaction of water with either the stainless steel working electrode or the reference electrode. For a planar area A, the amount of reactant which can be reach the surface in a time t can be predicted using the boundary conditions for semi-infinite linear diffusion, as $2AD_0^{1/2}C^*t^{1/2}/\pi^{1/2}$. This predicts that only .03 ppm of water could react on the working electrode surface overnight. The loss of water was observed in systems from which the reference electrode has been removed. In any event, since the potassium surface area is smaller than the working electrode a reaction with the reference electrode could not account for the observed loss of water.

A possible cause of the decrease in water concentration is the hydrolysis of PC, a reaction known to take place in the presence of acid or base. The products of the hydrolysis of PC are carbon dioxide and propylene glycol:

$$PC + H_2O = H_3C{-}CHOH{-}CH_2OH + CO_2$$

GC testing failed to confirm that a significant amount of water was consumed in this reaction. 1000 ppm water was added to PC which had been dried using Na/K alloy. If a significant portion of that water had been consumed in the hydrolysis of PC an increase in glycol concentration should have been observed. No propylene glycol was detected several days after water was added to the sample; the gc trace of that sample is shown in fig. 3.12, along with that of a sample to which no water had been added. Also shown are the chromatograms of Burdick & Jackson PC as purchased, and with 300 ppm of propylene glycol added.

These results showed no increase in glycol contamination. The only significant organic impurities seen were propylene oxide, propionaldehyde, and acetone. These are products of the anhydrous decomposition of PC and appear at greatly increased concentrations after Na/K drying. However, no increase in organic contamination could be attributed to the addition of water to dried PC. These results show that extensive hydrolysis does not take place in pure PC. They do not, however, account for any effects that the electrolyte may have on the solution. Using GC analysis for organic contamination in electrolytes would be meaningless, however, since the solvent decomposes in the column giving spurious peaks.

It is possible that water reacts with the PF_6^- anion, displacing a fluorine atom and producing HF. HF would be expected to be electroactive, however, and no new electroactive species were detected in the PC solutions in which the loss of water was measured. HF would also be highly reactive with other components of the system and would even react with glass, and might therefore disappear too quickly to be measured electrochemically. The elucidation of the reactions of water with the solvent and the electrolyte, a subject of considerable interest, was beyond the scope of this study.

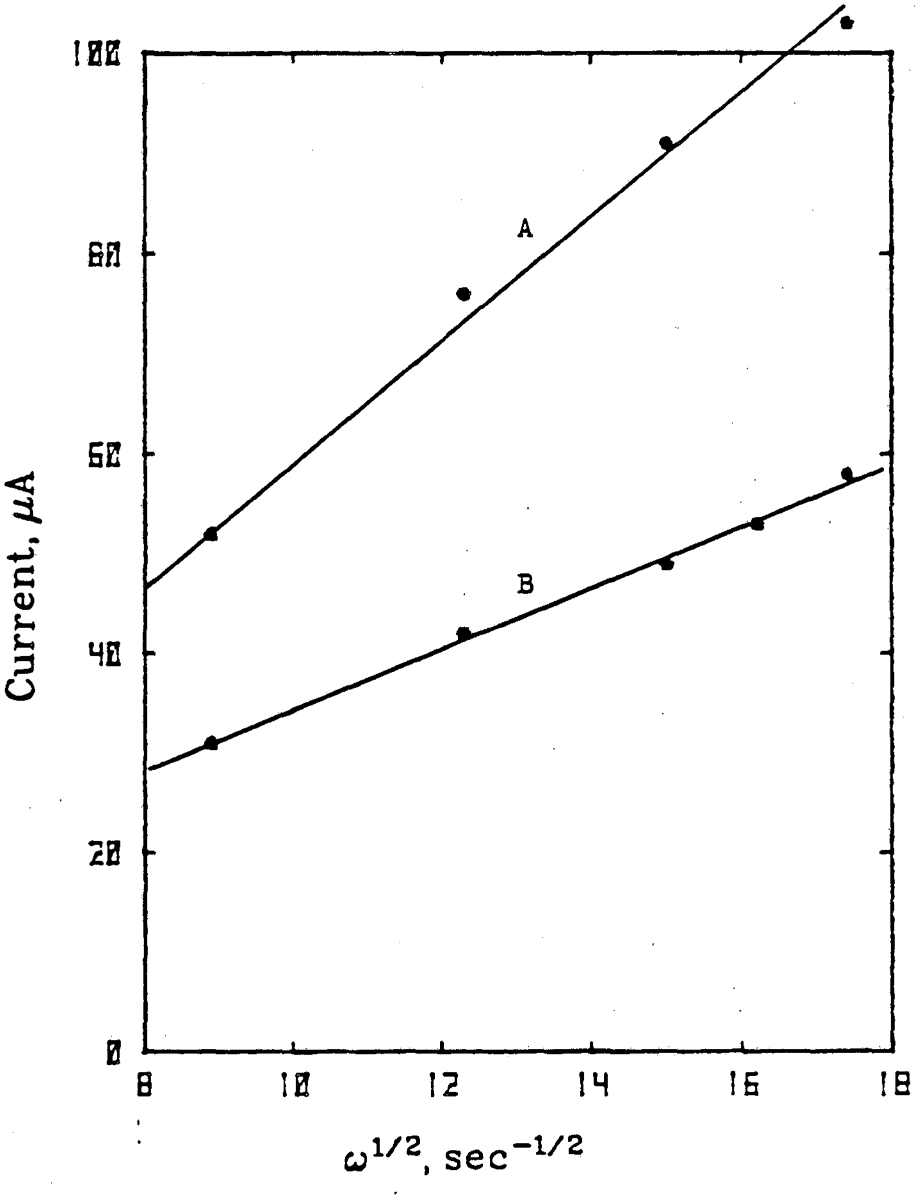

Figure 3.9: Plots of I vs. $\omega^{1/2}$ at 0.4V in 0.5M KPF_6 electrolyte showing an apparent decrease in water concentration after 3 days. Curve A=day 1, water conc.=25 ppm; Curve B=day 3, water conc.=15 ppm. Currents measured at a stainless steel rotating disk, area=$0.8cm^2$.

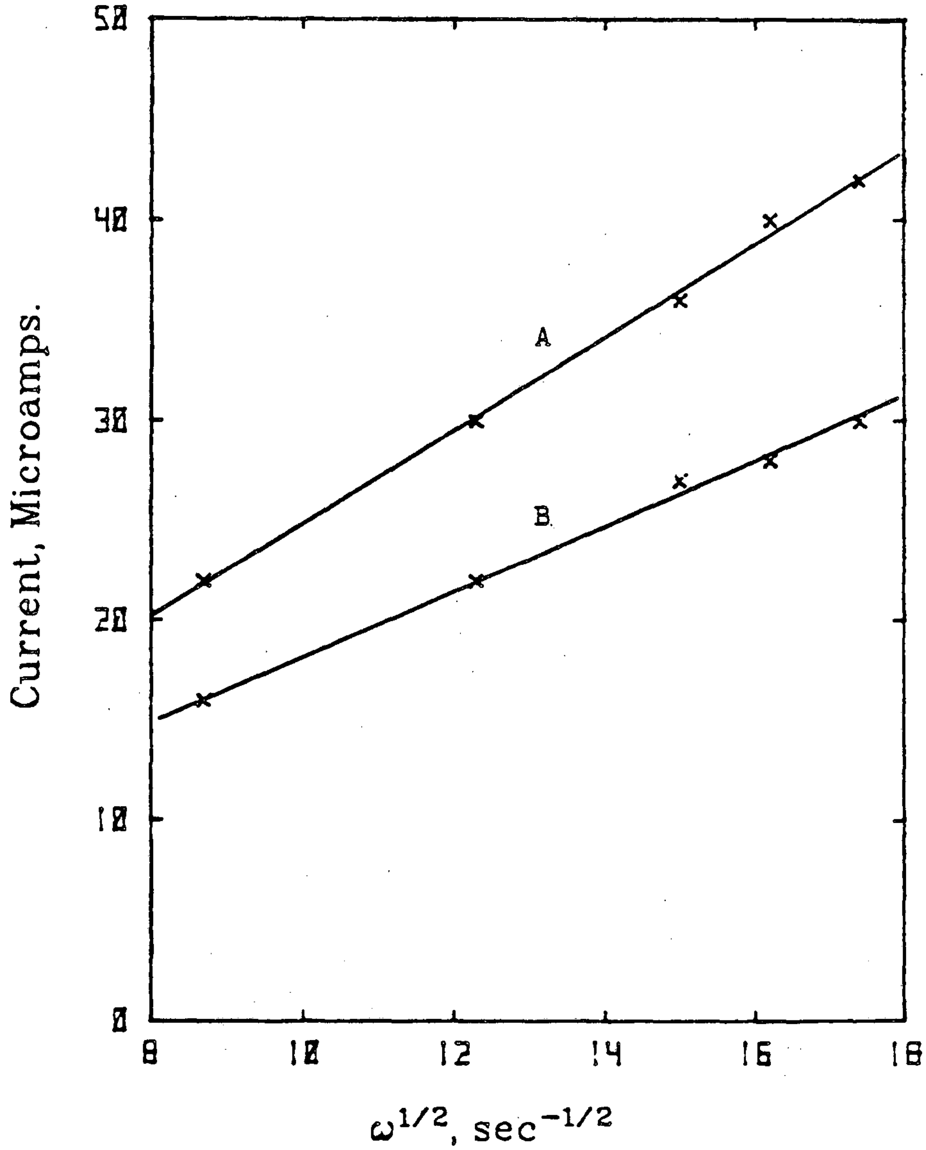

Figure 3.10: Plots of I vs. $\omega^{1/2}$ showing apparent decrease in water concentration; 0.5M KPF_6 solution; A=day 1, water conc.=10 ppm; B=day 2, water conc.=7.5 ppm. Currents measured at a stainless steel rotating disk, area=0.8cm^2.

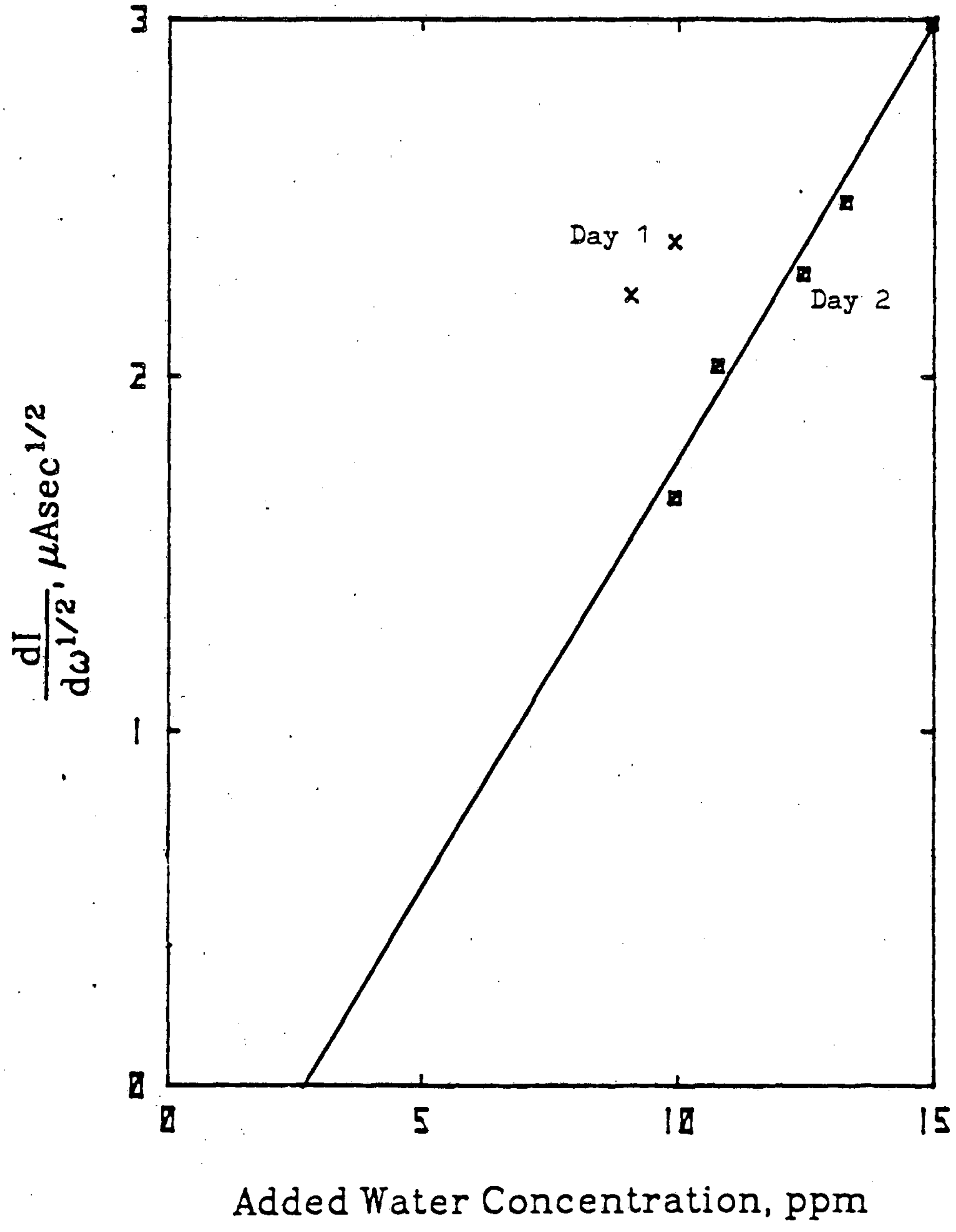

Figure 3.11: Levich slopes plotted vs. added water in 0.5M KPF_6 solution. The change in Levich slopes for additions of water on day one and day two are shown. Both the intercept of the points from day two, and the change in Levich slope from day one to day two indicate a loss of 2.5 ppm water overnight. Currents measured at a stainless steel rotating disk, area=0.8cm^2.

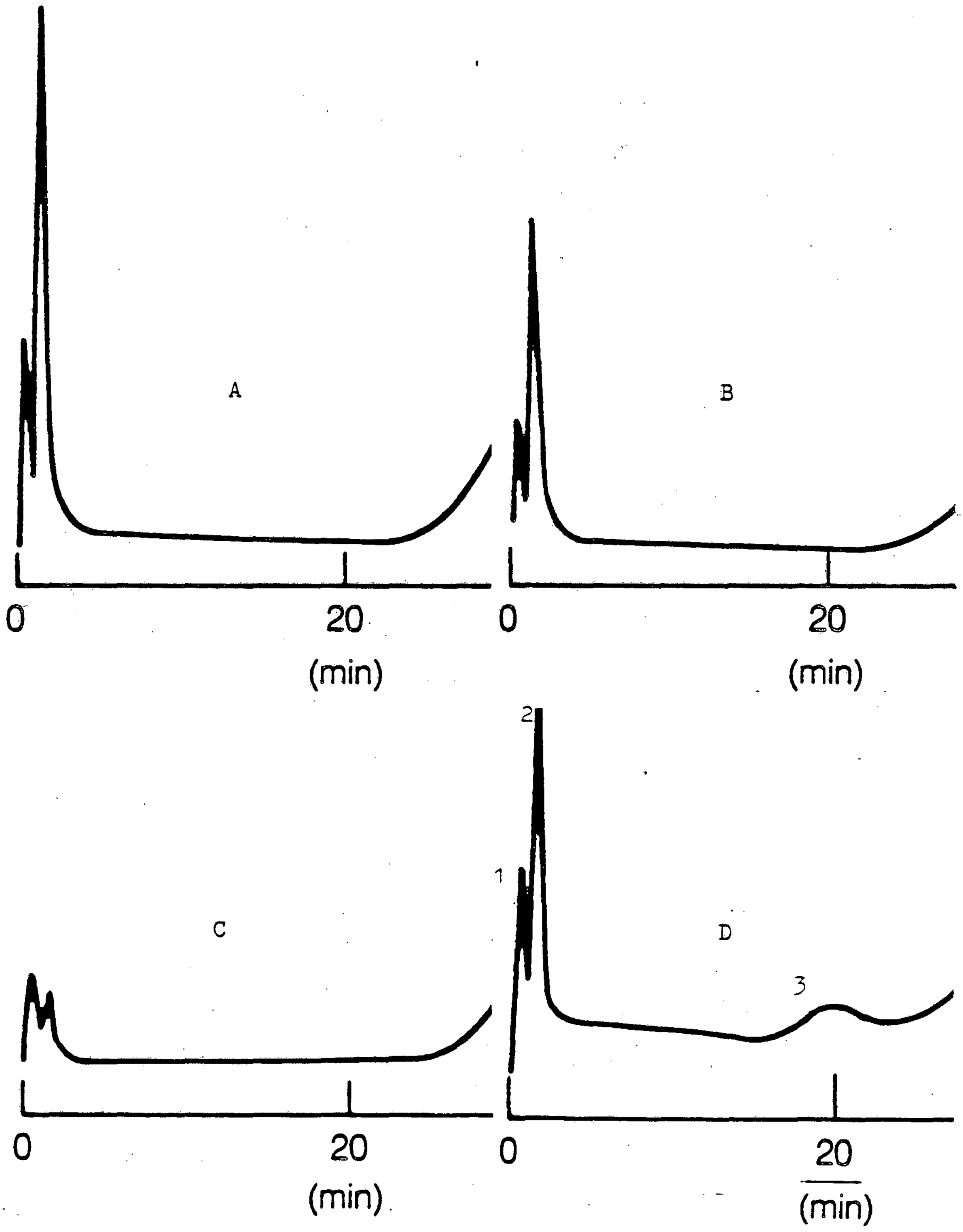

Figure 3.12: GC traces showing organic contaminants in PC. A) Na/K dried PC; B) Na/K dried PC + 0.1% water; C) Burdick & Jackson PC; D) Na/K dried PC +300 ppm propylene glycol. Peak 1: propylene oxide; Peak 2: acetone; Peak 3: propylene glycol.

3.2.2.3. $KAlCl_4$ Electrolyte

A similar procedure was used to study the electrochemical activity of water in 0.25M $KAlCl_4$ solution. The onset of a cathodic current was observed at +2.8V vs. K/K^+; no other cathodic reactions were observed in the range of +2.8 to +0.3V. As in the KPF_6 experiments several minutes had to be allowed for the limiting currents to stabilize. In this case the currents tended to drift downward for several minutes before reaching a steady state value.

The currents were measured at several rotation speeds after successive additions of water in the 0.5-10 ppm range. The $i_l/\omega^{1/2}$ plots are shown in fig. 3.13. The relationship is linear as in the case of the KPF_6 experiments, but with more uncertainty. The slopes of the Levich plots are plotted vs. added water concentration in fig. 3.14. This plot is also linear, but with some scatter. The Levich constant, calculated by least squares, is 4.1 $\mu Asec^{1/2}cm^3mol^{-1}$.

While the Levich constant for the cathodic reaction in this electrolyte is not significantly different from that in the KPF_6 the reaction potential of +2.8V indicates that a different reaction is taking place at the cathode. It has been found in solutions of $LiAlCl_4$ in sulfuryl chloride that water reacts with the $AlCl_4^-$ ion to produce HCl [21]:

$$H_2O + AlCl_4^- = AlCl_3OH^- + HCl$$

The formation of HCl was given by Law [1] as the reason for the dissolution of th stainless steel electrode in this solution. The behavior of HCl in PC has not been studied. However, the reduction of anhydrous hydrogen halides in dimethylsulfoxide (DMSO) was investigated by Michlmayr and Sawyer [22]. HCl, HBr, and HI gave well-defined cathodic potentiograms with identical reduction waves at -0.5V vs. SCE, corresponding to the reduction of hydrogen.

The diffusion coefficient calculated from the Levich equation is $1.0\text{x}10^{-5}$ cm^2/sec. This value is considerably higher than the value of

$4.3 \times 10^{-6} cm^2/sec$ found by Michlmayr and Sawyer in 0.1F tetraethylammonium perchlorate/DMSO solution. The difference is difficult to explain, since the viscosities of PC and DMSO are nearly equal. It is possible that the difference is due to the difference in the measurement method. The limiting current at a rotating disk is a function of the superficial area of the electrode, as opposed to the method of Michlmayr and Sawyer in which the calculated value of diffusivity depended on the measurement of a microscopic electrode surface area. More study of water in $KAlCl_4$ solution is needed, including further study of the diffusion coefficient.

3.2.3. Evaluation of Solvent and Electrolyte Drying

The limiting currents due to water reduction in KPF_6 solution solution were measured to determine the extent of water contamination in the electrolytes, comparing the Levich slopes to the constants drawn from figure 3.8. This analysis is useful, since almost no data exists for water contents in dried PC solutions, but several drawbacks must be kept in mind. For one, as shown above, water content can decrease over time in PC electrolytes. Another problem is the possibility of contamination of the electrolytes during handling in the glovebox. The amount of water contamination possible from dried glassware, filter paper, etc. is unknown.

Levich plots for 0.5M KPF_6 solutions dried using Na/K alloy and type 4A molecular sieves are shown in fig. 3.15. In each solution a significant amount of water was present. The water content of solutions dried using Na/K and molecular sieves was comparable . This is important, since drying with Na/K or other alkali metals often leads to degradation of the electrolyte as evidenced by a yellowish color. Molecular sieves are typically the desiccants of choice for liquids, being easier to handle and less reactive than chemical desiccants such as alkali metals and P_2O_5.

The choice of molecular sieve type for drying PC was based on an

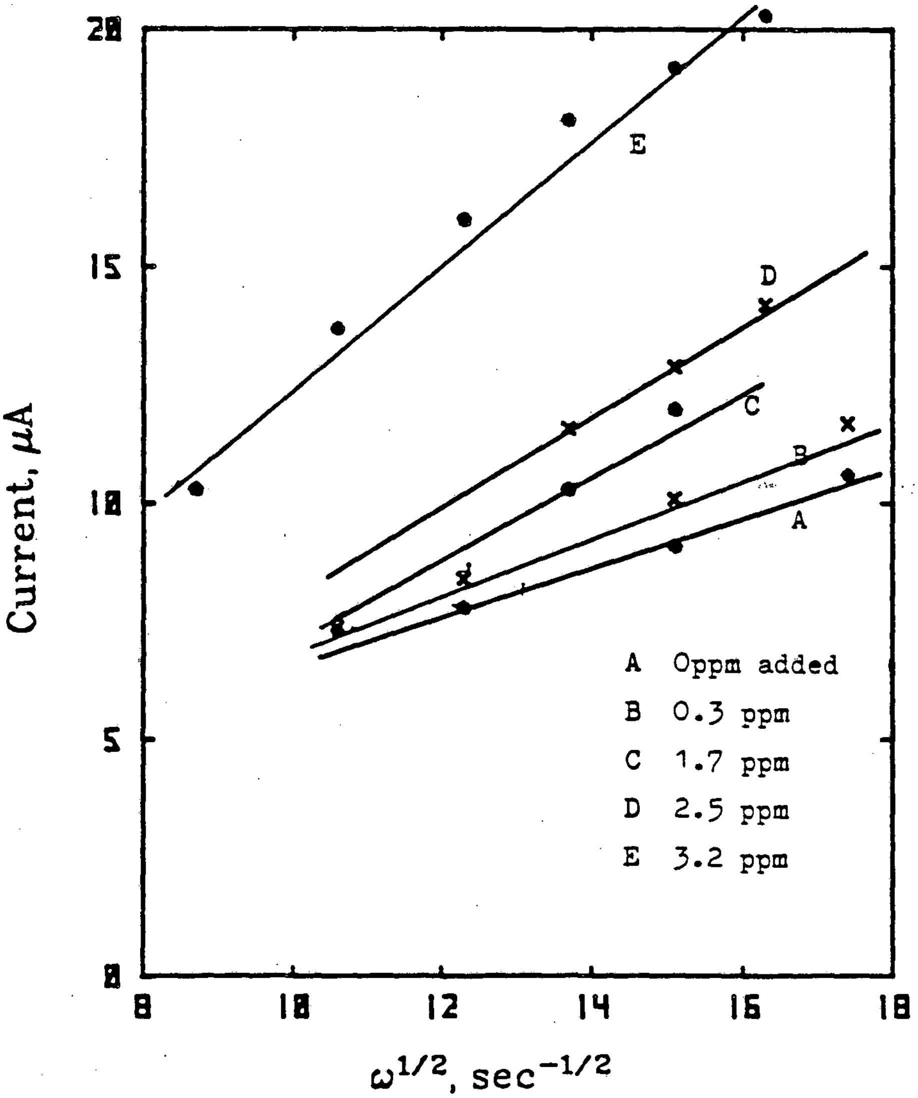

Figure 3.13: Levich plots of limiting current at +2.3V vs. K/K^+ in 0.25M $KAlCl_4$ electrolyte for varying concentrations of water; Stainless steel RDE; electrode area 0.08 cm^2.

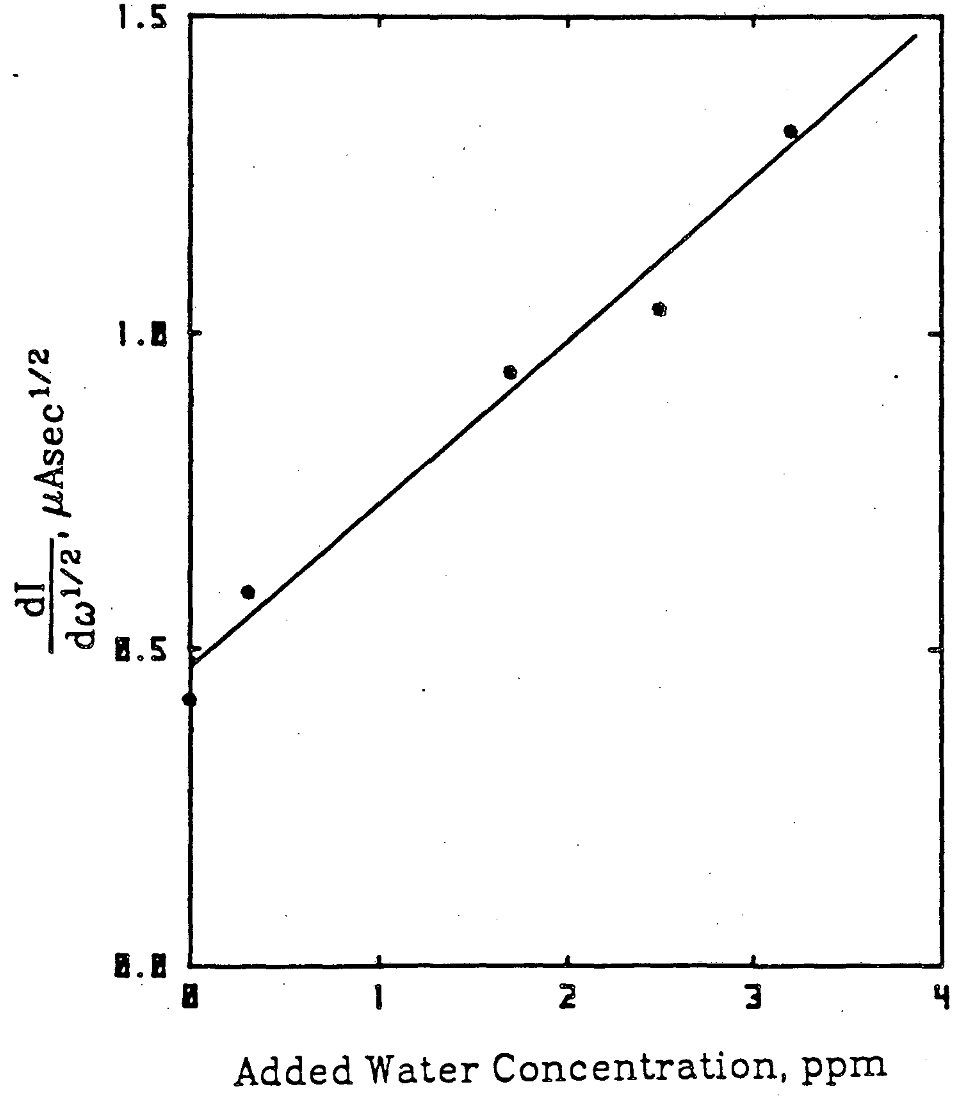

Figure 3.14: Slopes of the Levich plots from fig. 3.13 plotted vs. added water concentration.

experiment in which the temperature change of PC on exposure to several desiccants was measured. Type 13x molecular sieves and alumina have been used in this lab as the first step in the redistillation process. This was based on the assumption that the 13x sieves, with a pore size of 10 angstroms, would be able to remove light organic contaminants as well as water. When PC is run through the sieve column prior to distillation the bottom of the column becomes hot to touch. When 30 ml of Burdick & Jackson PC were contacted with 15g of type 13x molecular sieves or alumina, the temperature quickly rose by 12–15°C. This temperature rise is several orders of magnitude in excess of that expected from the absorption of 30 ppm of water, the amount found in the PC by GC analysis. Based on the heat of hydration of molecular sieves, 1 kcal/g H_2O, the temperature increase generated by the absorption of 30 ppm should be only .04°C. While the PC was known to be contaminated with some propylene oxide (approx. 50 ppm), clearly most of the heat generated was as a result of absorption of PC molecules.

By contrast, the temperature of 30 ml of PC brought in contact with type 4A molecular sieves rose by only 1.5°C. While still in excess of the temperature increase expected from the water content of the PC, this indicates far less interaction between the solvent and the sieves. The difference is important, since when PC is passed through a column of desiccant the first solvent to run down the column can get quite hot. Using type 4A sieves avoids the generation of heat which could contribute to the decomposition of PC. In addition, since fewer solvent molecules are being absorbed the type 4A sieves would have a greater capacity for water. As has been shown here, type 4A sieves are capable of drying electrolytes to close to one ppm in one stage.

Where the solvent was dried prior to the addition of supporting electrolyte, the extent of water contamination from the salt could be measured. In 0.5 M KPF_6 solution the limiting current due to water reduction was measured at 720 and 1080 rpm. The currents were 29 and 40 microamps, respectively, at the two rotation speeds. These figures both indicate an electrolyte water content of 15 ppm. That is a substantially larger amount of water than was found in the solution dried after the addition of the salt, and indicates that KPF_6 solutions will require drying no matter how dry the solvent is, if a water content in the low ppm range is needed. Based on the water content of the solution the water content of the salt was estimated as .02%. This figure is not unreasonable if one compares it to what information exists about similar salts [16].

The HCl content of the $KAlCl_4$ solution produced with Na/K dried PC was measured from the intercept of figure 3.13. The amount of HCl in the solution before the controlled additions of water corresonds to 1.5 ppm water, assuming that all of the HCl was present as a result of water contamination. This indicates that the salt is not a significant source of water contamination, since the amount of water indicated was close to the amount found in KPF_6 solutions which had been dried after the addition of salt. In the process of preparing solid $KAlCl_4$, $AlCl_3$ and KCl are fused at 500°C under dry helium. As the salts melt, residual water would react with the $AlCl_3$, producing volatile HCl. Thus the process for producing $KAlCl_4$ is self-desiccating. It is possible that the HCl detected by the limiting current measurements was present in the salt. Still, the low level of contamination demonstrates an advantage of using $KAlCl_4$ as a supporting electrolyte if dryness levels below 1 ppm are needed.

The possibility of water contamination during handling of the solutions inside the glovebox must be considered in assessing these figures. Since the water content of the glovebox atmosphere was consistently below 1 ppm the most likely sources of moisture are the materials used in the experiments. The glassware, filter paper, and the electrode itself were all carefully dried as described in section II. Given the dearth of techniques for measuring very low water concentrations, it is impossible to state what effect these materials had on the experiments. Rather, the figures for water content shown here are useful as an order-of-magnitude estimate of the amount of water which can be expected to be present in an electrolyte prepared under 'typical' research conditions.

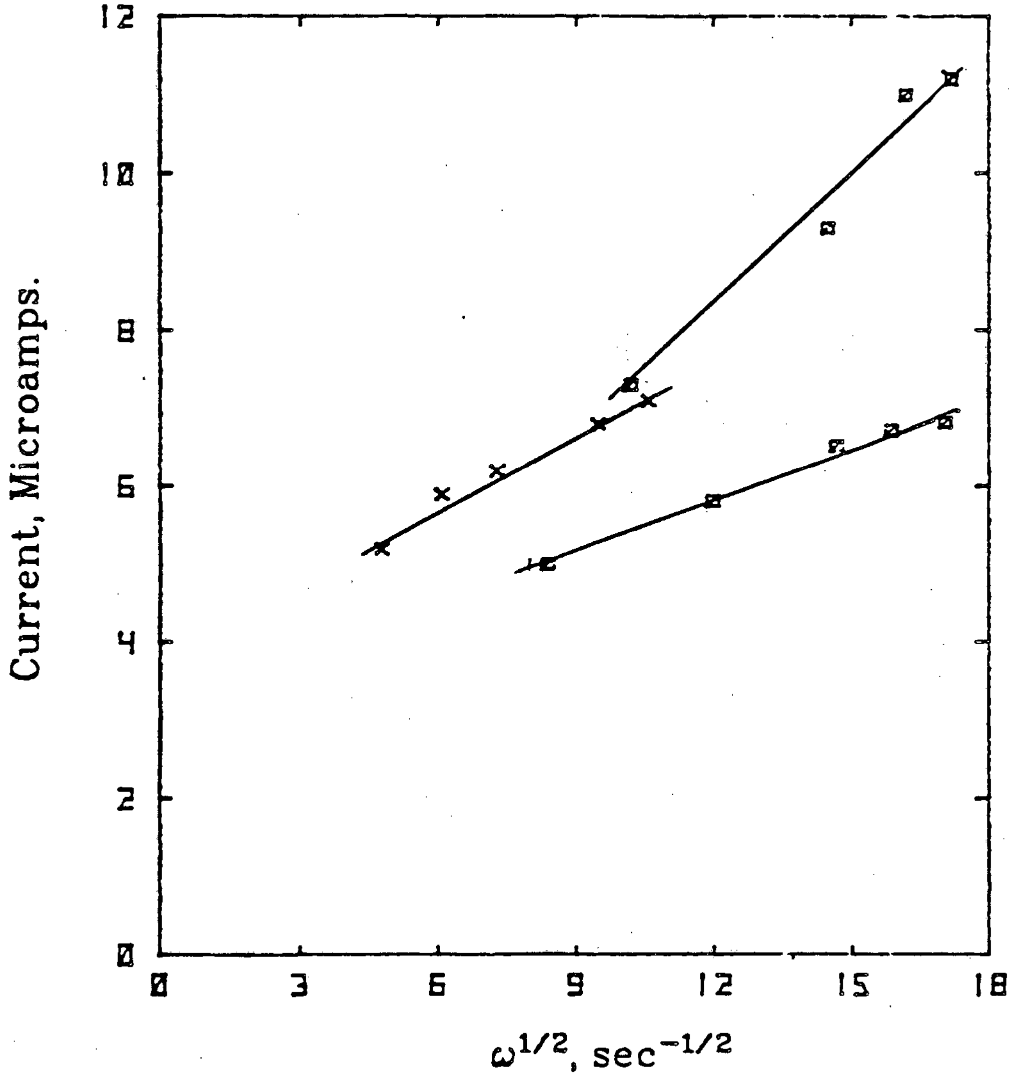

Figure 3.15: Levich plots of dried 0.5M KPF_6 solutions. A) Na/K dried, water content =2.2 ppm; B) Na/K dried, water content =0.9 ppm; C) dried over molecular sieves type 4A, water content =1.2 ppm. Currents measured at a stainless steel RDE, area =0.8 cm^2. Current measured at +0.4V vs. K/K^+.

V. Conclusions

Based on the foregoing work, the following conclusions are drawn:

1: The rate of mass-transfer controlled reduction of water to hydrogen and OH^- in KPF_6 solution can be measured at a rotating disk electrode. The cathodic current follows limiting current behavior at a potential of +0.4V vs. K/K^+. Limiting currents increase linearly with water concentration in the 5-20 ppm range, and yield a diffusion coefficient for water in the solution of 0.85×10^{-5} cm^2/sec, a figure higher than predicted from theoretical considerations.

2: Measurement of the limiting current due to water reduction in KPF_6 solution shows a gradual decrease in water concentration in the electrolyte with time. The reason for this is not understood.

3: Limiting current measurements for water in KPF_6 solution show that solutions dried using Na/K or molecular sieves contain 1-2 ppm water. It is possible that this water could be present due to contamination from materials used in handling the solutions in the glovebox. Significant water contamination is present if the supporting electrolyte is added to Na/K dried solvent, indicating that it is necessary to dry the solutions after the addition of the salt to reduce the water content to 1-2 ppm.

4: In $KAlCl_4$ solutions the limiting current due to the reduction of HCl, a product of the quantitative reaction of water with the $AlCl_4^-$ anion, has been measured. This current also responds linearly to increases in water concentration. Solutions of $KAlCl_4$ in Na/K dried PC contain 1.5 ppm water, indicating that little or no water is present in the salt.

In this work the measurement of limiting currents at a rotating disk electrode has been used to measure water concentrations in the 0-20 ppm range in PC electrolytes. This measurement technique could prove useful in studies of other nonaqueous electrolytes, since most other methods for trace determination cannot detect low ppm concentrations of water in liquids. With more accurate analysis of water concentration, it should be possible to better understand the effect of water in nonaqueous electrochemistry and evaluate methods of removing water from organic electrolytes.

This study does not answer all of the questions concerning trace water contamination in PC electrolytes. Other means for determining water content at low ppm concentrations would be useful for studying the reactions of water these solutions. F^{19} NMR spectroscopy shows promise for determining ppm levels of water and other protonated impurities if pure hexafluoroacetone were to become available.

IV. References

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Appendix: Evaluation of the Redistillation Process for PC

Vacuum distillation of PC has been used in the past to remove both water and organic contaminants from the solvent. In this section the water content of PC from several distillation runs are compared with reported results from other studies.

The process was described in detail by Hanson [2]. The vacuum distillation column (Semi-Cal series 3650, Podbielniak, Dresser Industries) was packed with stainless steel helices and kept sealed off from the atmosphere. PC (Burdick & Jackson, "Distilled in Glass") was first dried by passing 3 liters of the solvent over a column (stainless steel, 24" long, 2.5" i.d.) containing 600 cc of pretreated type 13x molecular sieves and alumina directly into the bottoms pot of the distillation apparatus. This process took about 2 hours It was then distilled at 1 torr in a flowing stream of dry helium with a bottom temperature of 140°C and a head temperature of 60°C . The middle 60% was collected for analysis and use.

The water content of PC from several distillation runs is shown in table A.1. Also shown are water concentrations of distillation runs on the same apparatus reported by Law [1] and Hanson [2]. All results were obtained using gas chromatography as described below. The difference between runs is probably due to contamination from handling of the distillation column and contamination of the sample during GC analysis.

Table A.1: Water content of redistilled PC

Date of Dist. run	H_2O content, ppm
6/13/84	12
6/19/84	<5
1/19/85	8
Law [1]	<1
Hanson [2]	<5-15

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