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Authors

Koppenhagen, J.E. Van Koppenha
Majda, M.

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Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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Structurally Heterogeneous Electrode Films of Polyacrylamide and Acrylamide/Vinylpyridine Copolymeric Gels. Mediation of Ascorbic Acid Oxidation

Juanita E. Van Koppenhagen and Marcin Majda[*]

Department of Chemistry
University of California
and the Center for Advanced Materials
Lawrence Berkeley Laboratory
Berkeley, CA 94720 (U.S.A.)

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[*] To whom correspondence should be addressed.

Introduction.

The recent development of numerous methods of reagent immobilization in polymeric films at electrodes has been driven to a large extent by potential electrocatalytic applications [1]. The use of polymers as electrode coating materials allows the attachment of large quantities of electroactive reagent. This increases the catalytic current over the value observed for electrodes derivatized with just a monomolecular layer of the same reagent. This simple strategy, however, requires efficient electron transport between the catalyst centers and the electrode, a process responsible for catalyst regeneration. This strategy also requires unimpeded access of substrate to all the catalytic sites within the electrode film. Unless these two conditions are met, the overall level of electrocatalytic current will be partially or completely limited by the rate of electron transport and/or the rate of mass transport within the electrode film. In a large majority of the reported cases dealing with mediated electrochemical reactions at polymer coated electrodes, the electrode film was found to be essentially impermeable [2 - 17]. In these cases the number of active catalytic sites is limited to those present in the outer-most part of the electrode film. Sometimes this behavior can be related to rapid electron transport and fast kinetics of catalytic reaction which, when combined limit the reaction layer thickens [5]. Most frequently, however, the low physical permeability of electrode films is directly responsible for such behavior of the system defeating the purpose of a multimolecular layer electrode assembly.

In an effort to deal with this problem, we have decided to design and synthesize polymeric matrices of controlled porosity and to test their behavior as electrocatalytic films. We have used polyacrylamide and acryl-amide/vinylpyridine copolymer gels as electrode films. The synthesis and

properties of polyacrylamide gels are well known through research in electro-phoresis and gel filtration chromatography, where these materials have been used extensively [17, 18]. The structure of these gels is heterogeneous in nature in that it consists of a fully permeable, three-dimensional network of polymer bundles and aqueous channels which remain essentially polymer-free. The polymer bundles consist of multiple strands of cross-linked polyacryl-amide. The bundle thickness and gel porosity depend primarily on the concen-trations of acrylamide and N,N'-methylene-bis-acrylamide, a cross-linking agent [20]. Polyacrylamide gels collapse and become impermeable upon transfer to solvents of dielectric constant lower than approximately 40 and when they are dried. They fully reswell when transferred back to aqueous media.

Most of the work presented in this paper deals with vinylpyridine/ acrylamide (VP/AC) copolymeric gels (see Figure 1). Their physical structure appears to be analogous to that of pure polyacrylamide gels. Incorporation of pyridine groups into the gel structure allowed us to exchange ferrocyanide ions into the VP/AC gels in acidic media. We present here our studies of the porosity of VP/AC gel films at electrodes as well as an account of a prelimi-nary investigation of the ferricyanide-mediated oxidation of ascorbic acid at VP/AC gel coated electrodes. Ascorbic acid was chosen as a model compound of well known chemical and electrochemical behavior [21, 22]. The oxidation of ascorbic acid by transition metal complexes proceeds by an outer-sphere mechanism of two consecutive one-electron transfer steps [23]. Recently, the mediated electrooxidation of ascorbic acid was also studied at polymer coated electrodes [10, 12-14]. In the last section of the paper we present an assessment of polyacrylamide gel films as an entrapment medium for macro-molecules.

Experimental Procedures.

Vinylpyridine/acrylamide gels were prepared by a radical polymerization of the monomers and N,N'-methylene-bis-acrylamide in the presence of ammonium persulfate and N,N,N',N'-tetramethylethylenediamine as the initiator-catalyst pair. Vinylpyridine content in the polymerization solution was varied from 5% to 25% of the total monomer concentration. The reported gel compositions are based on the elemental analysis of the polymerized gels. Small rectangular blocks of gel were thoroughly washed with water and dried at room temperature. Thin sections with surface area of approximately 0.2 cm^2 were cut with a microtome. Microtomy allows us to produce from a single block of gel hundreds of structurally identical gel sections 0.3 μm to 5 μm thick with 0.2 μm resolution. Individual sections of gel are first floated on water and then lifted off by an electrode and thus deposited on its surface. The gel films coated the entire surface of gold or glassy carbon disk electrodes. The adhesion of a gel film to the electrode surface becomes permanent after the first drying with a heat gun.

The dry thickness of the gel films deposited at the electrode surface as measured by a stylus profilometer is consistently 30% to 50% less than their original thickness before coating. The decrease in film thickness occurs during the floating and apparently reflects the lateral stretching of thin gel films at the water surface.

Permeability Studies.

The gel film porosity studies were performed with gels polymerized from a 15% (w/v) solution of monomers. Vinylpryidine constituted 22.9% of the monomer concentration. The thickness of the films was kept in the range of 0.4 μm to 2.0 μm. (The reported values of thickness are for the dry films unless specified otherwise). These films are readily permeable to $Fe(CN)_6^{3-/4-}$ ions

in neutral electrolytes in cyclic voltammetric experiments. Their presence at the electrode surface causes a 20% to 30% decrease of the voltammetric peak currents and an increase in the difference between the anodic and cathodic peak potential from 65 mV to 125 mV. This apparent permeability of the vinyl-pyridine/acrylamide gel films is in sharp contrast with polyvinylpyridine (PVP) films which are completely passivating under the same conditions [6, 24, 25]. The impermeable character of PVP films in neutral media is a result of their hydrophobicity and homogeneous structure.

Electrodes coated with the VP/AC films described above are also permeable to cationic species such as $Ru(NH_3)_6^{3+}$ and methyl viologen (MV^{2+}). In acidic media, the permeability with respect to $Ru(NH_3)_6^{3+}$ and MV^{2+} decreases compared to neutral solution, as judged from a 10% to 20% decrease in the height of the voltammetric peak currents.

More quantitative measurements of the film porosity were obtained from rotating disk electrode experiments. The rotating disk voltammograms were recorded in neutral 1.0 mM MV^{2+}, 0.1 M KCl solution at a glassy carbon disk electrode coated with 0.5 μm thick VP/AC gel film. The results are shown in Figure 2A. The corresponding Levich plots and Koutecky-Levich plots are shown in Figures 2B and 2C, respectively. The negative deviation from linearity of the Levich plots indicates that mass transport across the polymer film begins to limit the reduction current for higher rotation rates. The maximum value of the current limited by the film permeability, i_s, is the inverse of the intercept of the Koutecky-Levich plot (Figure 2C). Since i_s is directly proportional to film porosity, we have used this parameter to monitor changes in film permeability under different conditions. The experiments of Figure 2 were repeated at pH 2.5, where all pyridine groups of the VP/AC gel film are protonated. All other parameters remained unchanged. A sharp decrease in i_s

was observed (see data in Table 1). The increase in the swelled film thickness (as discussed below) accounts in part for this effect. Also, the mass transport is likely to be restricted by the repulsive electrostatic interactions between MV^{2+} and pyridinium charges. Based on literature data the average pore diameter of polyacrylamide varies from 10 Å to 80 Å depending on the acrylamide and bis-acrylamide concentrations used in the polymerization [20]. If the average pore diameter of our VP/AC gel films is of the same magnitude, the electrostatic repulsive interactions would indeed have an important effect on film permeability.

The determination of i_s was also repeated in the acidic MV^{2+} solution in the presence of 1 mM ferrocyanide ions which rapidly preconcentrate into the VP/AC gel film but which are not electroactive at the MV^{2+} reduction potential. As can be seen in Table 1, the magnitude of i_s under these conditions is noticeably higher than that measured in pH 2.5 with no ferrocyanide ions present. The increase upon incorporation of $Fe(CN)_6^{4-}$ ions into the film could be explained by the constriction of the gel bundles due to electrostatic cross-linking and the concurrent increase of the average pore diameter. At the same time, strong electrostatic interactions between pyridinium and $Fe(CN)_6^{4-}$ ions decrease the repulsive interaction of the pyridinium sites with MV^{2+} ions. This supports our model of the structurally heterogeneous VP/AC gel films.

A quantitative interpretation of i_s values involves a modified Fick's First Law equation:

$$i_s = nFAC_fD_f\rho \ / \ d \qquad (1)$$

where A is the electrode surface area, C_f and D_f are the effective concentration and the diffusion coefficient of MV^{2+} in the film and ρ and d are the porosity and the thickness of the swelled film. In view of the gel model of

the VP/AC films presented above, we can assume that C_f is equal to the MV^{2+} concentration in the bulk solution multiplied by the liquid fraction in the swelled gel, $1-(V_d/V_s)$, where V_d and V_s are the dry and swelled gel volumes. For the same reason D_f is assumed to be equal to the MV^{2+} bulk diffusion coefficient. We assumed further that there is no partitioning of MV^{2+} into the polymer bundles of the gel. This seems to be reasonable under conditions of low pH, where the bundles are populated with positively charged groups. This assumption also seems reasonable at neutral pH, where the bundles are poorly swelled and tight. Medium transfer experiments for both cases do not show any retention of MV^{2+} by the VP/AC films, supporting the above assumption.

The calculation of the film porosity, ρ from equation (1) requires a knowledge of the swelled thickness of the film. While the development of the method for the direct measurements of d is in progress, we will use here an assessment of d obtained from measurements of the dry and swelled volumes of various gel blocks.

The experimental values of V_s/V_d are 6.4, 8.8 and 8.4 for the 22.9% VP/AC gels swelled in neutral solution of 0.1M KCl, in 0.1M KCl solution at pH 2.5, and in 1.0mM $K_4Fe(CN)_6$ solution at pH 2.5, respectively. We have also assumed that the swelling process will have an identical effect on the gel films when attached at electrode surfaces. Since lateral expansion of the electrode films has not been observed, we assumed that the volume change occurs via an appropriate change in the film thickness. With these assumptions and with a MV^{2+} diffusion coefficient of 7.8×10^{-6} cm^2/s obtained by potential step chronocoulometry, the average film porosity was calculated as 0.49, 0.34 and 0.40, for the films swelled in neutral and in the acidic medium and in the acidic $K_4Fe(CN)_6$ solution as described above.

Due to the assumptions made in the calculation, the absolute values of the porosity can only be regarded as approximations. However, the relative magnitude of the film porosity and its changes with the solution pH and the film loading reflect the structural characteristics of the gel films. The 38% increase in the gel volume upon transfer from neutral to the acidic solution, $(V_s/V_d)_{pH\ 2.5}/(V_s/V_d)_{pH\ 7}$ is likely associated with an increase in the average pore diameter. At the same time our measurements showed a 29% decrease in the film porosity (see data in Table 1). Therefore, this decrease must be largely due to the electrostatic hindrance of the MV^{2+} transport across the gel film with charged pyridinium sites. Experiments with non-ionic, electroactive probes are under way in order to distinguish between the geometric and electrostatic factors influencing the apparent film porosity.

Mediated Oxidation of Ascorbic Acid.

The electrooxidation of ascorbic acid proceeds irreversibly at glassy carbon electrodes in pH 2.5, 0.1M KCl solution. As expected, coating the electrode with an approximately 1 μm film of 22.1% VP/AC gel causes no significant hindrance of the ascorbic acid transport as observed by cyclic voltammetry. Representative voltammograms of this process for the bare and the coated electrodes are shown in Figure 3.

Due to the high porosity of these gel films, ferrocyanide ions quickly enter into the protonated film. Figure 4A (dashed line) shows a voltammogram of the $Fe(CN)_6^{3-/4-}$ couple incorporated into a VP/AC gel electrode film recorded in 0.1 M KCl, pH 2.5 solution. The stability of the incorporated hexcyanoferrate species in the film with respect to leaching in pure supporting electrolyte is comparable to the stability of the highly charged anions in the PVP films [25, 26]. When the electrode of Figure 4A is transferred to a 1 mM solution of ascorbic acid one obtains the rotating disk voltammogram repro-

duced in the same figure by a continuous line. The mediation of the ascorbic acid oxidation by ferricyanide ions in the electrode film can be readily recognized at +0.2 V. At the same time, the direct electrooxidation of ascorbic acid diffusing across the electrode film is clearly evident by the wave at +0.6 V. Under the same conditions, the oxidation of ascorbic acid at an electrode coated with a PVP film loaded with ferrocyanide ions proceeds only at the potential of ferrocyanide oxidation, as shown in Figure 4B. The impermeability of the PVP film accounts for this behavior.

High permeability of the electrode films contributes to the efficiency of the mediation process by allowing a large number of bound ferricyanide centers to be accessible to ascorbic acid. We have tested this notion in a preliminary series of ascorbic acid mediation experiments with VP/AC gel films of varying thickness. The range of 0.4 μm to 1.2 μm was covered. Each time the electrode films have been saturated with ferrocyanide ions. As a result the total quantity of ferrocyanide ions is an indication of the film thickness. The results shown in Figure 5 demonstrate as expected a strong dependence of the mediation current on the film thickness as measured by the quantity of bound ferrocyanide ions. Detailed studies of the kinetic aspects of the mediated oxidation of ascorbic acid at VP/AC gel coated electrodes are in progress.

Entrapment of Polystyrenesulfonate in Polyacrylamide Gel Films.

Due to their distinctly heterogeneous structure cross-linked polymeric gels can be used as entrapment media for macromolecules. This methodology is commonly used in protein research [27]. The general strategy involves, simply, polymerization of a gel in the presence of the species to be incorporated. The entrapment effect may either depend on the size of the incorporated species relative to the average pore diameter of the gel, or it may involve a

partial entanglement of the entrapped species within the bundles of the gel. In either case entrapment in gels could provide a convenient means of immobilizing a broad range of macromolecules at electrodes, a task which otherwise may be difficult or impossible.

As a practical illustration of this concept, a polyacrylamide gel has been used to entrap polystyrenesulfonate sodium salt (PSS), MW 7×10^4. This anionic polyelectrolyte is water soluble and can only be used as an electrode film in nonaqueous solvents [28]. Thirteen and a half percent total monomer polyacrylamide gel was synthesized in the presence of 1.5% PSS. A block of the PSS/AC gel was thoroughly rinsed with water and dried. Thin sections were cut in a fashion analogous to the VP/AC gels described above. The electrode coating procedures were similar to those for VP/AC gel films.

Figure 6 summarizes our preliminary findings. The PSS/AC films were 0.96 μm thick when dry. The calculated quantity of the sulfonate groups in these films was 4.7×10^{-8} moles/cm^2. Incorporation of MV^{2+} ions is apparent in Figure 6. The quantity of MV^{2+} partitioned into the PSS/AC film, based on the integration of the cathodic current of the voltammogram in Figure 6B, is 3.6×10^{-9} moles/cm^2. This accounts for approximately 15% charge compensation of the sulfonate groups by MV^{2+}. Prolonged voltammetric cycling in MV^{2+}-free supporting electrolyte (Figure 6B) leads eventually to a complete loss of the electrochemical activity. If at that point the electrode is transferred to the original MV^{2+} solution, the same loading level as reported above is rapidly restored. This finding strongly indicates that PSS is permanently entrapped in the electrode film.

The simple experiments described here demonstrate the entrapment of macromolecules in porous gels as a means of their immobilization at electrodes. The extension of this concept to other polyelectrolytes, enzymes, micelles, solid particles, etc., is not difficult to envision.

Acknowledgment

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Table 1

Porosity of Vinylpyridine/Acrylamide Gel Films

electrode	$d_{dry} \times 10^5$ cm	i_s (pH 7.3)[a] mA cm^{-2}	i_s (pH 2.5)[b] mA cm^{-2}	i_s (pH 2.5)$_1^c$ mA cm^{-2}	ρ (pH 7.3)[d]	ρ (pH 2.5)[b]	ρ (pH 2.5)$_1^c$
1	5.3	0.880	0.476	0.489	0.47	0.33	0.34
2	5.8	0.927	0.508	0.643	0.54	0.38	0.48
3	3.8	1.022	0.521	0.664	0.39	0.26	0.32
4	4.9	1.180	0.622	0.751	0.58	0.41	0.46
					$\overline{0.49}$[e]	$\overline{0.34}$[e]	$\overline{0.40}$[e]

a. Measured in 0.1 M KCl, pH 7.3.

b. 0.1 M KCl, pH 2.5.

c. 0.1 M KCl, 1.0 mM $K_4Fe(CN)_6$, pH 2.5.

d. Film porosity factor calculated from equation (1); conditions as in a.

e. Average value of the film porosity for the four electrodes.

Figure Captions

Figure 1. Structural formula of a cross-linked vinylpyridine/acrylamide gel and a schematic representation of its physical structure.

Figure 2. (A) Steady-state rotating disk voltammograms at glassy carbon electrodes (A = 0.03 cm^2) coated with 0.58 μm VP/AC gel films in 1.0 mM MV^{2+}, 0.10 M KCl, pH 7.3 solution; (B) Levich plots of the limiting current values from (A); (C) The corresponding Koutecky-Levich plot.

Figure 3. Cyclic voltammograms recorded in 1 mM ascorbic acid, 0.1 M KCl, pH 2.5 solution at a glassy carbon electrode (dashed line) and at the same electrode coated with 0.8 μm VP/AC gel film (continuous line); v = 100 mV/s.

Figure 4. Quasi-steady-state rotating disk voltammograms at glassy carbon electrodes (A = 0.03 cm^2) in 0.10 M KCl, pH 2.5 solution (dashed line curves) and in the presence of 1.0 mM ascorbic acid (continuous line curves) in the same solution; v = 10 mV/s, ω = 400 rpm. (A) Electrode is coated with 0.5 μm VP/AC gel film with incorporated $Fe(CN)_6^{4-}$ ions; (B) Electrode is coated with ca. 0.2 μm PVP film containing $Fe(CN)_6^{4-}$ ions.

Figure 5. Dependence of the ascorbic acid mediation current on the thickness

of VP/AC gel films as expressed by the quantity of the bound ferro-

cyanide (see text). The mediation current was measured at quasi-

steady-state conditions described in Figure 4A.

Figure 6. Cyclic voltammograms at a gold electrode (A = 0.02 cm^2) (dashed

line) and at the same electrode coated with 0.96 μm PSS/AC film

(continuous line curves). (A) 1.0 mM MV^{2+}, 0.1 M KCl, pH 7.3,

v = 100 mV/s; (B) Medium transfer of the coated electrode from
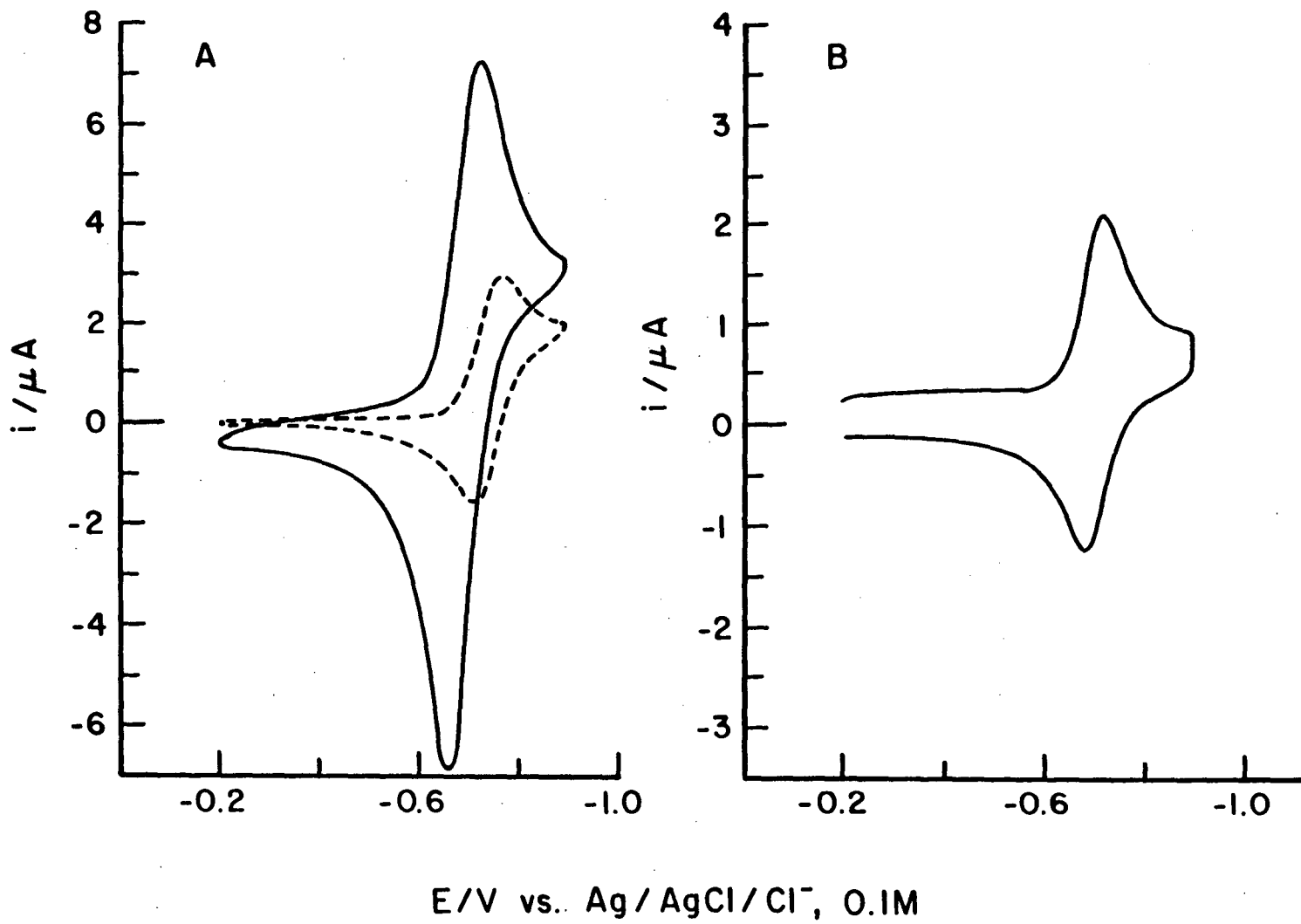
(A) to 0.10 M KCl, pH 7.3 solution, v = 20 mV/s.
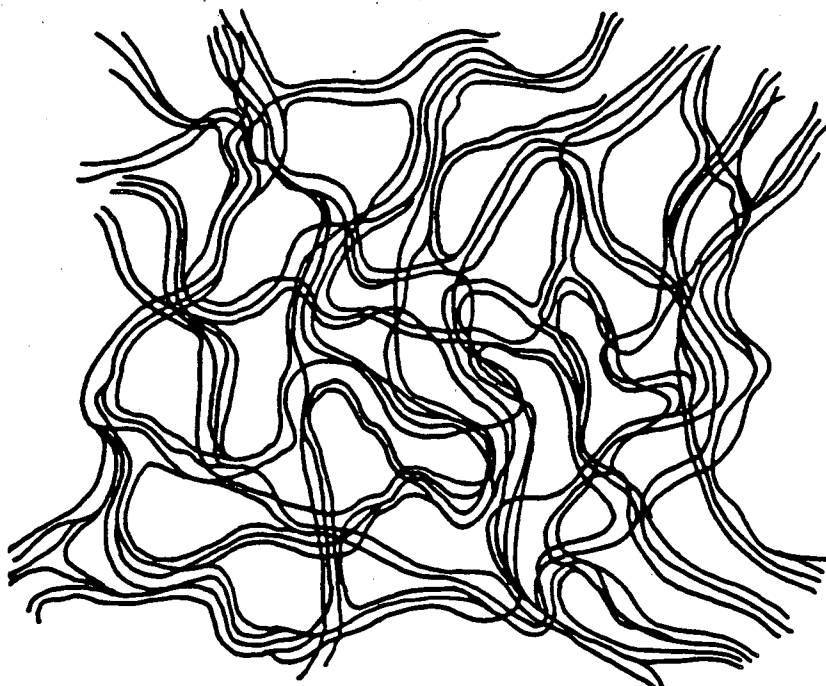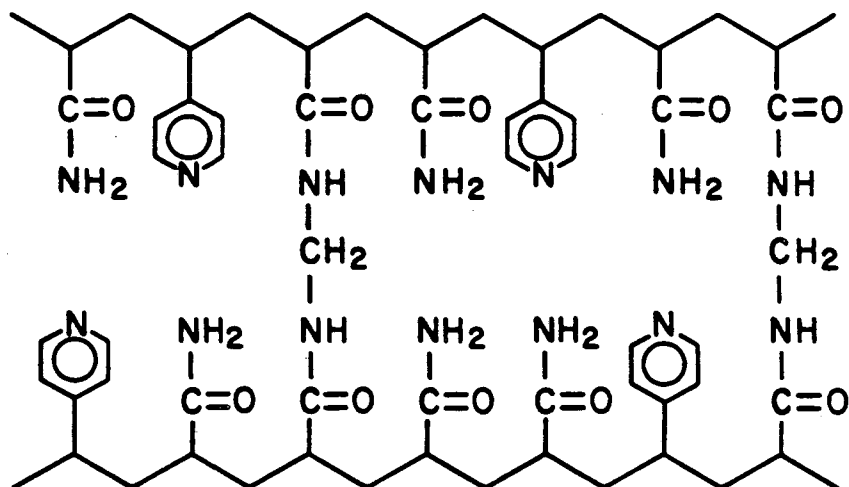
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Figure 2.
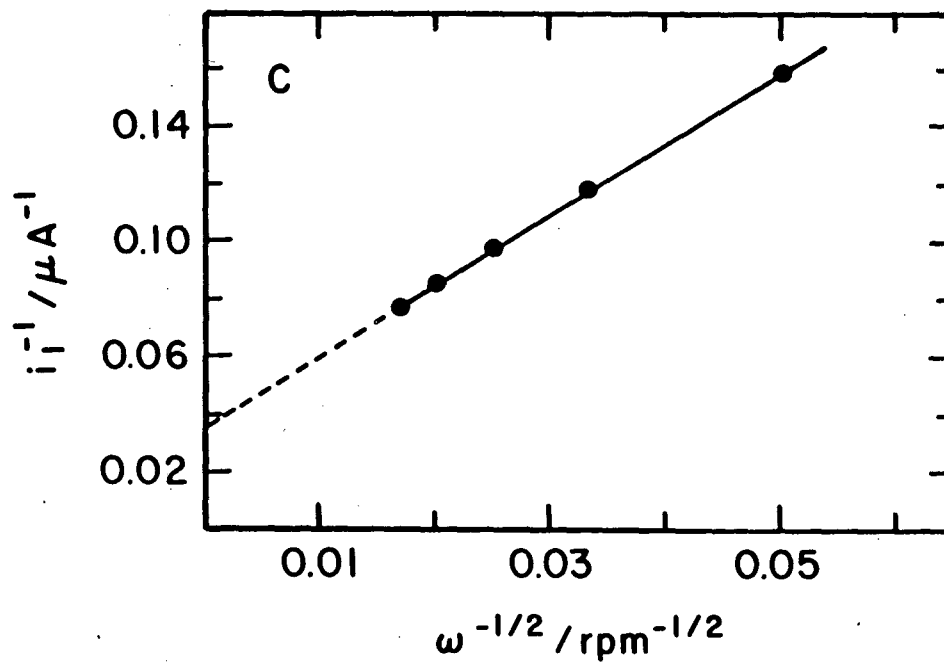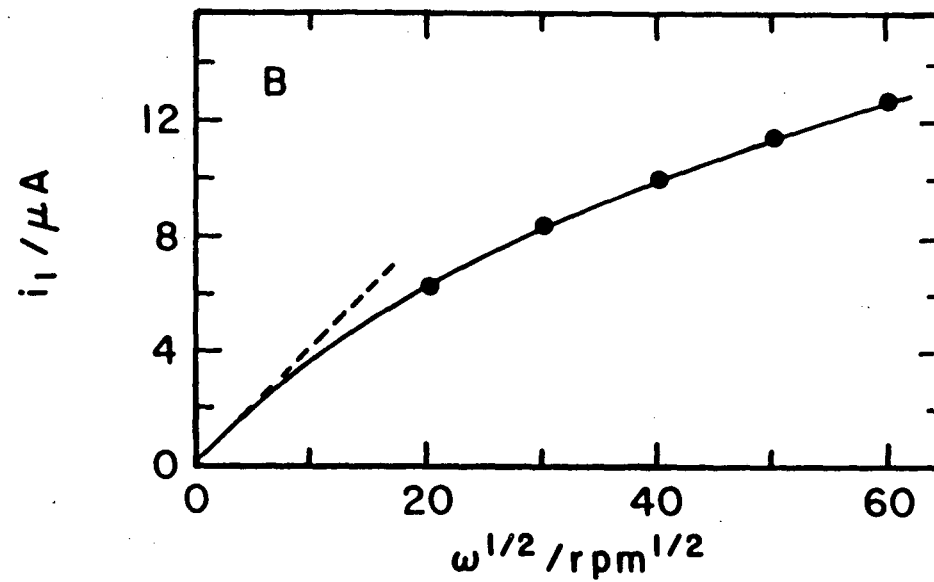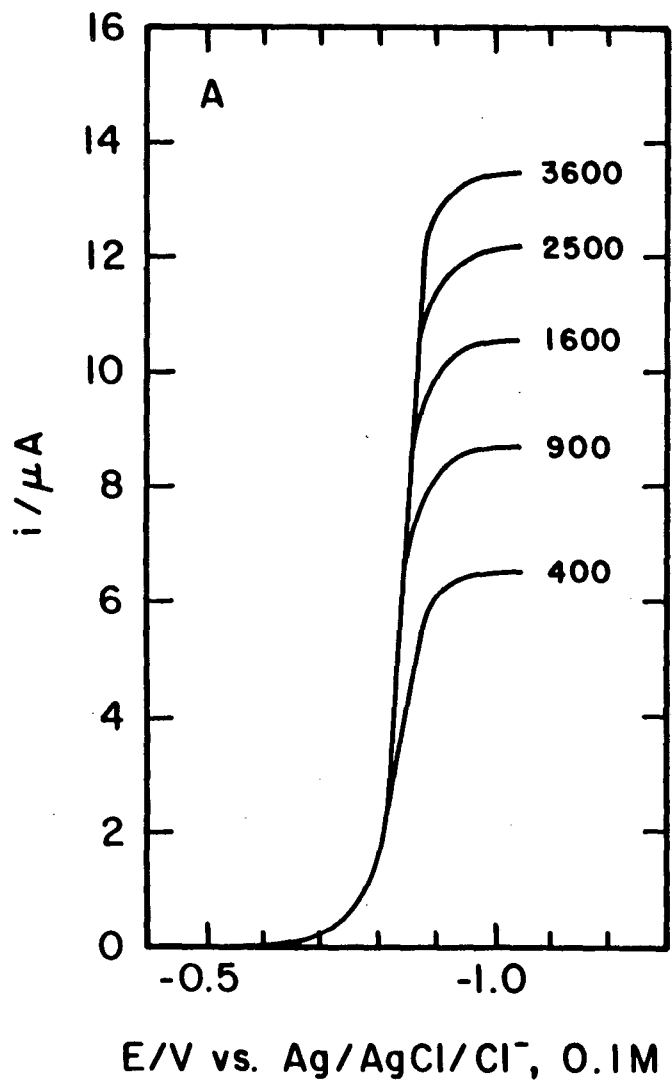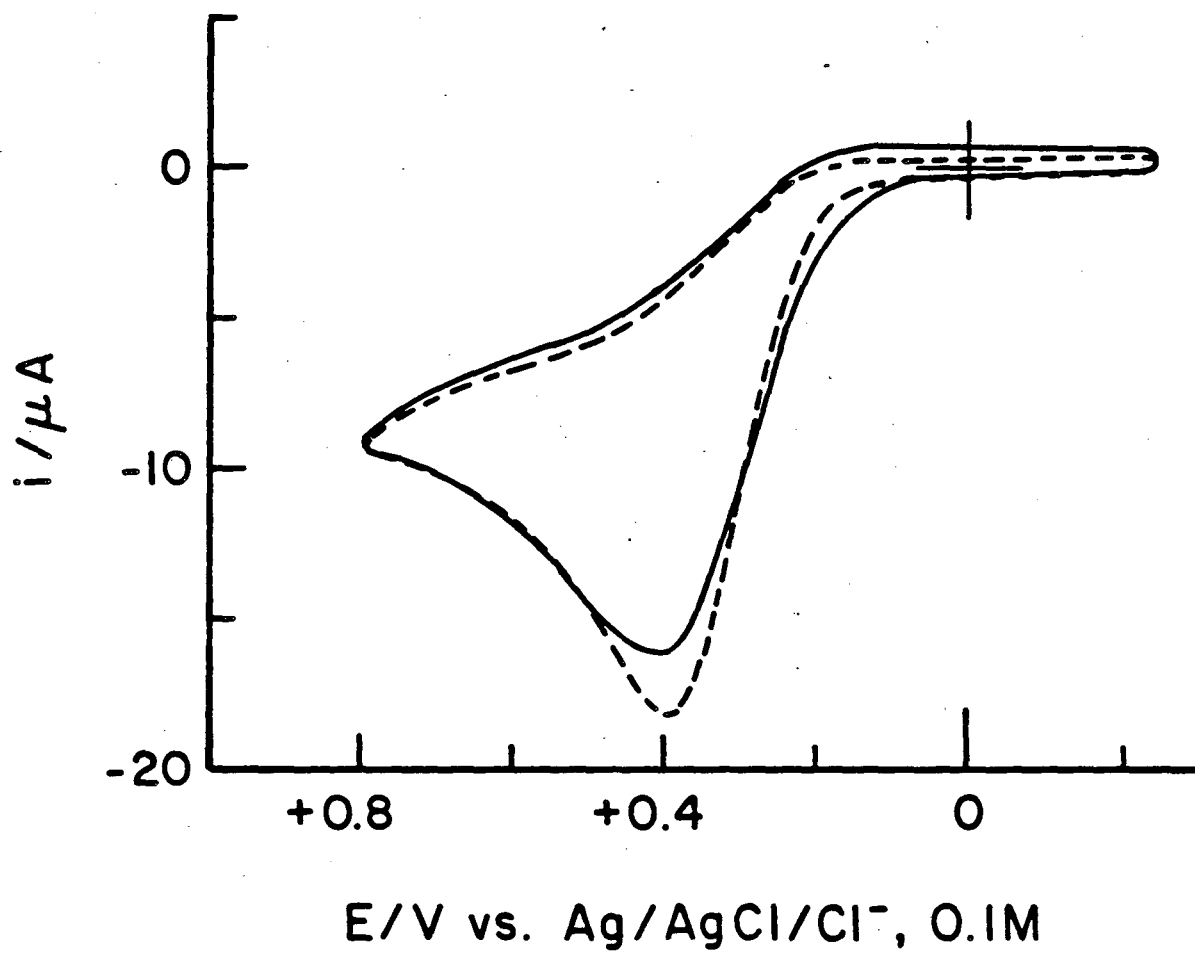
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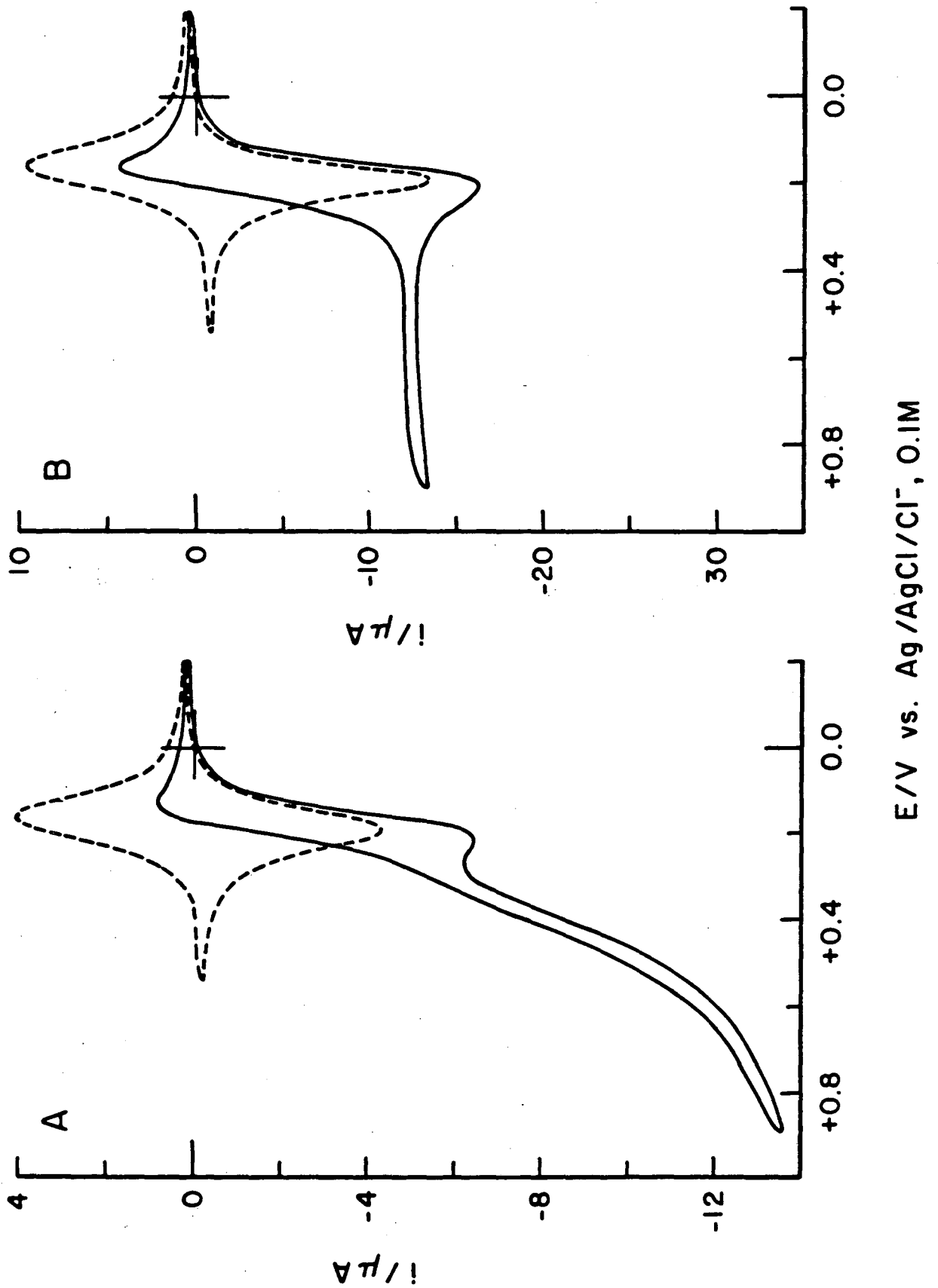
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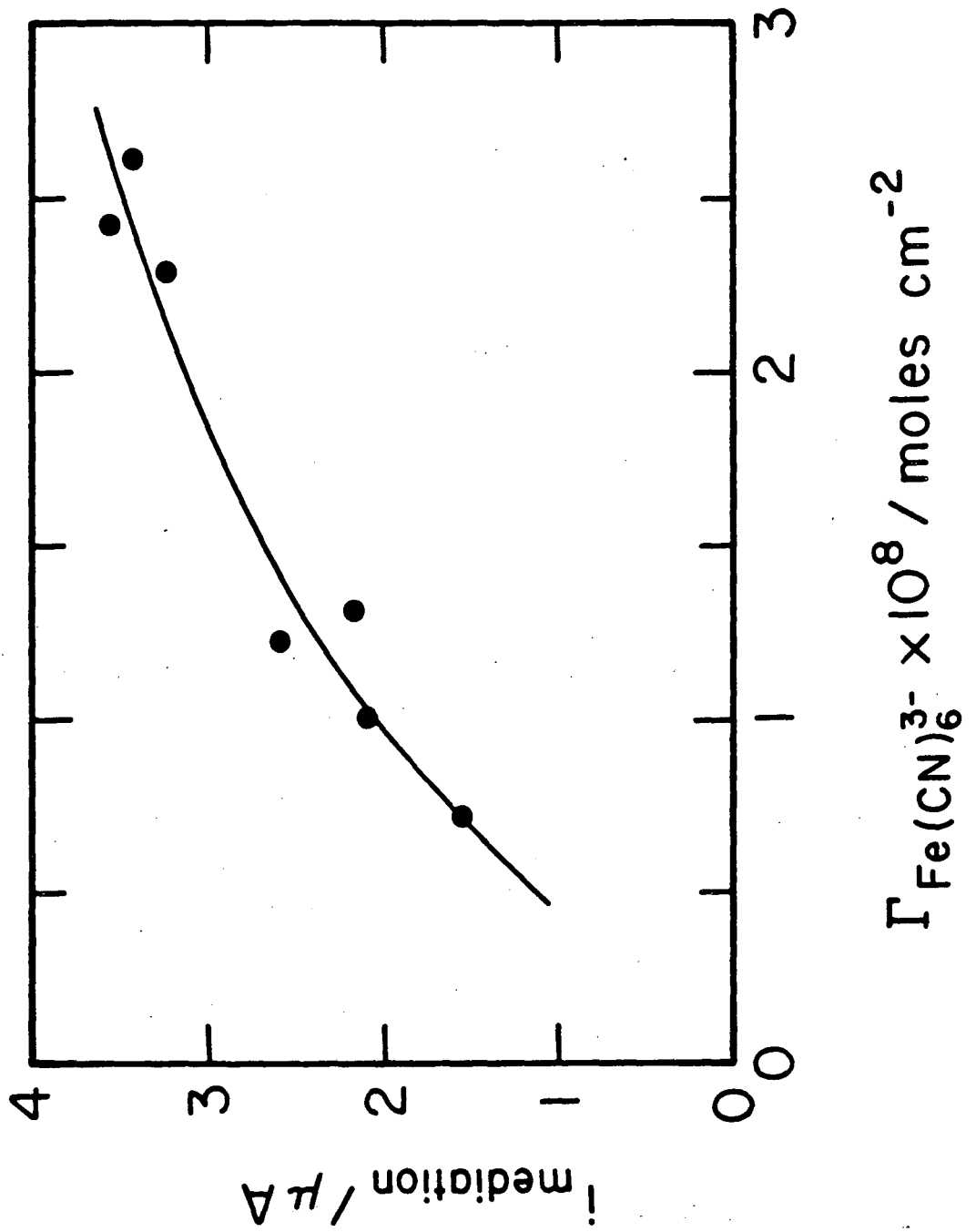
Figure 5.

Figure 6.

E/V vs. Ag/AgCl/Cl⁻, 0.1M

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720