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Publication Date
1986-10-01

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To be submitted to Journal of the Electrochemical Society

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October 1986

DISCLAIMER

ELECTROCHEMISTRY OF IODIDE IN PROPYLENE CARBONATE
I. CYCLIC VOLTAMMETRY MONITORED BY OPTICAL SPECTROSCOPY

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ABSTRACT

The electrochemistry of iodide in propylene carbonate (PC) was investigated using cyclic voltammetry. In an anodic sweep iodide is oxidized sequentially to triiodide and then to iodine according to

$$3I^- \rightarrow I_3^- + 2e^- \qquad \text{I}$$
$$2I_3^- \rightarrow 3I_2 + 2e^- . \qquad \text{II}$$
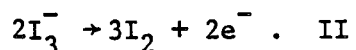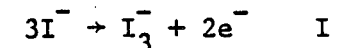
This mechanism was confirmed using UV visible spectroscopy in conjunction with cyclic voltammetry experiments at a thin gold mesh electrode. Potential Step experiments were used to measure a diffusion coefficient of 4×10^{-6} for iodine in a $KAsF_6$/PC electrolyte.

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1. Introduction

The behavior of highly electropositive metals such as the alkali and alkaline earth metals is an area of active research for applications such as in high-energy-density batteries, liquid-metal heat-transfer fluids, or light-weight alloy materials. The electrodeposition of these metals at ambient temperature requires the use of nonaqueous solvents that are both stable under potential differences in excess of 5 volts and capable of dissolving metal salts to form conducting solutions. In this regard, the feasibility of propylene carbonate (PC) as an electrolytic solvent for alkali metal deposition has been demonstrated[1][2] but compatible anodic reactions other than intercalation reactions have not yet been established. This paper describes a cyclic-voltammetry study of the anodic oxidation of iodide in propylene carbonate. This study is of particular interest, since to date there have been very few studies of halogen electrochemistry in propylene carbonate.

The electrochemical behavior of halogen couples depends strongly on the electrolytic solvent. Voltammetry experiments in iodide solutions in acetonitrile[3] for example, show four anodic waves, but only two waves are seen in iodide solutions in PC.[4] In each case, the reactions occurring at lower potential are described as triiodide formation followed by the oxidation of triiodide to iodine. In acetonitrile, the formation of a cationic iodide species has been postulated to account for the additional waves. The following reaction sequence has, therefore been hypothesized for iodide oxidation in PC in this study.

$$3I^- \rightarrow I_3^- + 2e^- \tag{I}$$

$$2I_3^- \rightarrow I_2 + 2e^- \tag{II}$$

Based on this mechanism and a difference of standard electrode potentials of 630 mV for the two reactions, a stability constant for I_3^- in PC of $10^{7.7}$ l/mol has been reported.[5]

The postulated reaction sequence is verified experimentally by determining spectroscopically the presence and concentrations of electrochemically generated iodine and triodide during the voltammetry measurements. In addition, the sequence is verified theoretically by comparing simulated voltammograms to experimentally determined voltammograms. Because of the complex stoichiometry of the reactions, a simple extension of the analytical analysis of Nicholson and Shain and others[6] is not possible, and therefore, the simulated voltammograms are calculated numerically. This work is presented in part II of this paper.[7]

2. Cyclic Voltammetry

Experimental

The electrochemical cells used for the voltammetry experiments were based on a design developed by C. Balfe,[8] in which a platinum counter electrode is embedded in the bottom of a single-compartment glass cell, as shown in Figure 1. All experiments were performed in a glovebox under a helium atmosphere at ambient temperature.

A thallium amalgam/thallium iodide reference electrode was used because salts in conventional reference electrodes such as silver/silver halide, calomel, or mercurous halides disproportionate to form soluble complexes in PC.[9] The design and construction of this electrode is similar to that described by Baucke and Tobias.[10] The electrodes were constructed by filling glass cups with ~2 ml of a saturated thallium amalgam (Alfa-Ventron, Thallium 1/8" wire, 99.999% pure; triple distilled mercury from Ballards, Quicksilver Products) to expose about one cm^2 of metal surface area to a saturated thallium iodide solution in PC. After drying at 150-200°C under a 1μ vacuum, the poorly soluble thallium iodide (ultrapure, Alfa Products) was equilibrated in PC. The reference-electrode compartment was connected to the cell by a short length of Teflon tubing. The open-circuit potential of this reference versus a freshly scraped potassium electrode was 2.14V and stable for several hours.

The working electrode was a planar platinum disc embedded in glass. It was constructed by melting the tip of a platinum wire to form a bead, encasing the bead in uranium glass to form a seal, and cutting the assembly with a diamond wheel to expose a circular cross-section of the platinum. The polished electrode has a surface of 0.0571 cm^2.

$KAsF_6$(0.5M) was used as a supporting electrolyte for all voltammetry experiments. Propylene carbonate was purified by treatment with activated alumina and molecular seives followed by vacuum distillation.[2] The salts, KI (Mallinckrodt Chemicals) and $KAsF_6$ (Alfa-Ventron), were analytical reagent grade. KI was recrystallized from distilled water and all salts were dried under vacuum (approximately 1 μm Hg) at elevated temperature for several days. Solutions were prepared by weight and the concentrations were checked by titration with silver nitrate. To avoid heating the solvent, concentrated solutions were prepared by first chilling the PC to near 0°C and adding the salt slowly while stirring continuously. Solutions prepared in this way were clear and colorless after filtration. The conductivity of the 0.5M $KAsF_6$ solution is 5×10^{-3} mho-cm^{-1} at 20°C.

The electrode potential was controlled by a potentiostat (Princeton Applied Research, Model 173 Potentiostat and Model 176 Current Follower) driven by a function generator (Princeton Applied Research Model 175). Data were collected with a fast (1 μ-sec/point) digital oscilloscope (Nicolet Model 4094) and with an XY recorder (HP Model 7046B with a time base). The oscilloscope was interfaced to a small desktop computer (HP 9825A) connected to peripheral equipment (HP 9885M disc drive, HP 9862A plotter) used to store and plot data.

Background Voltammetry Scans

To distinguish the current of the reacting ion from interferences such as electroactive impurities or capacitive effects, background voltammograms were obtained for all scan rates tested. These scans were featureless across the full voltage range and the currents were always at least an order of magnitude lower than those obtained with the electrolytes containing iodides.

Decomposition Potential of KAsF₆ Solutions

The anodic decomposition potential for a 0.5 M solution of KAsF₆ in PC was found to be 2.9V vs. Tll/Tl(Hg). Potassium deposition, the limiting reaction for a cathodic sweep, occurred at -2.18 V ($\pm$ 10 mV).

Window Opening Experiments

A sequence of voltammetry scans, taken by cycling each scan to progressively more anodic potentials, is shown in Figure 2 for a sweep rate of 100 mV/sec. Anodic and cathodic peaks are present for two reactions. The anodic peaks are denoted I and II as shown on the figure, and the primes indicate the cathodic reaction. The widely-spaced anodic peaks correspond to the formation and then subsequent oxidation of triiodide. These peaks are separated by 440 mV; this difference is independent of the sweep rate below 200 mV/sec. When the direction of the potential scan is reversed, iodine is reduced first to triiodide, then to iodide. The separation between the corresponding cathodic peaks, denoted I' and II', depends upon the history of the potential scan and the sweep rate. Figure 3 illustrates the shift of peak I' with the reversal of the potential scan. Although it appears in the same position at switching potentials of 1.7 and 1.9V, when the potential sweep reverses at 2.1V or greater, peak I' shifts in the cathodic direction. The reduction of triiodide to iodide is therefore very sensitive to the state of the electrode surface.

Sweep Rate Behavior

If the electrode reaction proceeds at a significantly faster rate than the transport of the reactant to the electrode surface, the peak potential is determined only by the thermodynamic potential and is independent of sweep rate. Kinetic limitations are indicated if the peak potential shifts with increasing sweep rate. Figures 4 and 5 illustrate the effect of sweep rates from 10 to 1000 mV/sec on the shape of the cyclic voltammogram[11] for a solution of 4.0×10^{-3} M KI and 0.5 M KAsF₆ in PC. The position of the first anodic peak (I) is shifted slightly with increased sweep rate; the reverse wave (I') is significantly offset under the same program. In

contrast, the position of the peaks for the reaction II (I_3^-/I_2) is nearly independent of sweep rate, indicating reversible behavior.

The effect of slow kinetics on the oxidation of iodide can be more clearly seen in experiments in which the voltage range is confined to the first peak. Figure 6 shows scans for sweep rates ranging from 1 mV/sec to 20 V/sec. The change in peak current as a function of sweep rate is shown in Figure 7. For a reversible wave, the value of the current at the peak is determined by the area of the electrode, the reaction stoichiometry, and the diffusion coefficient, according to

$$i_p = nFAc^* \left[\frac{\pi D_o nF}{RT} \right]^{1/2} \chi(\sigma t) \; b^{1/2}, \tag{1}$$

where $\chi(\sigma t)$ is a dimensionless calculated current function for the 3:1 stoichiometry,[12] and b is the sweep rate. Thus, for a given experiment, the peak current of a reversible reaction is only a function of the sweep rate. Sweep rates between 1 mV/sec and 500 mV/sec are shown in Figure 7A; the linear range extends to about 200 mV/sec. The deviation from reversibility can be seen in Figure 7B; the curve bends away from the linear region when the rate of the reaction is surpassed by the rate of the potential scan.

The width of the peak is also an indication of reversibility. Figure 8 shows the variation of the width of peak I with sweep rate. The value at the intercept is 52 mV; from his theory, Shuman predicts a value of 52.25 mV for a 3:1 stoichiometry.[12]

Discussion

The voltammetry experiments indicate that reaction I is sluggish in comparison to reaction II. In Part II of this paper,[7] the values of the kinetic parameters for these reactions are estimated by comparing simulated voltammograms to the data presented above. However, it is interesting to consider possible reasons for the observed behavior. It has been previously demonstrated that the surface of platinum is covered with an adsorbed layer of iodine and triiodide. For example, using the technique of thin layer chronopotentiometry, Hubbard, Osteryoung and Anson[13] have shown that about 2×10^{-9} moles/cm^2 of iodide ion or iodine are

adsorbed onto platinum. This adsorbed layer is not electroactive; i.e., it cannot be detected by reduction or oxidation near the reversible iodide/iodine potential. An additional 1×10^{-9} moles/cm^2 of iodine, but not iodide, are adsorbed in an electroactive state. This adsorbed layer is the likely reason for the disparity in forward and reverse reaction rates for peak I. In the anodic direction, the reactant and products are strongly adsorbed on the platinum surface and charge transfer is not impeded. In the cathodic direction, the triiodide has to be reduced at an iodine covered surface. Therefore, the large cathodic overpotential may be a measure of the additional energy required to overcome the adsorption energy of iodine.

3. Diffusion Coefficient of Iodide in PC

Potential step experiments were used to determine the diffusion coefficient of iodide in PC. The mathematical description of the current response to a potential step at a planar electrode in a stagnant solution is provided by the Cottrell equation. Under the assumption that a single electrode reaction occurs $(R \rightarrow O + ne^-)$, and that the potential step is sufficiently positive to assure that the surface concentration of R is zero, the current as a function of time is given by,[14]

$$i(t) = \frac{nFAD_R^{1/2}c_R^o}{3\pi^{1/2}t^{1/2}} , \qquad (2)$$

where D_R is the diffusion coefficient, and c_R^o is the bulk concentration of the reduced species. >From these experiments, and using equation 2, the diffusion coefficient of iodide in PC is found to be 4×10^{-6} cm^2/sec. It is difficult to assess the accuracy of this value. Popovych and Tomkins[15] report diffusion coefficients for iodide and triiodide in dimethyl sulfoxide (DMSO) and two different aqueous solutions. These values are listed in Table 1. Included in the table are diffusion coefficients reported by Nakanishi and Furusawa[16] for iodine in tetrahydrofuran (THF) and 1,4 dioxane, and for KI in various solvents reported by Janz and Tomkins.[17] As a general rule, the product of the viscosity and the diffusion coefficient (the Walden product) is approximately constant for a given solute in various solvents at the same temperature.

Obviously, this does not account for specific interactions such as hydrogen bonding or for the variation in the donor/acceptor properties of the solvents. These Walden products are given in the last column in Table 1. All values for iodide fall between 2.2 and 4.5×10^{-10} dynes/K. An average value is 3.2×10^{-10} dynes/K which is approximately the value in formamide. Assuming that this constant is valid for PC solutions, the "calculated" diffusion coefficient for iodide in PC is 3.9×10^{-6} cm^2/sec. This compares favorably with the measured value of 4×10^{-6} cm^2/sec. Also, the ratio of the diffusion coefficient of iodide to triiodide (approximately 2:1) is the same in DMSO, aqueous KI, and aqueous sulfuric acid solutions. If that same ratio holds in PC, the diffusion coefficient of triiodide in PC should be approximately 2×10^{-6} cm^2/sec.

Table 1 Diffusion Coefficients of Iodide, Triiodide, and Iodine					
Solute	Solvent (Donor No.*)	η_o (cp)	D $(10^6 cm^2/sec)$	Ref.	$\dfrac{D\eta}{T}$ $(10^{10} dynes/deg)$
Iodine	THF (20)	0.48	0.235	[18]	3.8
Iodine	1,4 Dioxane 3.8 (14.8)	1.19	9.6	[18]	–
Triiodide	DMSO (.8M $KClO_4$) (30)	1.96	3.7	[19]	2.4
Triiodide	Water (1.0 N H_2SO_4)	–	4.2	[19]	–
Triiodide	Water (0.1 M KI)	–	11.3	[19]	–
Iodide	DMSO (.8 M $KClO_4$) (30)	1.96	6.9	[19]	4.5
Iodide	FA (24)	3.03	3.0	[18]	3.3
Iodide	NMF (26.3)	1.65	4.7	[18]	2.6
Iodide	DMF (27.8)	0.796	8.3	[18]	2.2
Iodide	1 N H_2SO_4 (aq)	–	8.1	[19]	–
Iodide	1.5 M KI (aq)	–	22.0	[19]	–
Iodide	PC (15.1)	2.5	4.0	This work	3.4

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* All values for solvent donor numbers are from Gutmann.[18]

4. Spectral Electrochemical Experiments

In conventional cyclic voltammetry experiments, the identity of the reaction products is inferred from the position of the half-wave potential, the number of electrons transferred, and the stoichiometry of the reaction. If the reaction products or reactants are active in the UV-visible range, spectral electrochemical techniques can be used to track the course of reaction and directly identify the products as a function of potential. Thus, the electrode reaction is monitored simultaneously via the electrode current (as in a conventional cyclic voltammetry experiment) and by the UV-visible spectra. This technique was used to qualitatively confirm the reaction mechanism for the oxidation of iodide in PC derived from the cyclic voltammetry experiments.

Experimental

The cell design, originally developed by Carol Balfe[8] based upon work by Hawkridge[19] and Murray,[20] is illustrated in Figure 9. The working electrode is a fine (200 lines/inch, 0.1 mm thick, 78% transmission) electroformed gold mesh (Buckbee-Mears Co., St. Paul, Minn.). The counter electrode (platinum foil) and reference electrodes (thallium amalgam/thallium iodide) are located on the side of the working electrode. The reference electrode is the same as the one used in the cyclic voltammetry experiments. Light from the spectrophotometer (Hewlett-Packard Model 8450) is transmitted through the optically transparent working electrode to the detector. During the course of an experiment, the potential at the working electrode is ramped in a sawtooth wave at a rate of 1 mV/sec. A single spectral scan, from 200 to 800 nm, is completed in one second, so the electrode potential changes only one mV in the time interval of a single scan. Thus, each scan is essentially a "snap shot" of the solution absorbance at a given potential.

The path length for the gold minigrid electrode was 0.007 cm in this cell, calibrated using Methyl Red dye in an acidic propylene carbonate solution.[21]

Extinction Coefficients

The UV-visible absorption of triiodide and iodine in PC is shown in Figure 10. The triiodide spectrum is from a solution of equimolar (2×10^{-4}M) iodine and KI in PC. The iodine spectrum is from a solution of 0.15 F iodine in PC, and was taken in the thin layer cell described above. To eliminate any triiodide formed from the disproportionation reaction of iodine,[22] the working electrode was held at 1 volt anodic relative to the thallium/thallium iodide reference electrode. Triiodide absorbs in two sharp peaks at 292 and 363 nm. In contrast, iodine absorbs in a broad band at 462 nm and has a smaller band at 290 nm.

To convert the spectral information into concentration data, extinction coefficients are needed at the wavelength of maximum absorbance, λ_{max}, for each species. This information, along with the path length of the cell, specifies the absorbance as a function of concentration according to Beer's Law,

$$Absorbance = \epsilon \, \ell \, c$$

where ϵ is the extinction coefficient, c is the concentration, and ℓ refers to the path length of the cell.

A compilation of extinction coefficients from Johnson[21] is presented in Table 2. Triiodide absorbs very strongly in the visible range. For example, at 292 nm, concentrations as low as 5×10^{-6} M triiodide can be detected in a 1.0 cm cuvette. In contrast, this technique is relatively insensitive to iodine concentration.

Table 2 λ_{max} and Extinction Coefficients for Iodine and Triiodide in Propylene Carbonate at 25 °C		
Molecule	ϵ, 1/mole-cm	λ_{max}, nm
Iodine	837 (462 nm) 59 (363 nm) 315 (293 nm)	462
Triiodide	1053 (462 nm) 24091 (363 nm) 44881 (293 nm)	363, 293

Results

Figure 11 shows the anodic portion of the cyclic voltammetry scan of 6.7×10^{-3} M KI and 0.5 M KAsF$_6$ in PC at 1 mV/sec. The potential sweep is initiated at 0.5V (approximately open-circuit potential), switches from anodic to cathodic at 1.7V, and switches from cathodic to anodic at -0.1V. Despite the fact that the cell geometry is completely different, the shape of the voltammogram is qualitatively the same as that in the corresponding conventional voltammetry experiment. However, background reactions from etching of the gold electrode by iodine slightly alter the cathodic portion of the sweep.

The spectral results of the experiment are presented in the form of a series of UV-visible scans taken at 30 second (or 30 mV) intervals throughout the potential sweep. The first sweep, taken at open circuit, was stored and automatically subtracted from all subsequent scans. Figure 12A shows the first portion of the anodic sweep, starting at 0.5V. Except for a negative peak, which corresponds to the disappearance of iodide (at 230 nm), little activity is observed until the potential reaches almost 1V. >From 0.80 to 1.24V the triiodide absorbance increases monotonically with each scan, reaching a maximum at 1.24V. >From this point to the end of the anodic sweep the triiodide absorbance decreases, as shown in Parts C and D. This behavior is consistent with the oxidation of triiodide to iodine in this potential range. The behavior of

the molecular iodine as a function of potential can be seen using a more sensitive absorbance scale. Figure 12 D and E show the development of the iodine peak from a shoulder of the triiodide peak at 1.37V to a single large broad peak at 1.7V, corresponding to the conversion of triiodide to iodine. Unfortunately, the extinction coefficient of triiodide at 462 nm is of the same order of magnitude as that of iodine, so the concentration variation of iodine is not directly apparent. To follow the change in concentration of iodine, the absorbance due to triiodide must be subtracted. The spectral response of the cathodic sweep was similar, showing the formation and disappearance of triiodide.

The information presented above is summarized in Figure 13 in a plot of the fractional conversion of iodide to triiodide and iodine as a function of time (or potential) throughout a single sweep of the cyclic voltammetry experiment. The fractional conversion is defined as the concentration of the iodine species divided by the concentration for 100% conversion to that species. Thus,

$$\text{Fractional Conversion of } I_3^- = \frac{[c_{I_3^-}]}{3\,[c^o]} \tag{3}$$

$$\text{Fractional Conversion of } I_2 = \frac{[c_{I_2}]}{2\,[c^o]} \tag{4}$$

where c^o is the initial concentration of iodide. The concentration of iodine is calculated by subtracting the contribution of triiodide at 462 nm. This figure illustrates the concentration changes during the course of the reaction as triiodide is first formed from the oxidation of iodide, then oxidized to produce iodine. When the potential sweep reverses, the iodine is reduced back to triiodide which is, in turn, reduced to iodide. The slight dip in iodine concentration at 1.7V is probably due to the corrosion of the gold electrode by iodine.

The results of these spectral electrochemical experiments clearly confirm the chemical reaction mechanism postulated from the cyclic voltammetry experiments.

5. Conclusions

In summary, the electrochemical behavior of the iodide/triiodide/iodine system was investigated in propylene carbonate using the technique of cyclic voltammetry. It was found that iodide is oxidized in two electrochemical steps; triiodide is formed first (Reaction I) and then the oxidation proceeds to iodine (Reaction II). The kinetics of the two reactions differ markedly. The rate of reaction I is much faster in the anodic direction than in the cathodic direction. In contrast, reaction II is reversible below sweep rates of 1 V/sec. Spectral electrochemical experiments confirm this sequence of reactions. However, in view of the complexity of the reaction system, cyclic voltammetry experiments can represent only the first step toward understanding the details of the reaction sequence. Rotating ring-disc experiments to detect triiodide at the ring, or pulse techniques could provide further insight into the reaction mechanism.

List of Symbols

A	Electrode area, cm^2
b	Sweep rate, V/s
c_i	Concentration of species i, mol/cm^3
c^o	Concentration in bulk of solution
D_i	Diffusion coefficient of species i, cm^2/s
i_p	Current density at peak maximum, ma/cm^2.
ℓ	Path length of spectralelectrochemical cell, cm
n	Charge number for reaction
$\chi(\omega t)$	Dimensionless current function
η	Viscosity (cp)
ϵ	extinction coefficient
λ	wavelength, nm
$V - \Phi_{ref}$	Electrode potential relative to a saturated Tl/Tl(Hg) electrode in the electrolyte solution, V

FIGURE CAPTIONS

Figure 1.   Electrochemical cell and reference electrode.

Figure 2.   Cyclic voltammetry of 0.004 M KI in supported (0.5 M $KAsF_6$) PC solution. Initial potential is 0.6V. The anodic switching potential of each successive scan increases by 100 mV. Voltages are referenced to the Tll/Tl(Hg) reference electrode in PC.

Figure 3.   The effect of the anodic switching potential on the position of Peak I'. Solution: 4.3×10^{-3}M KI, 0.5 M $KAsF_6$, 100 mV/s.

Figure 4.   Effect of sweep-rate from 10 mV/s to 200 mV/s. (a) 200 mV/s, (b) 100 mV/s, (c) 50 mV/s, (d) 20 mV/s, (e) 10 mV/s. Solution: 4.3×10^{-3}M KI, 0.5 M $KAsF_6$.

Figure 5.   Effect of sweep-rate from 100 mV/s to 1000 mV/s. (a) 1000 mV/s, (b) 500 mV/s, (c) 200 mV/s, (d) 100 mV/s. Solution: 4.3×10^{-3} M KI, 0.5M $KAsF_6$.

Figure 6.   Variation of Peak I with sweep-rate. (a) 1 mV/s, (b) 2 mV/s, (c) 5 mV/s, (d) 10 mV/s, (e) 20 mV/s, (f) 50 mV/s, (g) 100 mV/s, (h) 200 mV/s, (i) 500 mV/s, (j) 1000 mV/s. Solution: 4.3×10^{-3} M KI,0.5 M $KAsF_6$

Figure 7.   Change in peak current for Peak I as a function of the square root of the sweep rate. (A) Slow sweep-rates from 1 mV/s to 500 mV/s. (B) Range is 1 mV/s to 20 V/s.

Figure 8.   Change of peak width for Peak I with sweep-rate.

Figure 9.   Electrochemical cell containing optically-transparent, thin-layer electrode. The dimensions of the gold mesh electrode are shown.

Figure 10.   UV-Visible absorption spectra of triiodide and iodine in PC at 25° C. Triiodide solution: equimolar (2×10^{-4} M) iodide and iodine. Iodine solution: 0.15 M. From reference [22].

Figure 11.   Anodic portion of voltammetry scan of iodide solution $(6.7 \times 10^{-3}M$ KI, 0.5M KAsF$_6$ in PC) taken in thin-layer cell.

Figure 12.   UV-Visible spectra taken during the anodic voltammetry sweep in the thin layer cell. In each figure an insert shows the variation of the applied potential for the given spectra. Initial potential: 0.50V (vs. TlI/Tl(Hg) reference) (a) 0.50V to 0.80V, (b) 0.83V to 1.22V, (c) 1.25V to 1.40V, (d) 1.37V to 1.46V, (e) 1.70V.

Figure 13.   Fractional conversion of iodide to triiodide and iodine during a single voltammetry scan.

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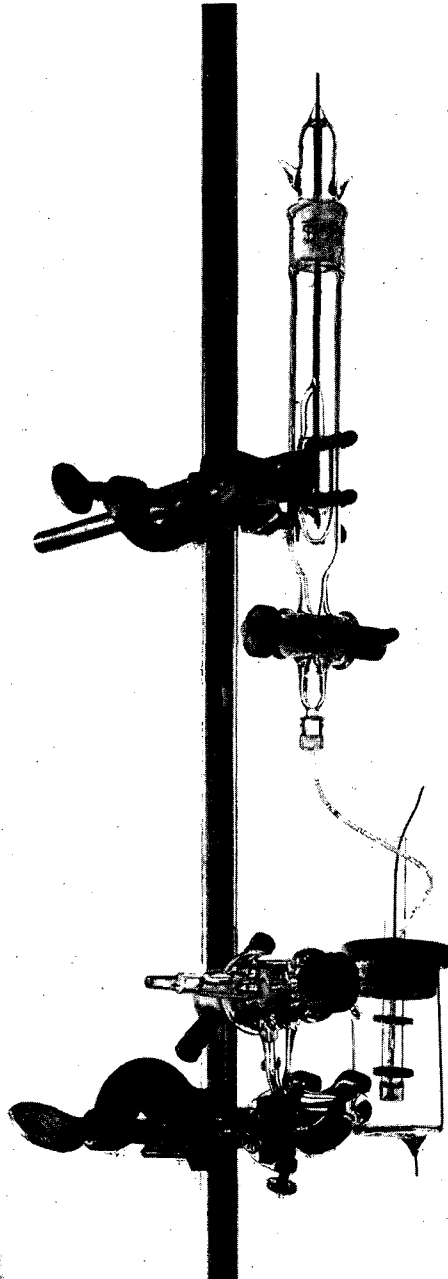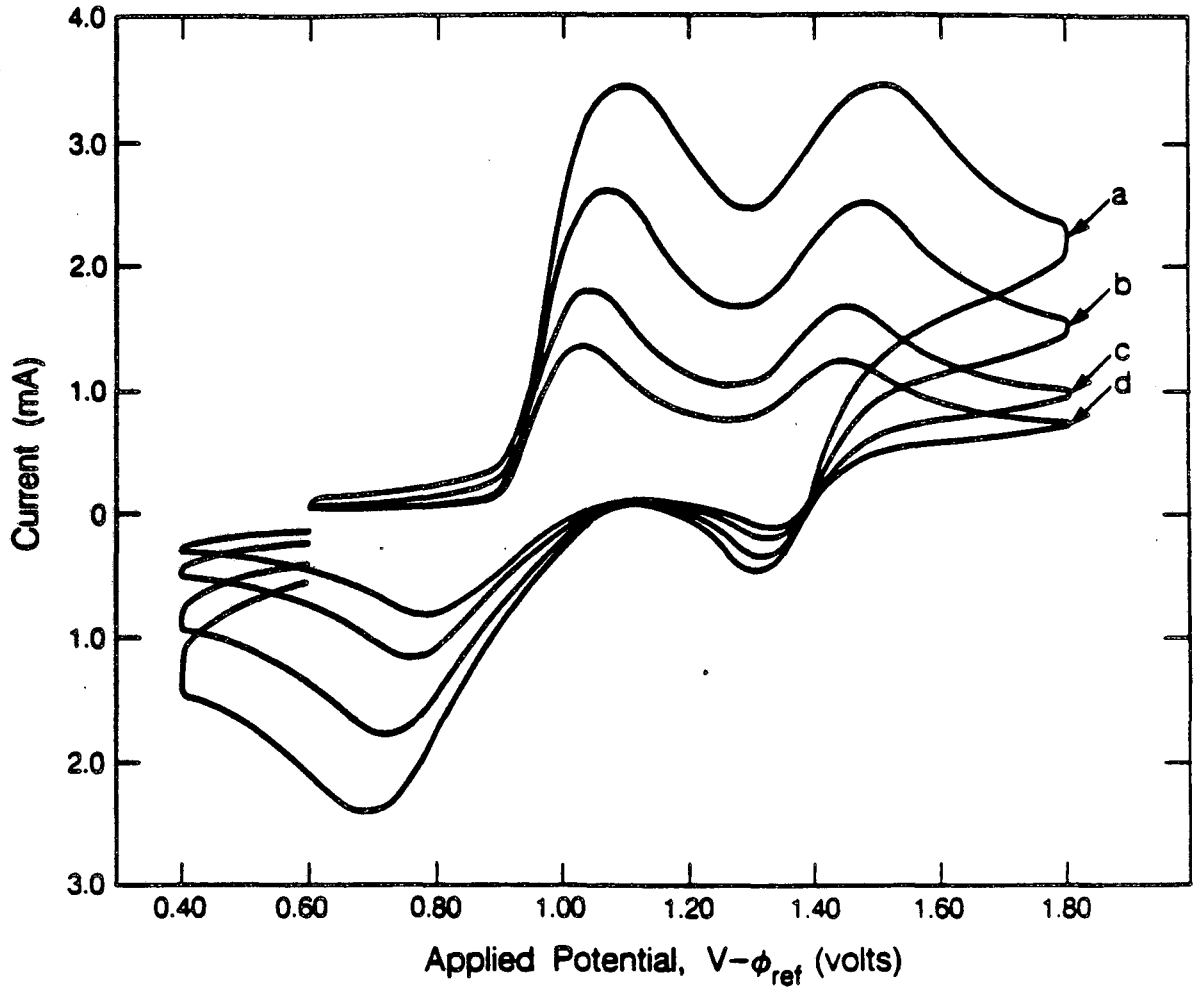
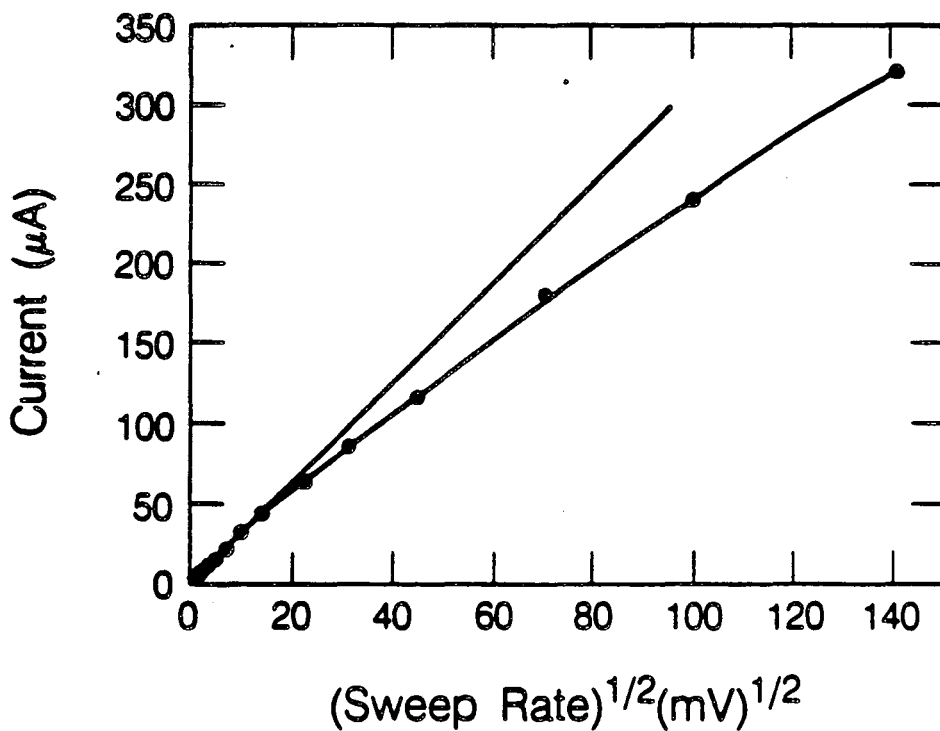CBB 830-9691

Figure 1
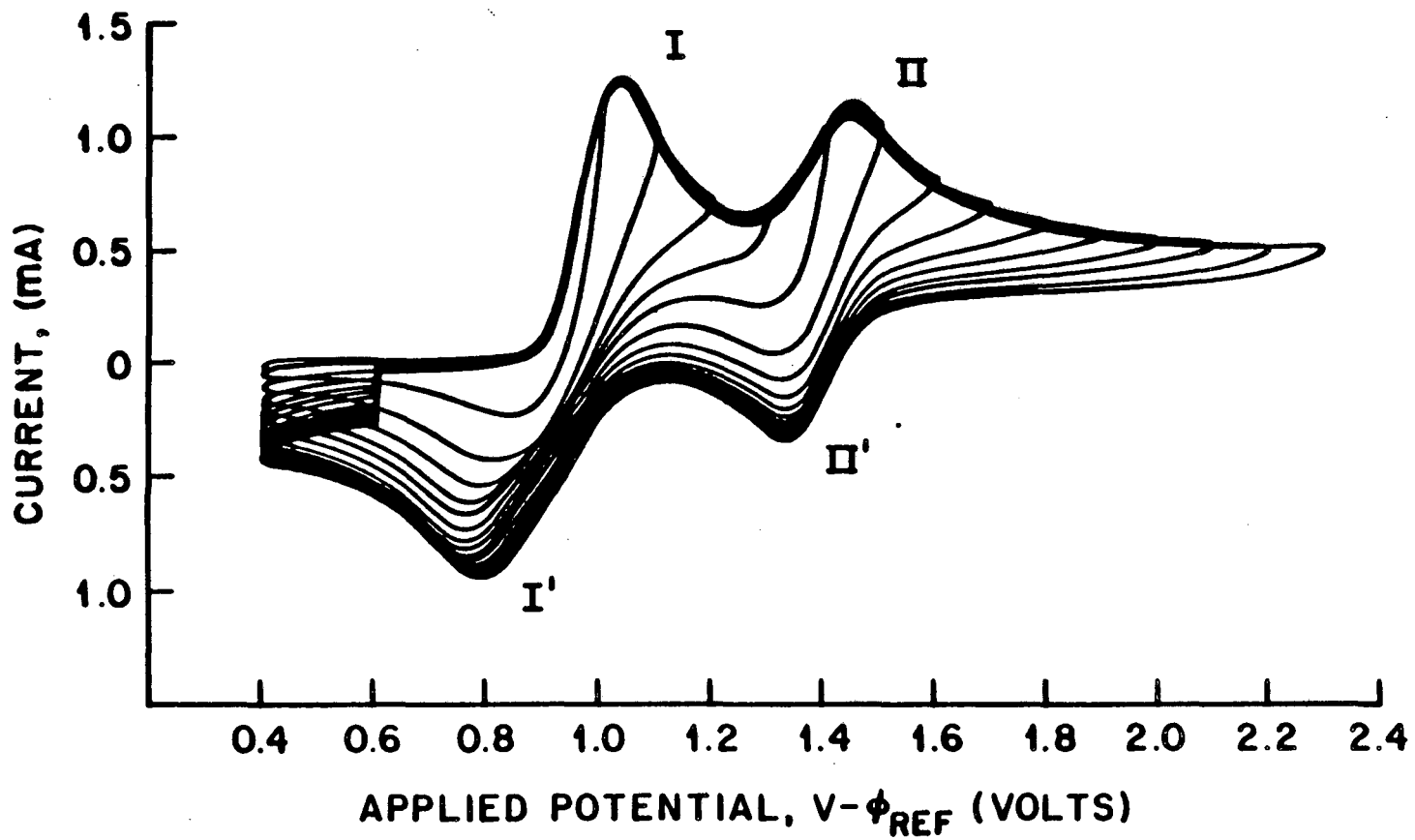
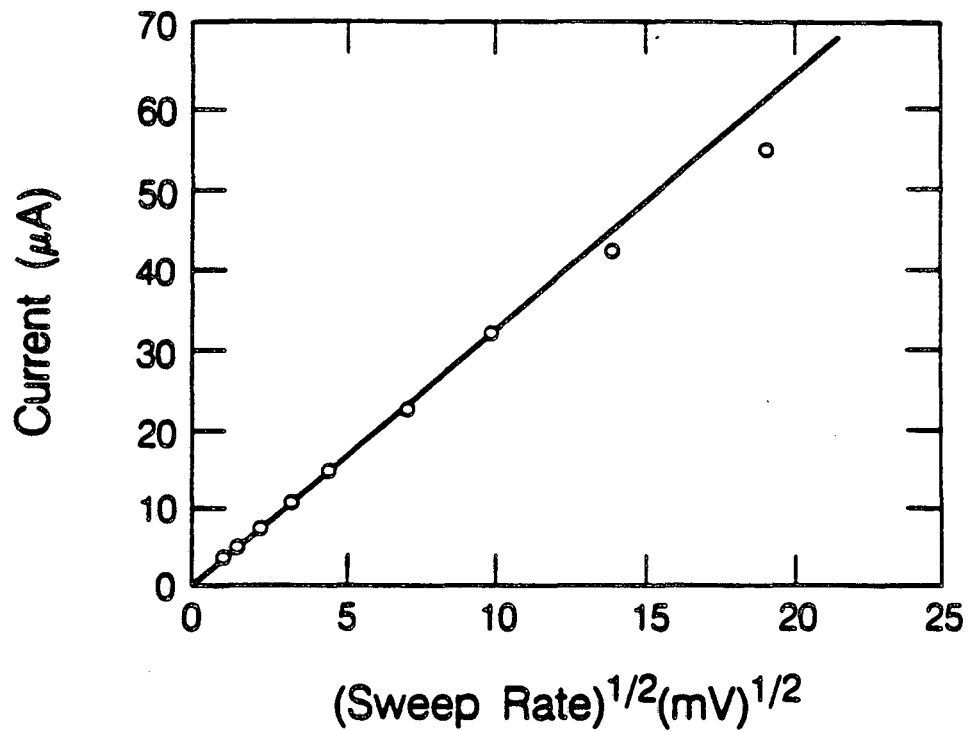Figure 2
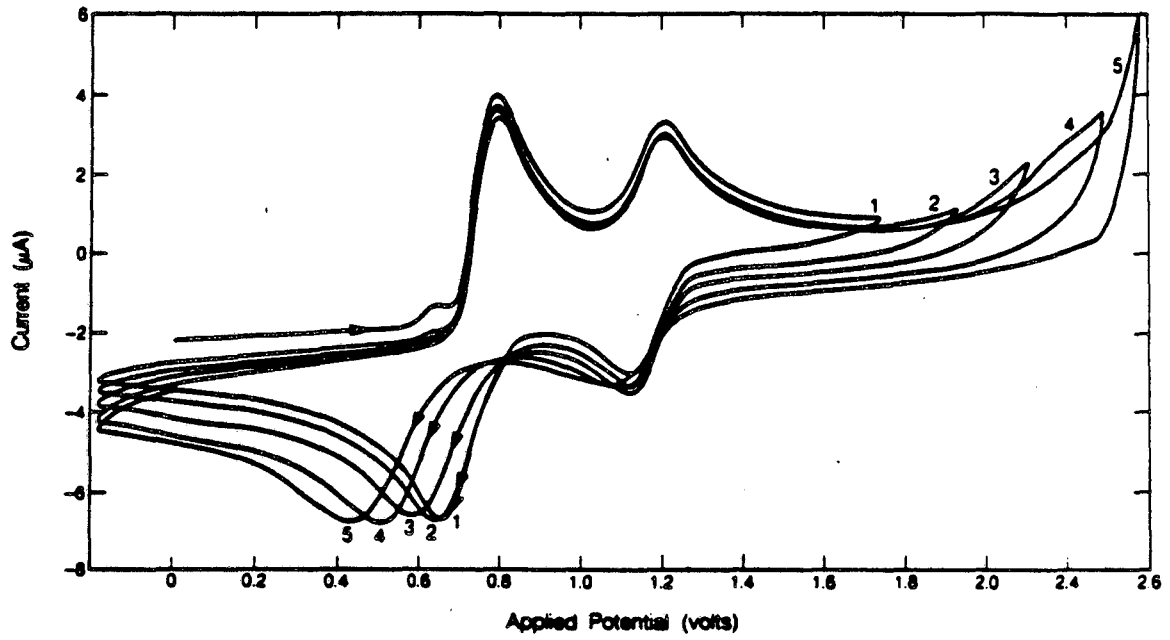
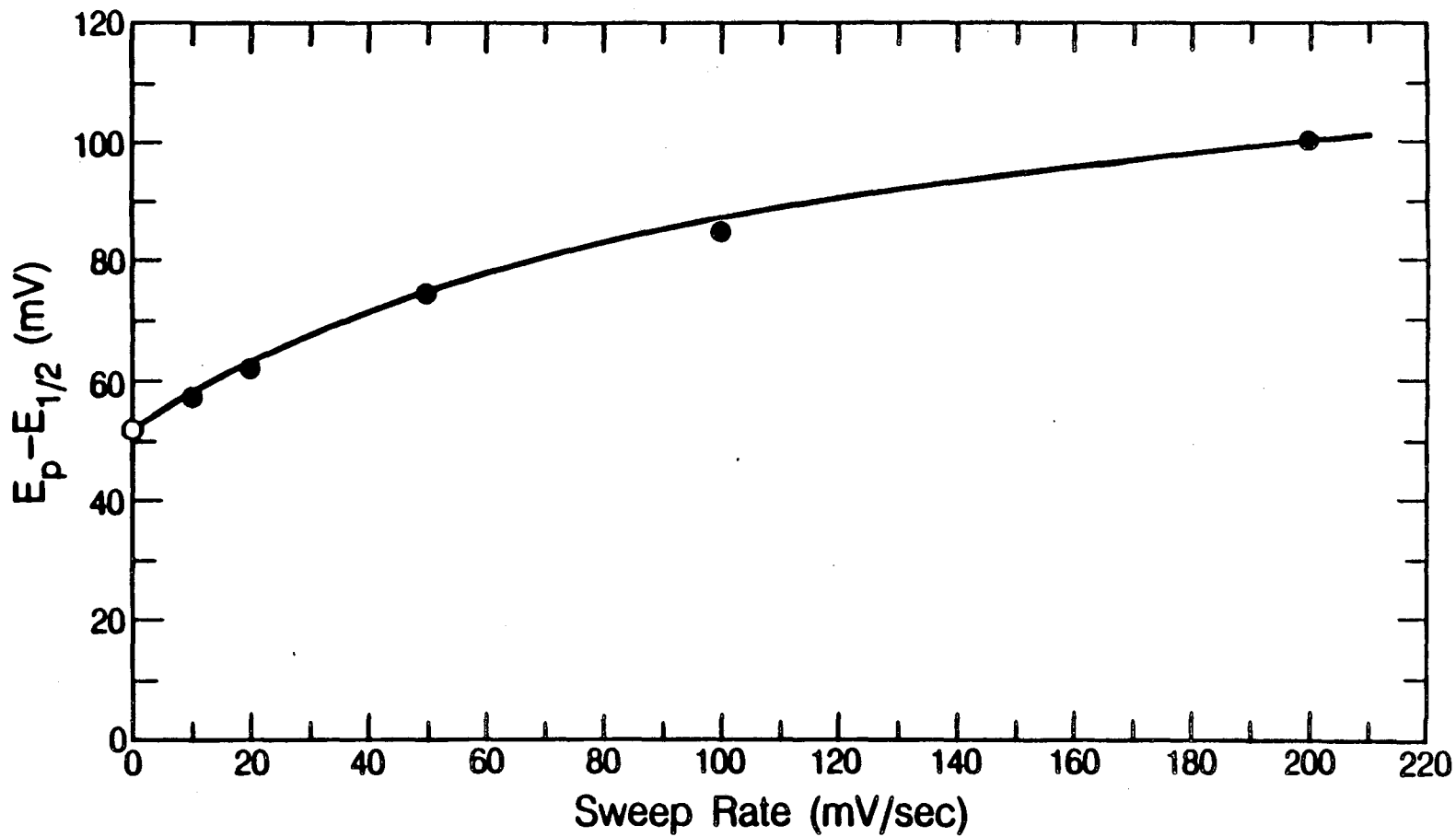Figure 3

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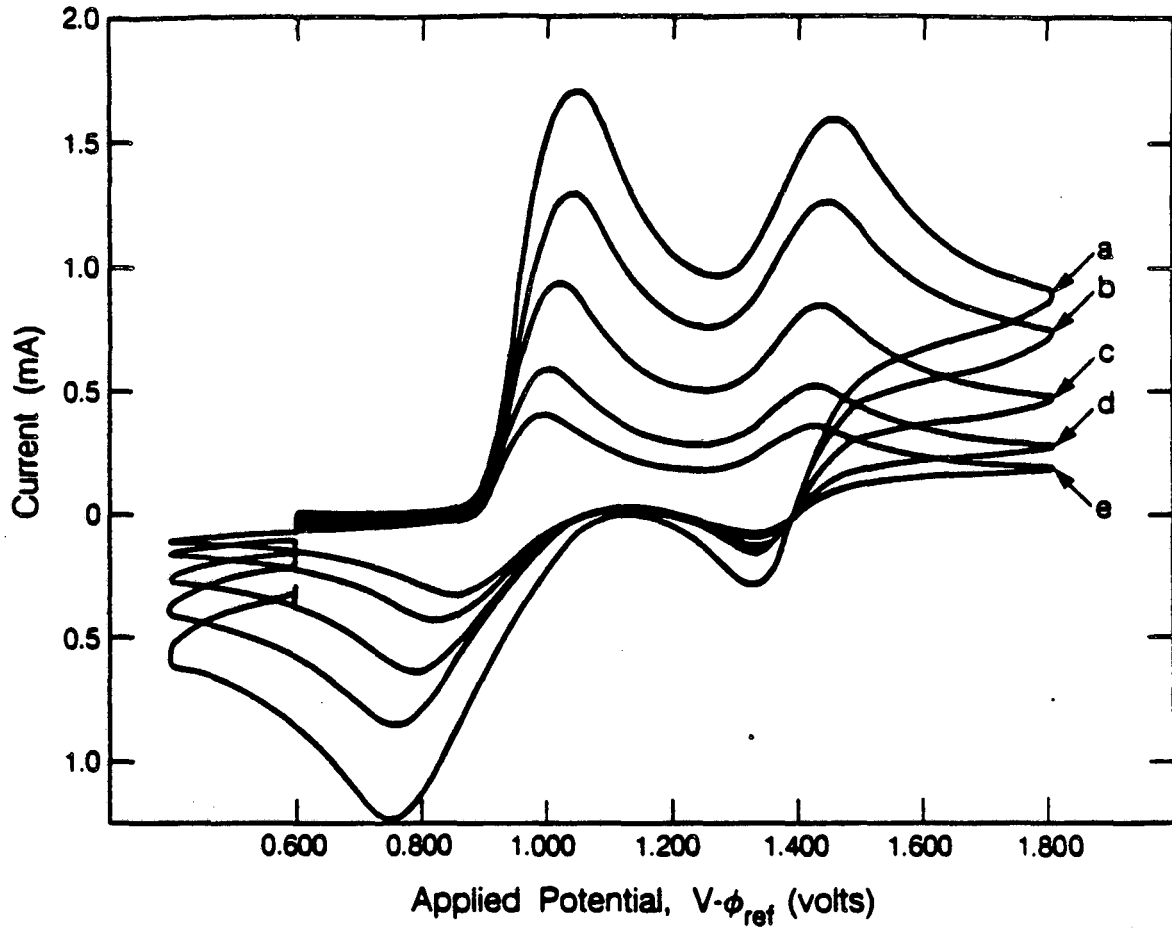
Figure 4

XBL 847-7202

Figure 5

XBL 847-7203

Figure 6
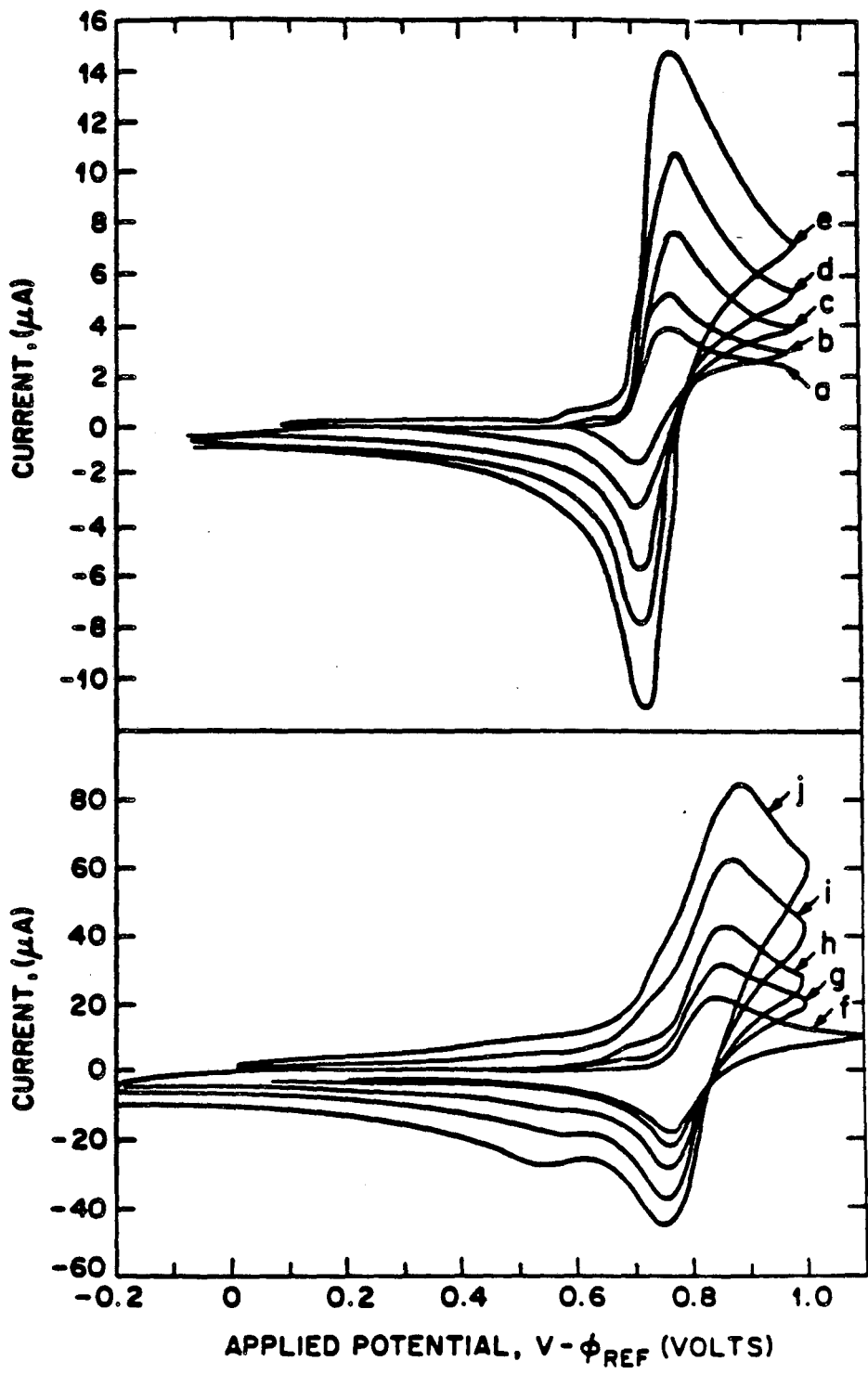
XBL 849 10807

Figure 7

XBL 847-7736

Figure 8

WORKING ELECTRODE

COUNTER ELECTRODE

UV VIS LIGHT BEAM

2.54 μ

100 μ

100 μ
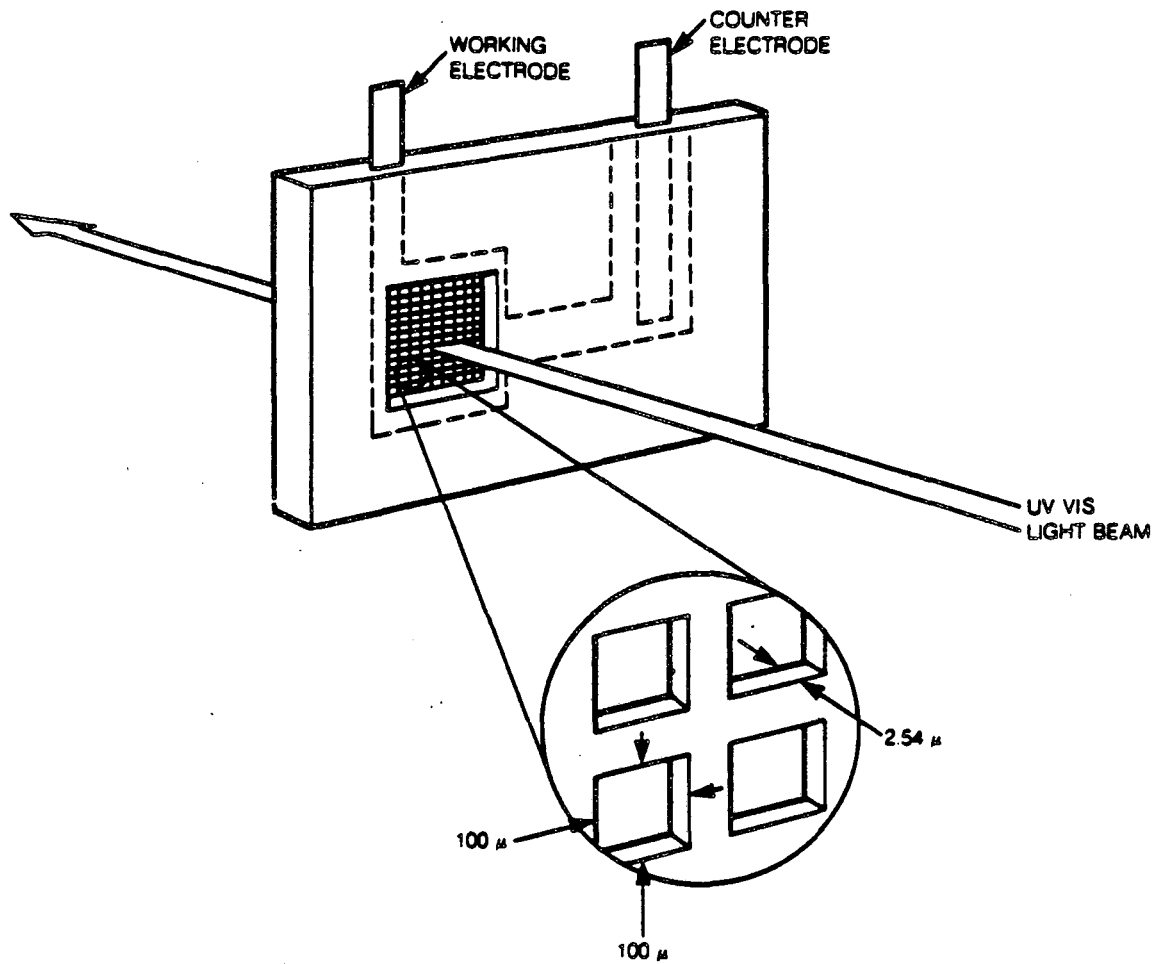
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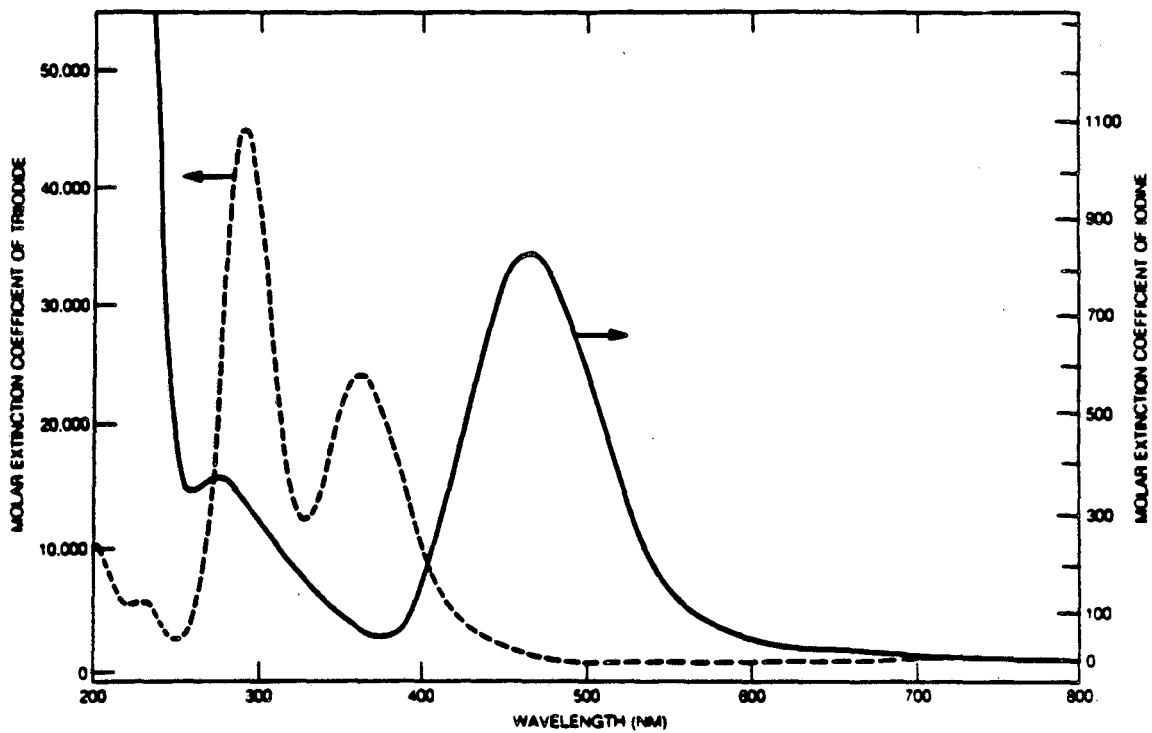
Figure 9

XBL 845-8938

Figure 10

Figure 11

(a)

(b)

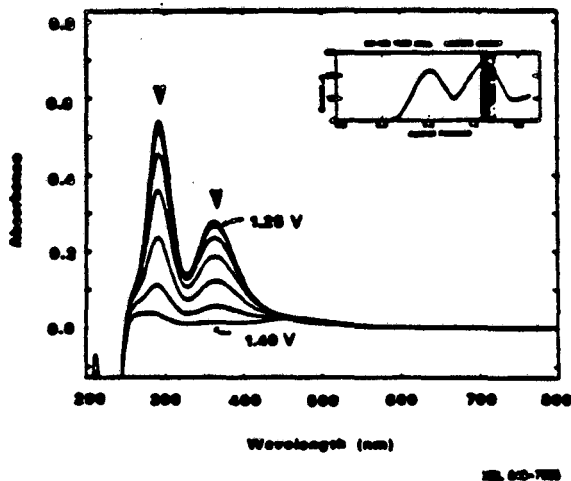(c)

(d)

(e)

Figure 12

Figure 13