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R.T. Atanasoski, H.H. Law, R.C. McIntosh, and C.W. Tobias

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Electrochemical Analysis of Trace Amounts of Water in Propylene Carbonate Electrolytes

by

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ABSTRACT

Cyclic voltammetry and limiting currents to a RDE have been used for the determination of the water in the 0.3 to 20 ppm range, in PC electrolytes. Carefully dried solutions yielded voltammetric peaks proportional to the amount of water added. In KPF_6 electrolytes, the cathodic current corresponding to the reduction of water was at 0.48 V, while in $KAlCl_4$ solutions the reduction occurred already starting at 2.8 V, both relative to a K/K^+ reference. At these potentials, the current to a RDE showed Levich type dependence on rpm and was proportional to the concentration of water in the range of 0.5 to 20 ppm. The calculated diffusion coefficients of water are higher than expected: at 25°C, D_{H2O}= 8.5 ± 2 x 10^{-6} cm^2/s in 0.5 M KPF_6, while in 0.25 M $KAlCl_4$ D_{H2O}, 10 ± 2 x 10^{-6} cm^2/s.

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The determination of the water content of nonaqueous solvents is of fundamental importance for electrochemical studies in these media. The nature of the electrode process in nonaqueous systems could be altered substantially by the presence of water, especially so when reactive metals are involved. In a proposed process for electrowinning of potassium from potassium chloride in propylene carbonate(PC) electrolyte with aluminum anodes[1], the electrodeposition of potassium should not proceed at all if the water level is above 14 ppm[2]. The detection and removal of water at the ppm level is, however, a difficult problem. Water is miscible with PC (up to 8 wt%); the highly polar nature of the solvent makes the removal of the last traces of water difficult. More importantly, only few analytical methods have been shown to be suitable for the accurate determination of water at concentrations below 10 ppm. The determination of water in the presence of ionic solutes is even more difficult.

Electrochemical reduction of water in nonaqueous systems offers a direct method of determining water content since the standard reduction potential for water is much lower than that of active metals, such as 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 SCE 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 concen-

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trations (20-500 ppm, ~0.01-0.1M). In voltammetric experiments the anodic and cathodic peaks for water appeared at 1.3 V and 2 V vs. Li/Li^+, which is in the same potential range vs. SCE as found by Dey[3]. 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 [2,5,6] 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, Jansta et al. 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, products of the decomposition of PC. Unlike the reaction studied by Dey[3], and by Burrows and Kirkland[4], this reaction was found to be irreversible. The height of this cathodic peak was used to estimate water content of the solution. Water levels as low as 0.01 ppm could be detected. The reproducibility, however, was poor even at higher concentrations(below 20 ppm) and quantitative results could not be compared with theoretical expectations because of the undefined mass transport conditions.

Direct comparisons 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. Still, several observations can be made about the above studies. The reduction potentials for water were more negative than would be expected. For comparison, in aqueous solution the standard potentials for the two reactions (water and potassium reduction respectively) are -0.828 V and -2.924 V, a separation of 2.1 V. In Burrows and Kirkland study, the potential for water reduction in PC electrolyte was much closer to the alkali metal reduction and the difference was only 1.4 V. In KPF_6 solutions with water content below 20 ppm, Jansta

et al.[2] found that water reduction took place at a more negative potential, 1 V to 0.5 V vs. reversible potassium potential.

The interactions of trace water with both the solvent and the ions in the electrolyte could affect its reduction potential. Cogley et al. [7] 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.

Abolin and Kedrinskii[8] suggested that lithium is attacked by two different mechanisms, depending on water content. Geronov et al.[9] proposed that the presence of salt in PC reduces the activity of water. According to Plekhanov et al.[10], the effect of the water content on the cathodic current efficiency for lithium deposition was found to be stronger in $LiAlCl_4$ than in $LiClO_4$. More recently, Avdalyan and Povarov[11] found that in the presence of water the cathodic peak current was independent of the rotation rate of a disk electrode but was dependent on the sweep rate and on water concentration. They postulated that water in low concentration (below 0.1M) serves only as a proton donor and is not reduced cathodically, providing that the electrolyte contains an alkali metal salt. This is in contradiction to the work reported previously[2-4], in which the cathodic peak due to water reduction was reported.

The purpose of this work is to determine water at concentrations below 1 ppm to 20 ppm and its behavior in PC electrolytes using cyclic voltammetry and limiting current measurements. Besides the earlier work of Jansta et. al. [2], this question does not seem to have been getting the attention which it deserves.

EXPERIMENTAL

All experimental procedures including electrolyte preparation were performed in a dry glove box under helium atmosphere. The water content of the helium gas was continuously moni-

tored and maintained below 2 ppm by recirculating the gas through a gas purifier (Kewanee Scientific Engineering 2C1982) to remove moisture and oxygen.

Two different grades of PC were used as a starting material. Technical grade propylene carbonate (Jefferson Chemical Company), after passing through a column of dried molecular sieve (Linde, 13X) and alumina (aluminum oxide, Woelm basic, ICN), was finally purified by vacuum distillation at 3 mm Hg. This is similar to the general practice[12]. The first 10% of the distillate was discarded. The middle 60% was transferred to the glove box for use without further purification. As determined by gas chromatography(GC) analyses, we found that the distillate contained less than 1 ppm of water using the thermal conductivity detector and less than 5 ppm of propylene glycol using the flame ionization detector.

The higher grade propylene carbonate, "Distilled in Glass," was purchased from Burdick and Jackson, with a stated water content of 20 ppm. Further purification of this solvent was performed by drying with sodium-potassium alloy. The Na/K(70/30) alloy was filtered through a small hole to remove oxides prior to use. The alloy, approximately 5 g per 50 ml, 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 several days and the alloy was filtered out to obtain the clear solution. This procedure for the preparation of the solvent was applied prior to all RDE experiments.

The supporting electrolytes used in this work were KPF_6 and $KAlCl_4$. The 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; the salt gave clear colorless solutions in PC after drying at a vacuum of 10 μm Hg at 250 °C for 2 days and filtering through a glass fiber filter as well.

In the experiments with a classical distillation purification of the solvent, an additional step in the electrolyte pretreatment was performed. Before the deliberate addition of water, preelectrolysis for a period of 48 hours was performed. Solid potassium anode was dissolved at 1

mA/cm^2 and potassium was redeposited at the large surface area platinum electrode, providing a fresh potassium surface be in contact with the electrolyte all the time.

$KAlCl_4$ has been shown to be suitable for use in electrodeposition of potassium in PC [1]. The salt was prepared in this lab using a procedure outlined by Law[13]: KCl and $AlCl_3$ were fused together under dry helium at 500 °C in a quartz tube, and the melt was cooled, evacuated and stored under 1 mm Hg vacuum. When excess KCl was present, $KAlCl_4$ solutions could be cloudy and were filtered prior to use.

The reference electrode used in this study was a potassium capillary electrode described earlier[1,13]. 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. All potentials here-to-fore are referred to K/K^+ immersed in the solution under investigation.

The working electrodes used were a vibrating Pt electrode and rotating disk electrodes. The vibrating Pt electrode was simply set-up: the free hanging end of an insulated 1.3 mm diameter Pt wire was hit by the fast spinning teflon stirring bar. For rotating disk experiments two electrode materials were used: a stainless steel electrode embedded in teflon disk and a Pt electrode in an epoxy resin disk. The electrode area in both cases was 0.078 cm^2. All working electrodes were polished with 1 μm 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 Pt electrodes were cleaned in 0.1 M HNO_3, rinsed with deionized water, and dried in the vacuum oven (see refs. 13 and 14 for details).

The electrolyte volume was 12 ml for the cyclic voltammetry experiments and was 27 ml for the rotating disk electrode studies. The effect of water was determined by adding a known quantity of water to the system under investigation. A known quantity of water was first dissolved in PC, so that 3 μl of this solution added to the cell containing 20 ml electrolyte increased the water concentration in the cell by 1 ppm by weight.

RESULTS AND DISCUSSION

Cyclic Voltammetry Studies

Reproducible and consistent results were obtained at all the electrodes examined. The effect of an addition of only 0.33 ppm of water on the cyclic voltammograms is illustrated in Fig. 1. The background curve was recorded after the Pt working electrode had been kept at 0.25 V for 48 hours and the potential was cycled for approximately one hour until no further change was observed. There is no pronounced peak in the background curve. As a result, the starting voltammogram (the inner curve in Fig. 1) represents a rather featureless curve over a wide span of potential. The changes due to the addition of water appeared slowly and became more evident with each subsequent cycle. It took six minutes or twelve cycles for a series of approximately 15 identical voltammograms with well developed peaks to appear. Since these experiments were performed with strong stirring, the slow changes could not be due to the distribution of water throughout the solution. The current of the two peaks then started decreasing steadily. It took several hundred cycles to reach the same shape as prior to addition of water.

The presence of water effected dramatic changes in the voltammograms. There were two related current peaks: the cathodic at 0.25V and the anodic at 2.75V. The anodic peak has not been reported so far, whereas the cathodic peak due to water in the very negative potential region has been previously described in the literature [2,15]. The cathodic and anodic peaks were mutually dependent(Figs. 2 & 3). The influence of the sweep rate on the peak heights is presented in Fig. 2. The voltammograms were obtained after the addition of 1 ppm of water and were recorded during the period in which reproducible curves with fully developed peaks were obtained. It appears that (i) the area under the peaks is directly proportional to the sweep rate, and (ii) the ratio of the areas of anodic and cathodic peaks remains constant. Along with the fact that the peak separation is 2.5 V, this suggests that the product of the reduction reaction due to the addition of water does not diffuse away and is bound to the surface and oxidized in the anodic region. With cycling, the electrode active area was enlarging until an equilibrium was attained. The charge associated with each peak is about 45 μC, corresponding to only one

fifth of a monolayer coverage. This charge is related to the bulk water content, since the charge of the fully developed peaks with 0.33 ppm of water (Fig. 1) is approximately 15 μC. The maximum of the peak current is also directly proportional to the water content.

More insight to the interdependence of the peaks could be obtained by shifting the anodic limit of the scan in the negative direction to the onset of the anodic peak (Fig. 3). The omission of the anodic peak resulted in a faster disappearance of the cathodic peak, suggesting that the electrode surface was gradually blocked. To probe the passivity of the electrode surface, more water was added. The peak was shifted more positive, from 0.2 to 0.45 V and the maximum of the peak current was slightly lower than that of the sweeps with higher anodic limit, i.e., with the anodic peak in. Thus the surface film was "transparent" to newly added water, which mean that the electrode was blocked in the previous runs. In addition, there was no delay in establishing the maximum peak current, confirming that the distribution of water throughout the solution under strong stirring was fast. The extinguishing of the water effect on the voltammograms in the narrower potential span was much faster. The cathodic current maximum in the potential range of 0.03V-1.08V is proportional to the quantity of added water (Fig. 4). Indeed the relationship between the water present and the cathodic current is linear. The currents obtained in the 0.3-3 ppm H_2O region after the subtraction of the background, are presented in Fig. 5. As expected for the presence of such low concentrations of water, a linear relationship was observed, suggesting the diffusional limitation of the reacting components. The straight line passing through the origin suggests that there was no detectable water present (down to less than 0.1 ppm) before any of the experiments, i.e, the system consumes water in such a manner that its presence could not be detected by the potential sweep method.

The data presented are in general agreement with those presented by Jansta et al.[2], proving that even with this simpler and more commonly used method of electrolyte preparation one can obtain good results. The peaks in the potential sweep data can be explained tentatively by hydride formation. The potential of hydride ion formation from hydrogen (-2.23 V standard aqueous potential[16]) corresponds to the onset of the cathodic peak (Fig. 2). The hydride could

be formed from the recombination of adsorbed atomic hydrogen with elemental potassium, deposited at the working electrode via an underpotential mechanism. This assumption is supported by the sharp rise of the cathodic current after the water reduction peak, but below the reversible potential of potassium. The potassium hydride, probably insoluble in PC, formed on the electrode surface and could be subsequently oxidized creating the anodic peak. Thus the formation of hydride could cause the two peaks observed.

RDE Studies

The potential sweep analysis provides a method for determining the water content up to 3 ppm. The linear relationship between the concentration of water and the cathodic current at 0.48 V (Fig. 5) implies that the reaction is under diffusional transport control. Thus we investigated the reaction of water with limiting current measurements using rotating disk electrodes.

The voltammograms from slow potential scans (2 mV/s) at a stainless steel RDE are shown in Fig. 6 for several rotation speeds. The steep increase of the current occurred between 0.8 V and 0.5 V in agreement to the cyclic voltammetry data; limiting current behavior would be expected at potentials below 0.5 V. These voltammograms do not show limiting current behavior. To determine whether limiting current behavior was followed in the potential range of 0.1 to 0.4 V, currents were measured at several rotation speeds at 0.1 V, 0.3 V, and 0.4 V, after allowing several minutes to reach a steady state. The results of these measurements are shown in Fig. 7 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 0.4 V, and that true limiting current behavior is followed. Thus the absence of a plateau in the current vs. voltage curves of Fig. 6 appears due to the mass transport not reaching a steady state.

Once it was established that limiting current behavior was followed at 0.4 V, their values were measured by stepping the potential to 0.4 V. Using this procedure several minutes had to be allowed for the currents to increase slowly to constant values which were recorded. Typically currents drifted upward by several μA before reaching steady state.

The response of the current measured at 0.4 V to additions of water in the range of 1-15 ppm at a single rotation speed is shown in Fig. 8. The relationship is linear, as predicted by the Levich equation, with a slope of 53.6 $A-cm^3/mol$. There is some scatter in the points at the lowest concentration which could be related to the transient features seen in the voltammograms.

A more complete and precise calibration for water is shown in Figs. 9 and 10. The limiting currents (I_l) 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 Fig. 9. These curves are linear at rotation speeds up to 2800 rpm, indicating that a true limiting current is being measured. The lines show 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 $I_l/\omega^{1/2}$ slopes are plotted vs. added water concentration in Fig. 10. The slope of Fig. 10 gave the Levich constant, $I_l/(C\omega^{1/2})$. This was calculated by least squares to be 3.6 $\mu As^{1/2}cm^3mol^{-1}$. The same constant based on least squares fit of Fig. 8 is 3.1 $\mu As^{1/2}cm^3mol^{-1}$. The difference in the two figures (15%) could be due to the greater uncertainty in Fig. 8. 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. 10 was used for calibration purposes. The 95% confidence limits of the slope of Fig. 10 were $\pm 11\%$, indicating an excellent linear fit.

The electrochemical activity of water in 0.25M $KAlCl_4$ solution was also investigated with limiting current measurements using rotating disk electrodes. The onset of a cathodic current was observed at +2.8 V vs. K/K^+; no other cathodic reactions were observed in the range of +2.8 to 0.3 V. 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. 11. The relationship is linear as in

the case of the KPF_6 electrolytes, but with more uncertainty. The slopes of the Levich plots are plotted vs. added water concentration in Fig. 12. This plot is also linear, but with some scatter. The Levich constant, calculated by least squares, is 4.1 $\mu As^{1/2} cm^3 mol^{-1}$.

While the Levich constants for the cathodic reaction in $KAlCl_4$ and KPF_6 electrolytes are not significantly different, the potentials where the two reactions occur are two volts apart. Different reactions must have occur. In KPF_6 solutions, similar current response was observed on stainless steel and Pt electrodes, demonstrating that the electrode material does not play a major role. The formation of potassium hydride is likely to be the reaction, as discussed earlier. In $KAlCl_4$ solutions, the HCl from the hydrolysis of $AlCl_4^-$ [17] is likely to provide the hydrogen ions for the reduction process. 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 [18]; HCl, HBr, and HI gave well-defined cathodic potentiograms with identical reduction waves at -0.5 V vs. SCE, corresponding to the reduction of hydrogen ions.

Diffusivity of Water

In KPF_6 solution, the diffusivity of water was calculated, based on a solution density assumed equal to that of PC and a solution viscosity of 3.8cP[19] and was found to be 8.5 x 10^{-6} cm^2/s. The correlation of King et al.[20] is often used to estimate molecular diffusivities in nonaqueous solvents:

$$D_{AB} = 4.4x10^{-12}[T/\mu_B][V_B/V_A]^{1/6}[\Delta H_B/\Delta H_A]^{1/2} \quad m^2/s$$

where:

T = Temperature, °K
μ_B = solvent viscosity, cP
V_A, V_B = solute and solvent molal volumes, cm^3
$\Delta H_{A,B}$ = solute and solvent molar heats of vaporization

This gives an estimate of 0.4 x 10^{-5} cm^2/s 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 0.6 x 10^{-5} cm^2/s. One possible reason why the King equation predicts a diffusivity 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 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 takes 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.[21] using NMR and IR spectroscopy at fairly high concentrations of water (0.1-3.5 M). In this work 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 does not seem that water molecules are strongly bonded in PC-water complexes, which means that water should not react at such negative potentials.

The situation is further complicated by the addition of an electrolyte. One major effect of adding a solute is the increase of the viscosity of the solution. Another factor which could be important is that some of the hydrogen bonding sites on the PC molecule (i.e. carbonyl groups) are participating in the solvation of cations. Since a liquid solution of PC is approximately 11 M in PC, a significant fraction of the electron donor sites would participate in the solvation of cations in a 0.5 M 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. Cogley et al.[7] 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 1 the literature values of diffusion coefficients of water in several polar solvent are listed, along with the calculated values of $D\mu/T$. It can be seen that $D\mu/T$ is much higher for 0.5 M KPF_6 than for most of the solvents listed, with the exception of aniline. Aniline 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 $D\mu/T$

calculated in this work for water in 0.5 M KPF_6/PC is unusually high but not physically impossible in an organic solvent.

In $KAlCl_4$ solution, the diffusion coefficient calculated from the Levich equation is 10 x 10^{-6} cm^2/s, higher than the value of 4.3 x 10^{-6} cm^2/s found by Michlmayr and Sawyer[18] in 0.1 F tetraethylammonium perchlorate/DMSO solution. Since the viscosities of PC and DMSO are nearly equal, it is possible that the discrepancy is due to different measurement methods.

Reaction of Water with Electrolyte

Similar to the findings in the potential sweep experiments, water was found to gradually "disappear" from the electrolyte in the RDE experiments as well. 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; the decreases in water content took place after the alloy had been removed by filtration.

In a 0.5 M KPF_6 solution, Levich plots were obtained after 10 ppm of water was added and one day later (Fig. 13). The water content at day 2 was calculated to be 7.5 ppm, indicating a loss of 2.5 ppm. Then more Levich plots were obtained with extra additions of water. In Fig. 14, Levich slopes are plotted vs. added water concentration. The y-intercept of the points of day 2 is negative, confirming the loss of water to be 2.5 ppm. This shows that the decrease in limiting current measured was not due to the loss of active electrode area.

A possible cause of the decrease in water concentration is the hydrolysis of PC [23], a reaction known to take place in the presence of acid or base:

$$PC + H_2O = H_3C-CHOH-CH_2OH + CO_2.$$

Gas chromatographic analysis failed to confirm that a significant amount of water was consumed in this reaction. An amount of 0.1% 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 solvent. Fig. 15 shows the GC traces of the Na/K dried PC, of the same PC with 0.1% water added, of PC as received from Burdick & Jackson, and of the Na/K dried PC with 300 ppm of propylene glycol added. These results show 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. Thus extensive hydrolysis does not take place in pure PC. They do not, however, account for any effects that the solute may have on the solvent. Using GC analysis for organic contamination in electrolytes is not meaningful since the solvent decomposes in the column giving spurious peaks.

CONCLUDING REMARKS

Results of voltammetric experiments and of rotating disk studies show a self-consistency and reproducibility with one important feature in common: a current response proportional to the quantity of water added to the electrolyte, clearly indicating mass transport control of its reduction at the cathode. The rotating disk data in KPF_6 solutions could be considered as a main accomplishment in this respect, with nearly perfect demonstration of Levich type of behavior.

There is, however, an important question left to be answered in order to correlate the results which are reflecting the bulk behavior of water(such as its diffusivity), with its electrode reaction taking place at the very negative potentials. Is water reacting like any other low level impurity in PC with the only limitation being its rate of diffusion? A strong interaction with PC will contribute to the very negative potential for water reduction; however, this does not go along with the high diffusivity of water found in the RDE study. Hence, additional factors, such as the properties of the electrode surface have to be considered.

Most of the published results[24,25] as well as our experimental evidence[26] suggests that at potentials of 0.4 V vs. potassium reversible potential, the electrode surface is covered with some type of a film. If nothing else, a film due to the reduction of the solvent until a layer adequate

for preventing further attack is formed. The presence of water could be considered as an additional source for passivation. However, the passive film has to be somewhat transparent to water reduction, at least at the beginning of the reaction. The cyclic voltammetry experiments show an increase of the activation state of the electrode proportional to the water content and suggests that the electrode surface undergoes substantial adjustment to the amount of water present. Though the RDE experiments reveal mass transport control and the results are not affected by the state of the surface activation, the extended period of time required to get these electrodes to reach steady state suggests that some adjustment of the electrode surface takes place as well. Further non-electrochemical studies of this multicomponent system are required in order to answer this type of question. A direct spectroscopic study of the film formation on the electrode surface should help to distinguish the interaction between PC and water in the bulk and at the electrode surface.

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Table 1
Values of Diffusivity for Water in Various Solvents

	D $cm^2/s x10^5$	T °C	μ cP	$D\mu/T$ dynes/° $x10^{10}$
Ethanol	1.10	25	1.10	4.10
Methanol	2.20	20	0.60	4.50
Pyridine	1.50	20	0.97	5
Acetone	5.50	25	0.32	5.90
n-Propyl Alcohol	0.80	20	2.30	6.30
Aniline	0.70	25	4.40	10.30
0.5M KPF6/PC	0.85	25	3.80	10.80

All single solvent D and μ values are from [22]; the electrolyte value for D is from this work; Electrolyte μ value is from [19].

FIGURE CAPTIONS

Fig. 1. Cyclic voltammograms of a vibrating Pt electrode (1.14 cm^2) in pre-electrolyzed 0.5 M KPF_6 before (dashed lines) and after the addition of 0.33 ppm of water; outer curve: twelveth cycle; 260 mV/s; reference electrode: K/K^+ in same solution.

Fig. 2. Effect of sweep rate on cyclic voltammograms of a vibrating Pt electrode in 0.5 M KPF_6 with 1 ppm of H_2O; (1) 65 mV/s, (2) 130 mV/s, (3) 260 mV/s.

Fig. 3. Influence of potential range on cyclic voltammograms of vibrating Pt electrode in 0.5 M KPF_6 with 0.33 ppm of H_2O; 260 mV/s; outer curve--first cycle after the anodic limit was made more positive(see Fig. 1 for comparison); dashed lines-eighth cycle.

Fig. 4. Effect of the amount of added water on cyclic voltammograms of vibrating Pt electrode in 0.5 M KPF_6; (1) before the addition of H_2O, (2) 1 ppm H_2O, (3) 2.33 ppm H_2O; 200 mV/s.

Fig. 5. Dependence of cathodic current (Fig. 4 at 0.48 V, background subtracted) on the amount of water added.

Fig. 6. Current vs. voltage curves for slow (2mV/s) potential scans in 0.5 M KPF_6 solution; stainless steel rotating disk electrode(0.078 cm^2) A) 1000 RPM, B) 2000 RPM, C) 2880 RPM. Reference electrode: K/K^+.

Fig. 7. Current vs $\omega^{1/2}$ measured at several potentials in 0.5 M KPF_6 solution containing 6.05 ppm added H_2O; stainless steel rotating disk electrode(0.078 cm^2).

Fig. 8. Current vs. added concentration of water in 0.5 M KPF_6 solution; current measured at 0.4 V vs. K/K^+; stainless steel rotating disk electrode(0.078 cm^2); 2880 RPM.

Fig. 9. Current vs. $\omega^{1/2}$ in 0.5 M KPF_6 solution containing containing 6.5 - 25 ppm of added water; current measured at 0.4 V vs. K/K^+; stainless steel rotating disk electrode(0.078 cm^2).

Fig. 10. Slopes of Levich plots from Fig. 9 vs. added concentration of water.

Fig. 11. Levich plots of limiting current at 2.3 V in 0.25 M $KAlCl_4$ electrolyte containing 0 - 3 ppm of added water; stainless steel rotating disk electrode(0.078 cm^2).

Fig. 12. Slopes of Levich plots from Fig. 11 vs. added concentration of water.

Fig. 13. Current vs. $\omega^{1/2}$ for showing apparent decrease in water concentration; (A) day 1, 10 ppm H_2O added, (B) day 2; 0.5 M KPF_6 solution; stainless steel rotating disk electrode(0.078 cm^2) at 0.4 V.

Fig. 14. Slopes of Levich plots vs. added concentration of water for showing apparent decrease in water content; 0.5 M KPF_6 solution; Day 1, from Fig. 13.

Fig. 15. GC traces showing organic contaminants in PC. (A) Na/K dried PC, (B) Na/K dried PC+0.1% H_2O, (C) Burdick & Jackson PC, (D) Na/K dried PC+300 ppm propylene glycol: peak 1, propylene oxide; peak 2, acetone; peak 3, propylene glycol.

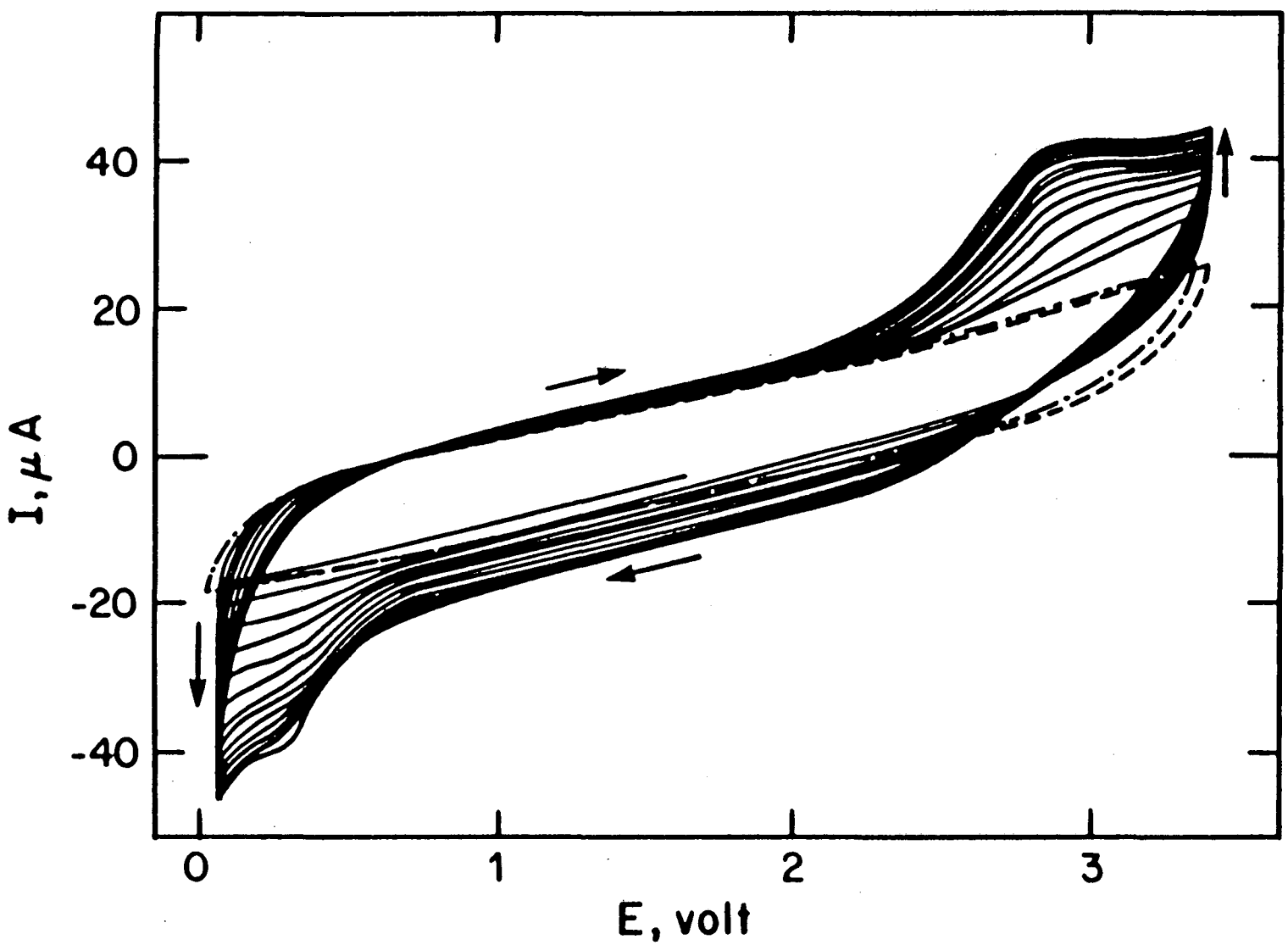

Fig. 1

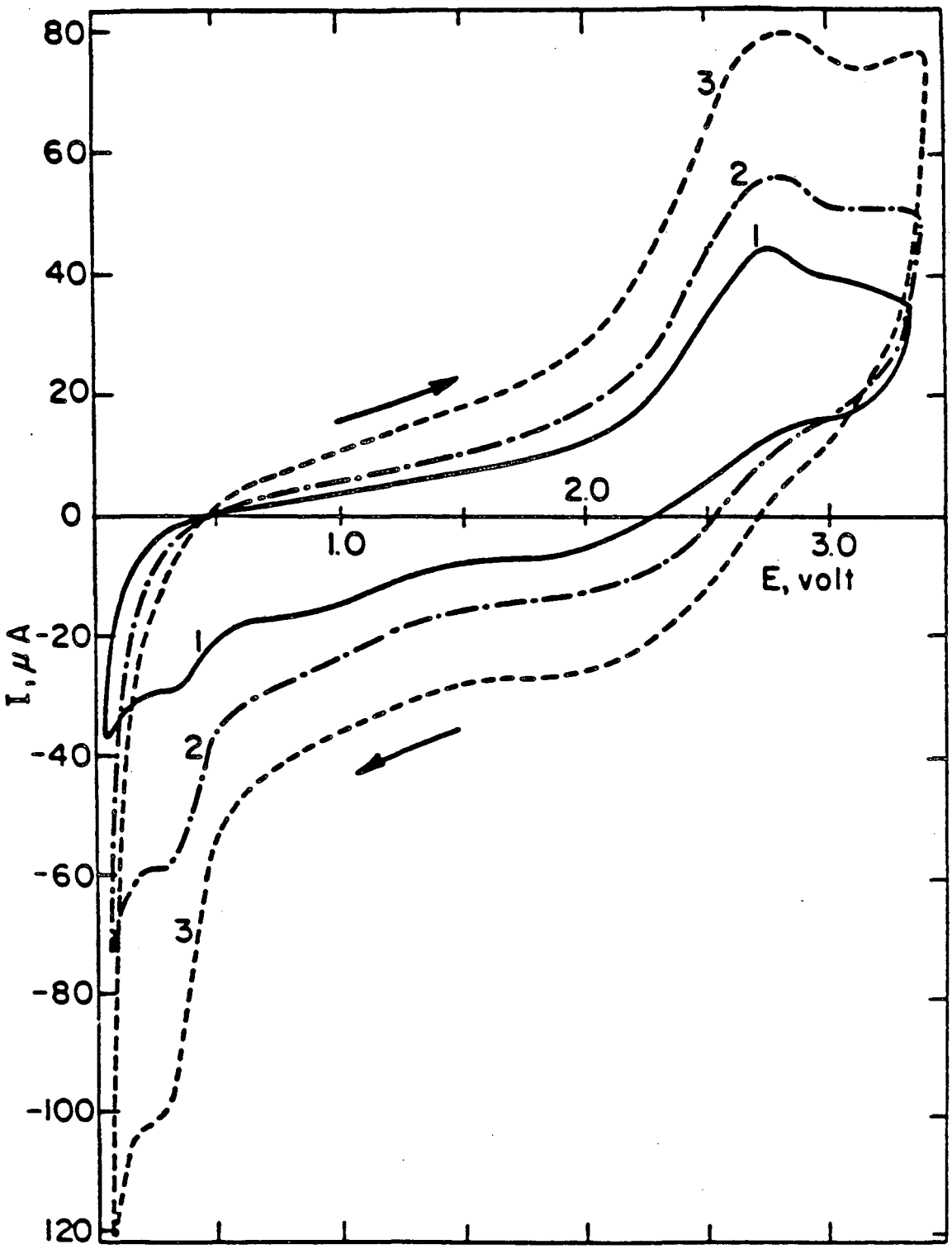

Fig. 2

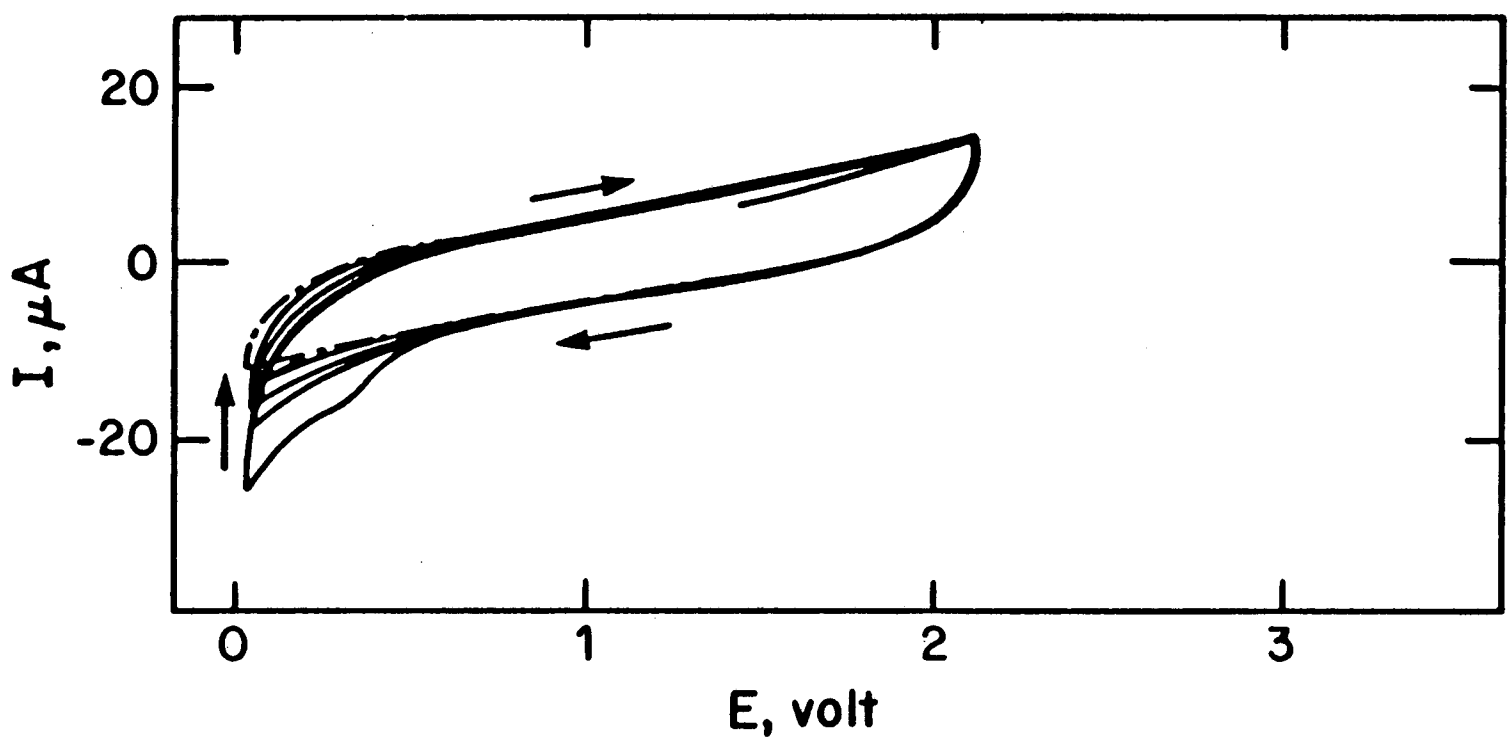

Fig. 3

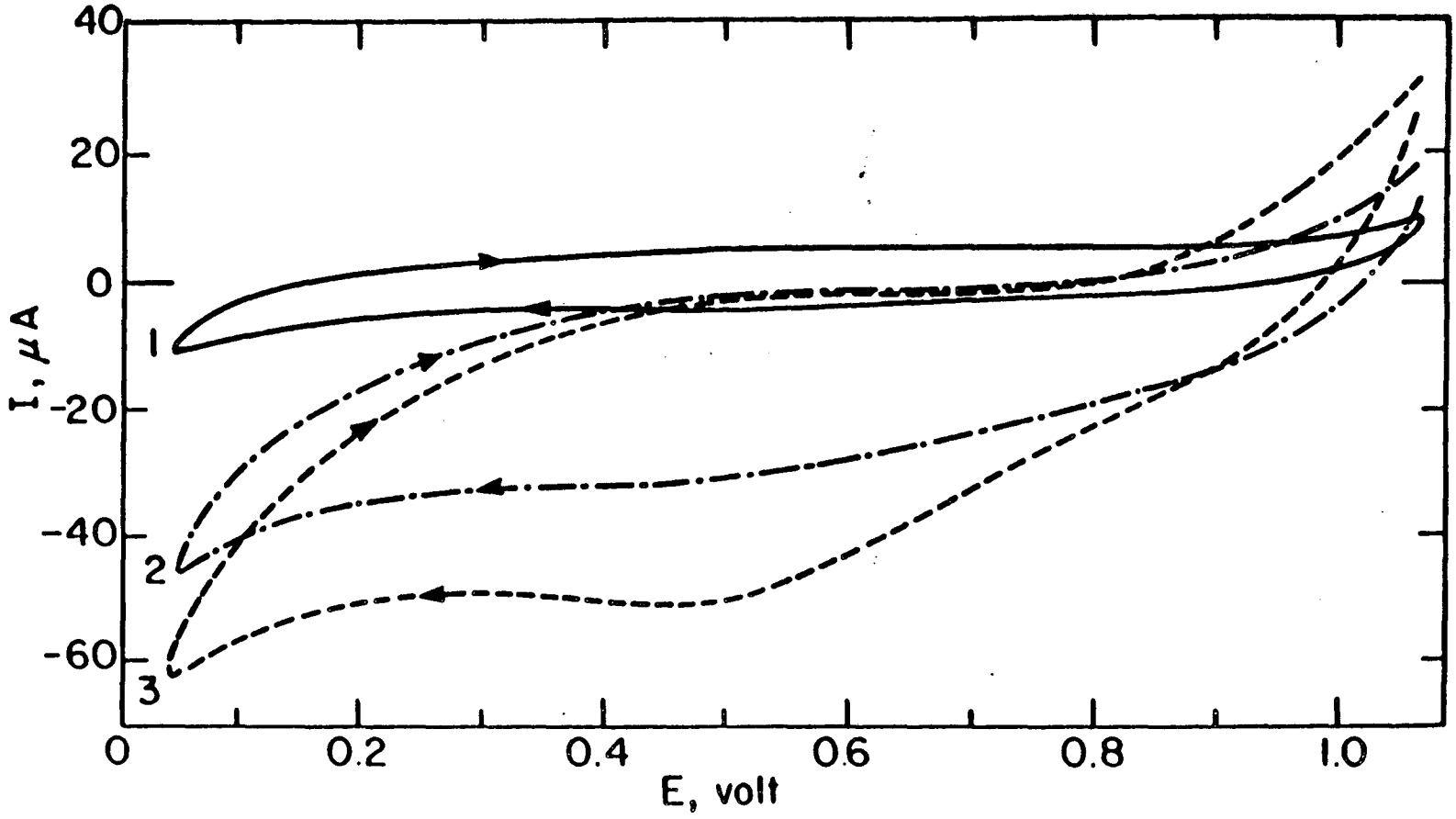

Fig. 4

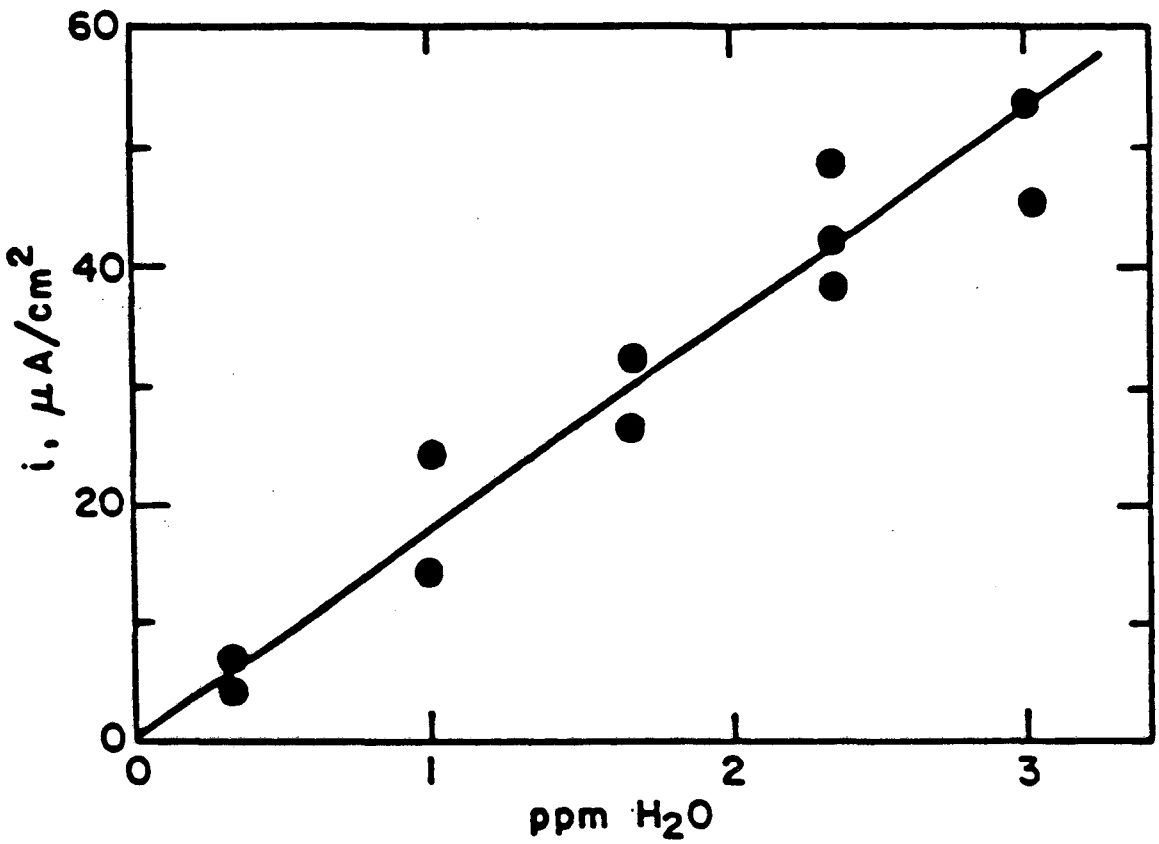

Fig. 5

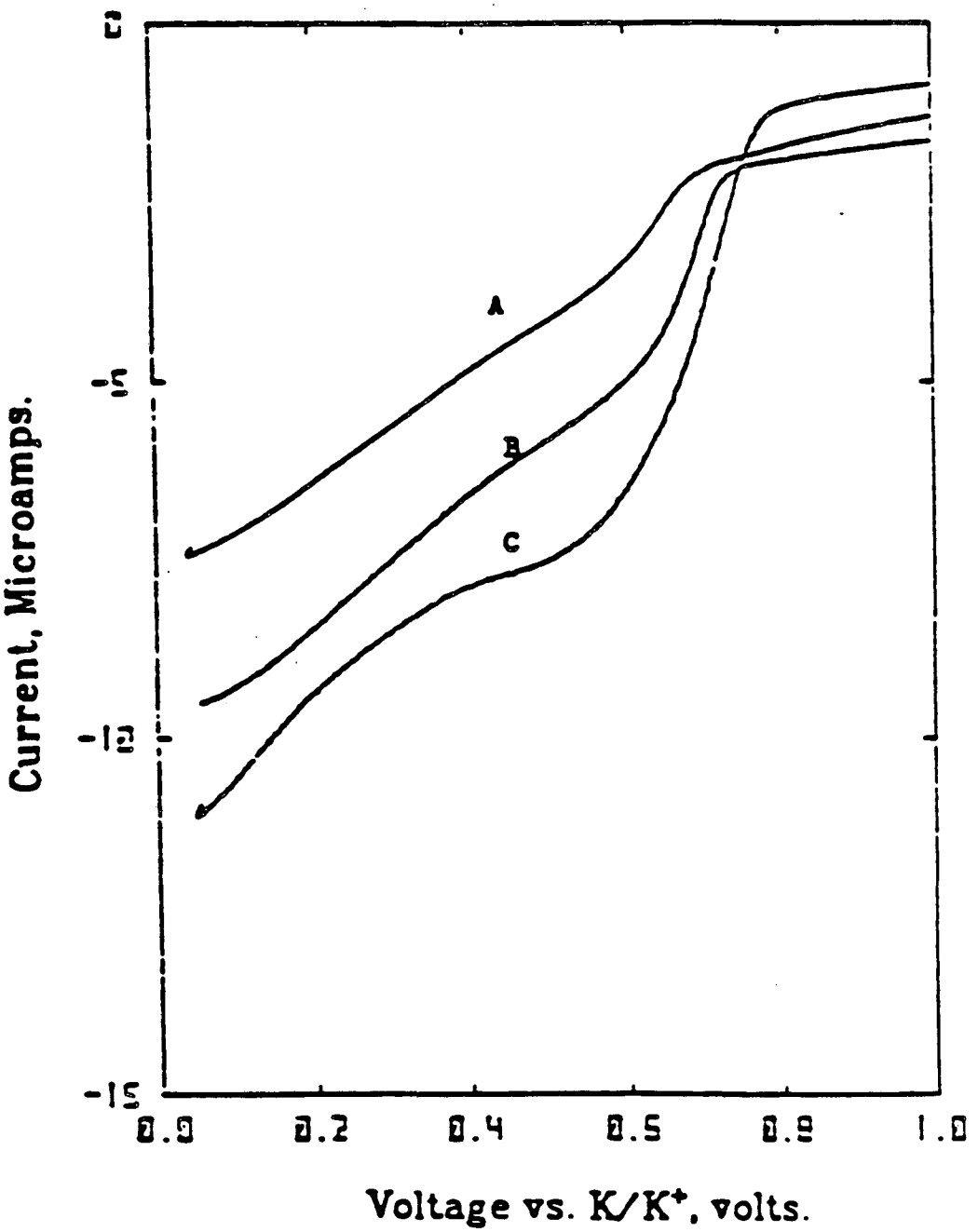
0
-5
-10
-15
0.0
0.2
0.4
0.6
0.8
1.0
A
B
C
Current, Microamps.
Voltage vs. K/K+, volts.

Fig. 6

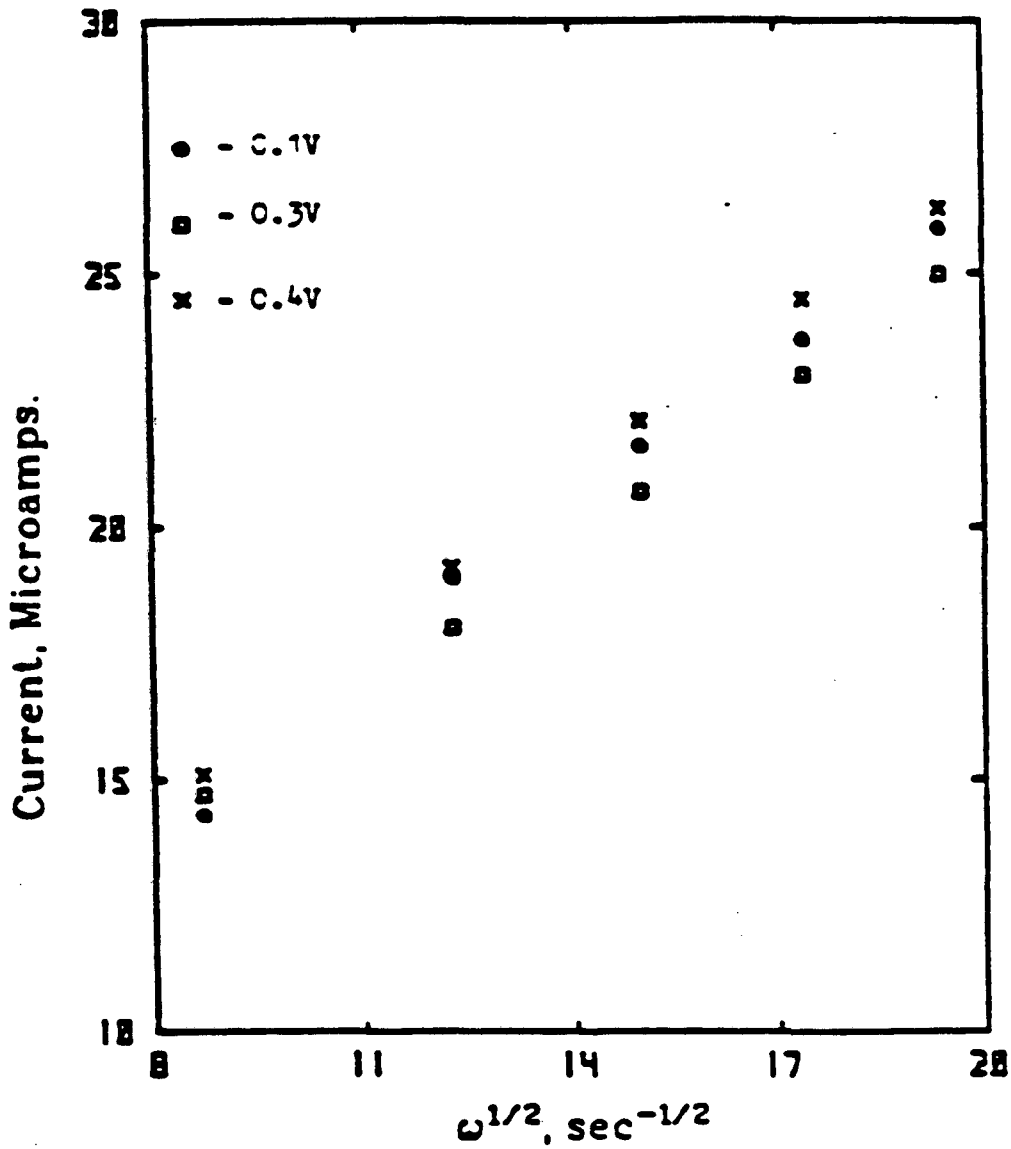
30
25
20
15
10
8
11
14
17
20
● - 0.1V
■ - 0.3V
× - 0.4V
Current, Microamps.
$\omega^{1/2}$, $sec^{-1/2}$

Fig. 7

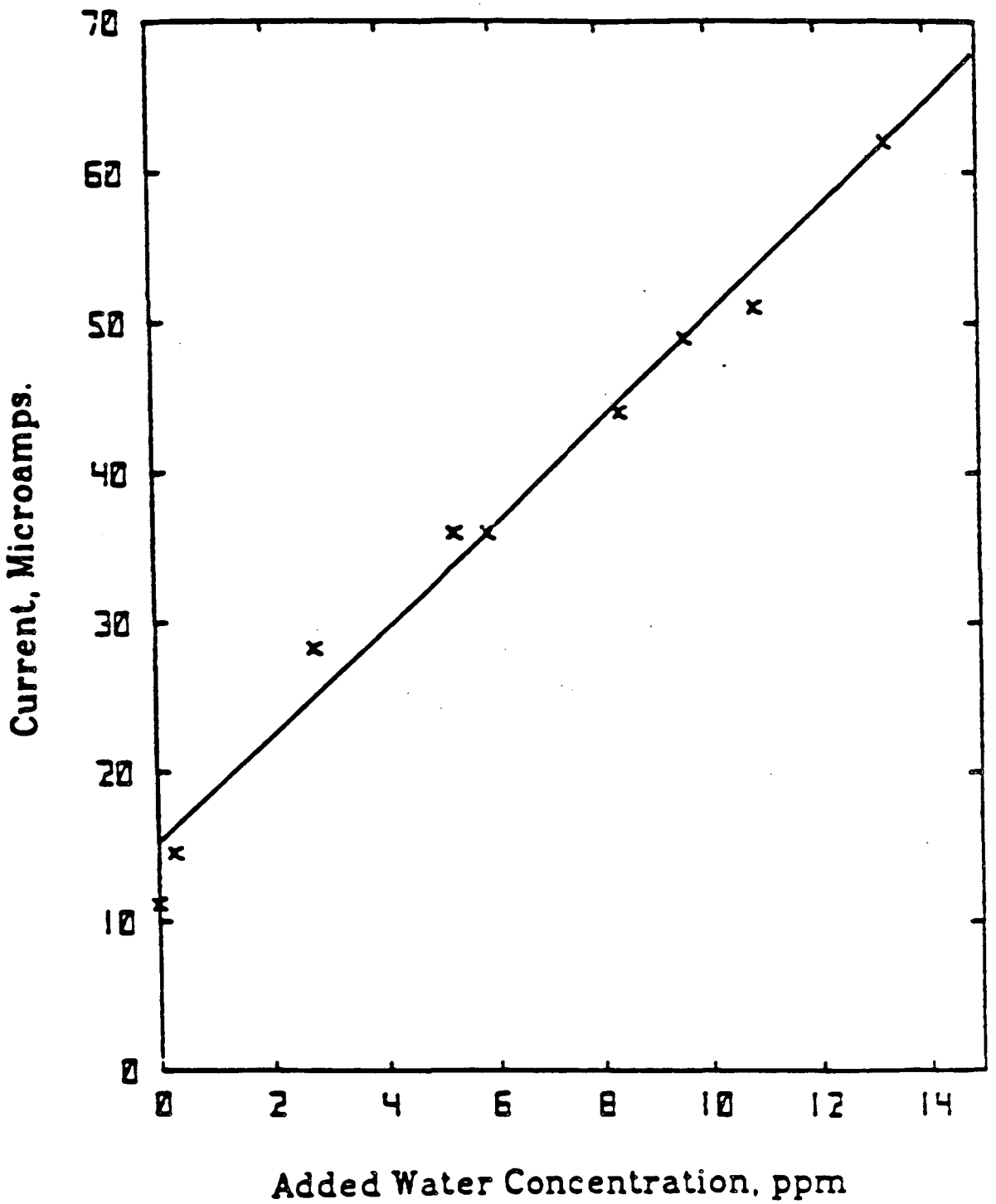
70
60
50
40
30
20
10
0
Current, Microamps.
0
2
4
6
8
10
12
14
Added Water Concentration, ppm

Fig. 8

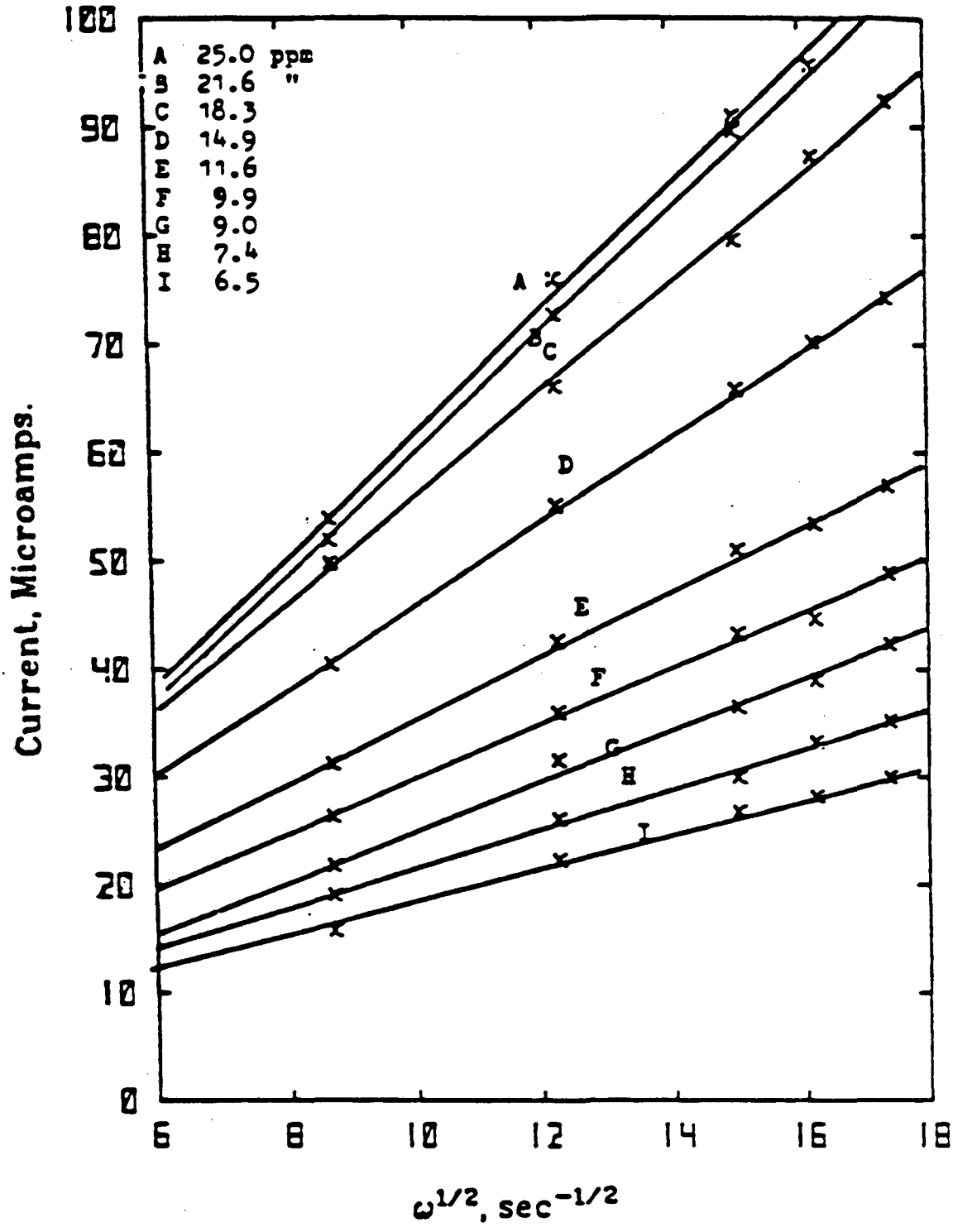
A 25.0 ppm
B 21.6 "
C 18.3
D 14.9
E 11.6
F 9.9
G 9.0
H 7.4
I 6.5
Current, Microamps.
$\omega^{1/2}$, $sec^{-1/2}$
0
10
20
30
40
50
60
70
80
90
100
6
8
10
12
14
16
18

Fig. 9

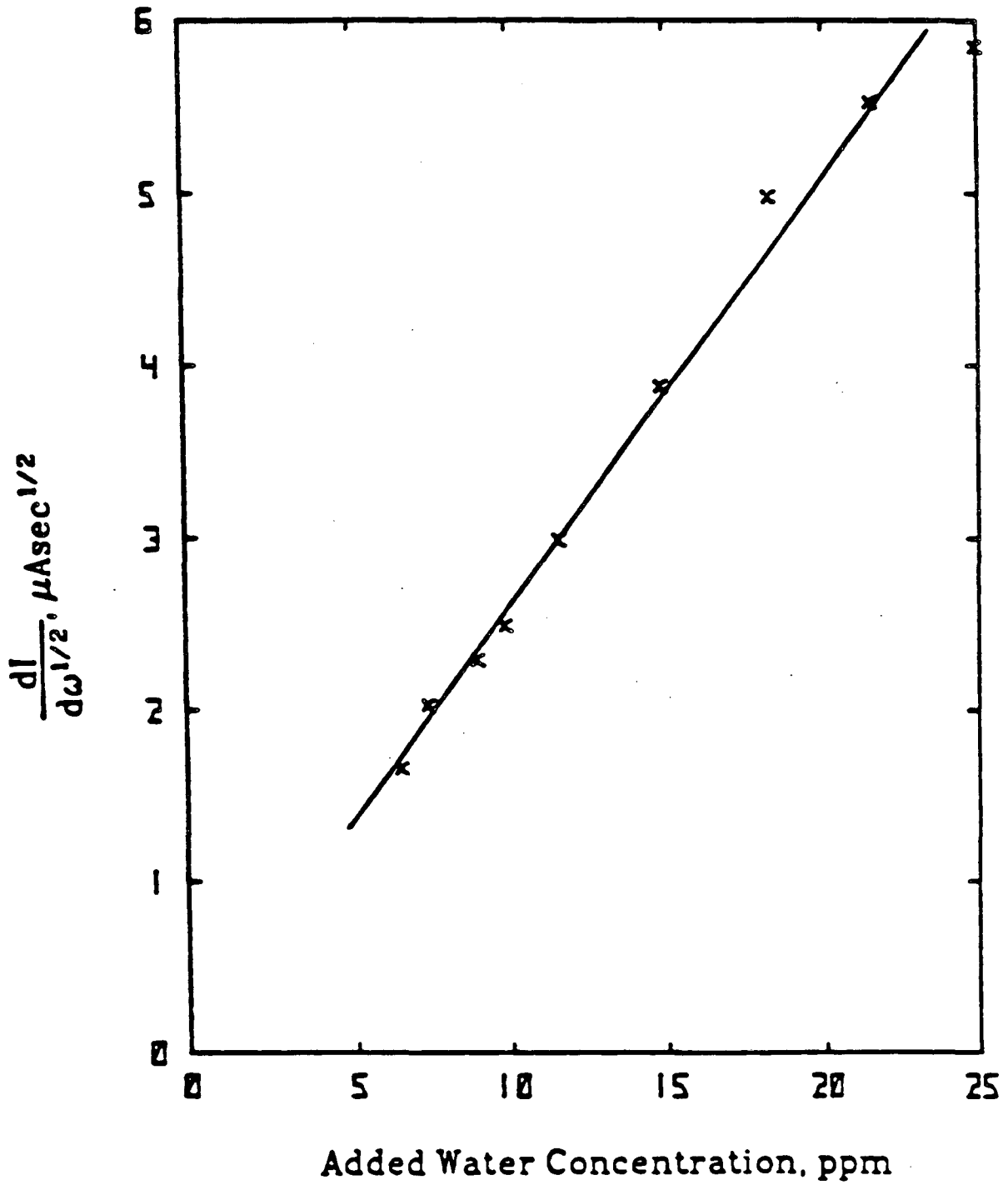
6
5
4
3
2
1
0
0
5
10
15
20
25
$\frac{dI}{d\omega^{1/2}}$, $\mu Asec^{1/2}$
Added Water Concentration, ppm

Fig. 10

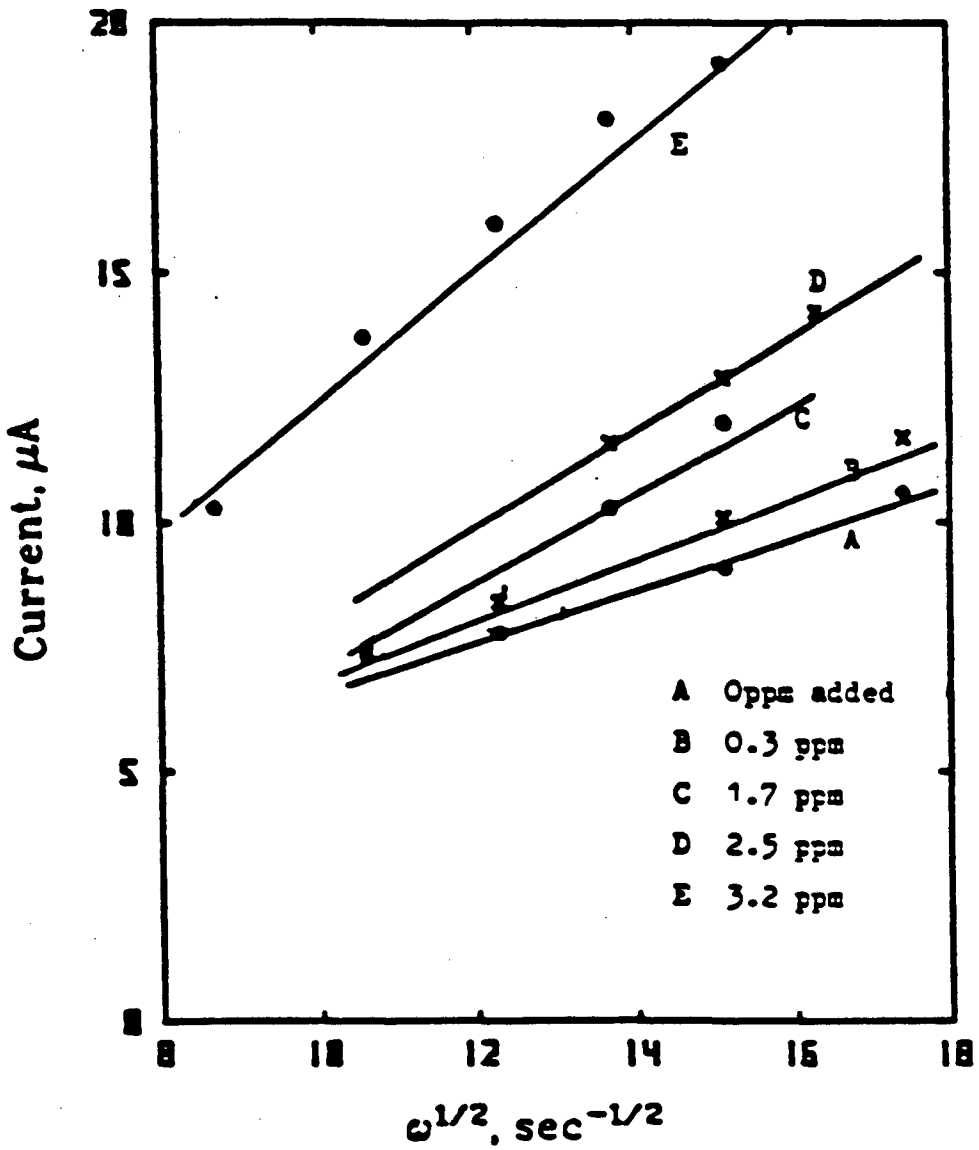
20
15
10
5
0
8
10
12
14
16
18
Current, μA
ω^1/2, sec^-1/2
E
D
C
B
A
A 0ppm added
B 0.3 ppm
C 1.7 ppm
D 2.5 ppm
E 3.2 ppm

Fig. 11

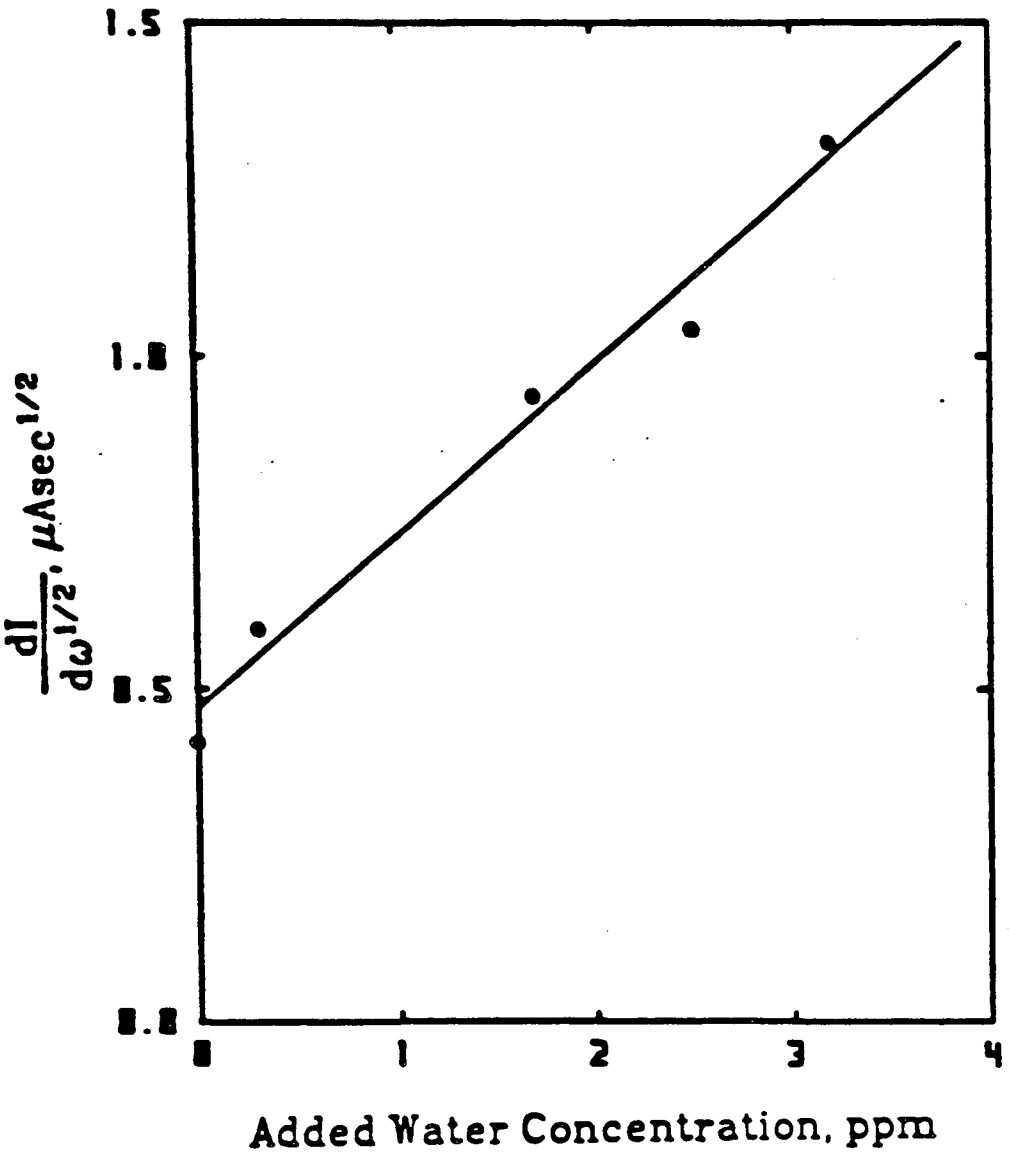
1.5
1.0
0.5
0.0
0
1
2
3
4
$\frac{dI}{d\omega^{1/2}}$, μAsec$^{1/2}$
Added Water Concentration, ppm

Fig. 12

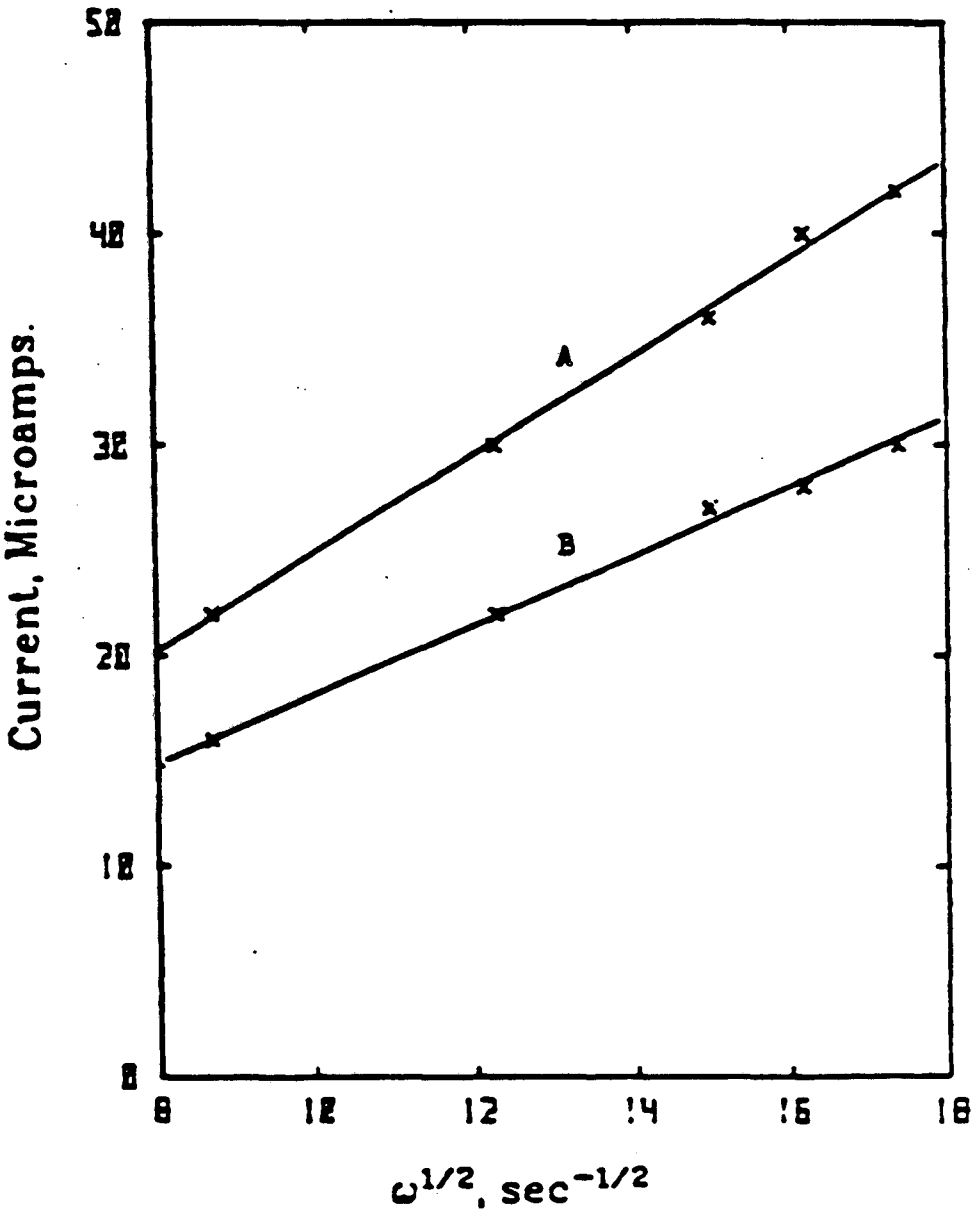
50
40
30
20
10
0
8
10
12
14
16
18
A
B
Current, Microamps.
$\omega^{1/2}$, $sec^{-1/2}$

Fig. 13

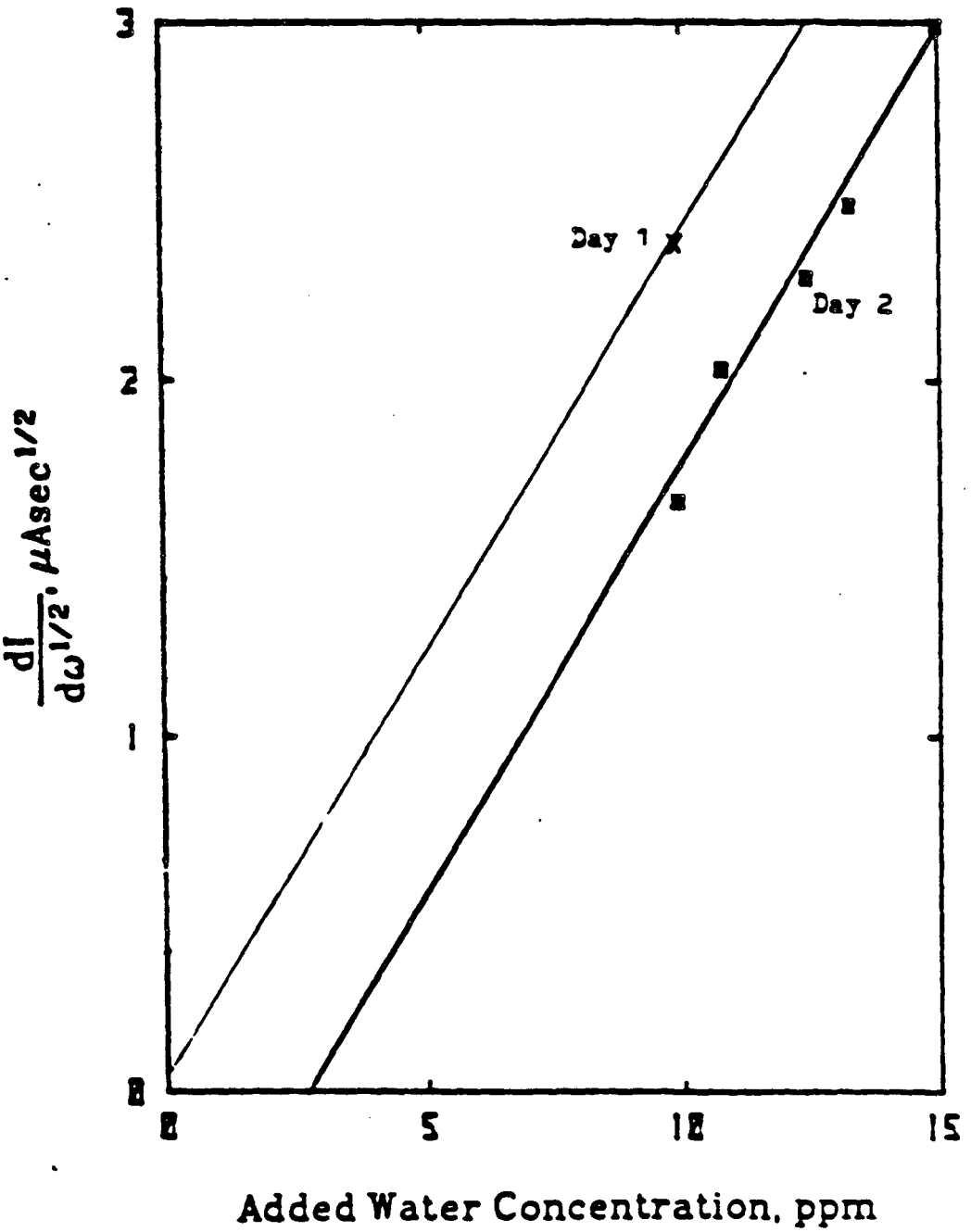
3
2
1
0
0
5
10
15
Day 1
Day 2
$\frac{dI}{d\omega^{1/2}}$, $\mu Asec^{1/2}$
Added Water Concentration, ppm

Fig. 14

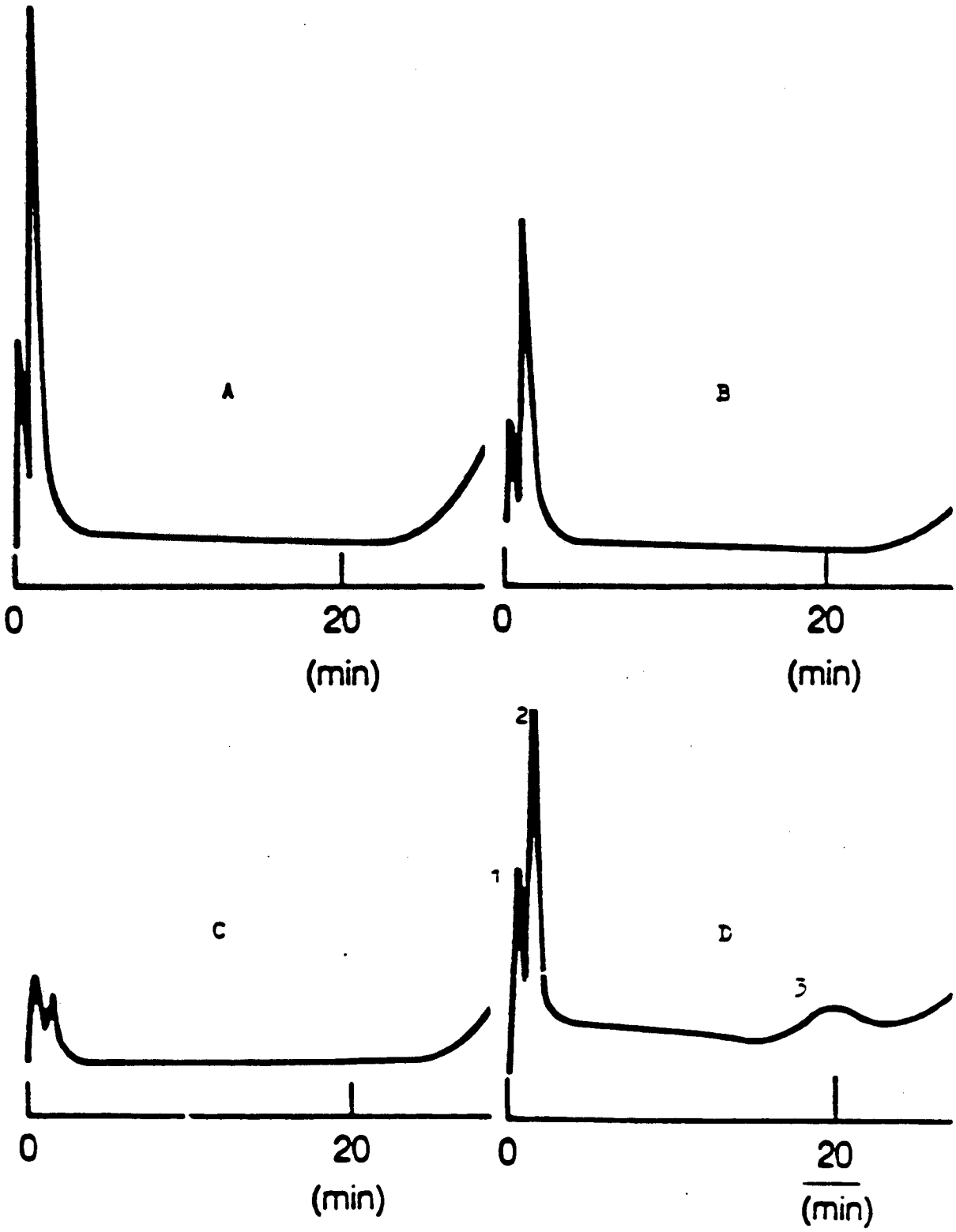

Fig. 15

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