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Polymer Films on Electrodes. 22. Electrochemical, Spectroscopic, and
Transmission Electron Microscopic Studies
on Morphological Changes in Films of Polymeric Surfactants.

By

Yu-Min Tsou, Hsu-Yang Liu, and Allen J. Bard

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The University of Texas at Austin
Department of Chemistry
Austin, Texas 78712

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Polymer Films on Electrodes. 22. Electrochemical, Spectroscopic, and
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Yu-Min Tsou, Hsu-Yang Liu, and Allen J. Bard
Department of Chemistry, The University of Texas
Austin, TX 78712

Abstract

An electroactive polymeric surfactants with pendent long-chain viologen redox groups, PCMS-VC₁₆, was synthesized, by the reaction of poly(chloromethylstyrene) with N-hexadecyl-4(4'-pyridyl)pyridinium bromide. Films of this polymeric-surfactant on glassy carbon electrodes were studied by electrochemical, spectroscopic (absorption-probe), and electron spin resonance techniques. The results suggest that upon reduction of the viologen groups in aqueous solution, the structure of the polymeric surfactant becomes more compact, probably because of reorganization induced by a decrease in the coulombic repulsive interaction. Spherical domains formed by the aggregation of the long-chain hydrocarbon groups were observed in the transmission electron micrographs of both the oxidized form and reduced form of the polymeric surfactants.

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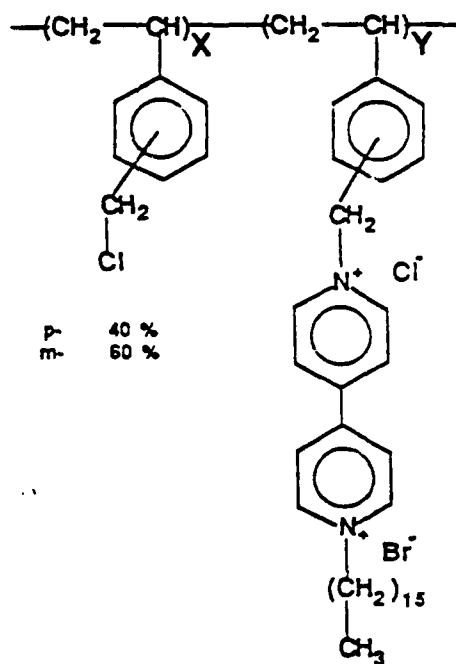


INTRODUCTION

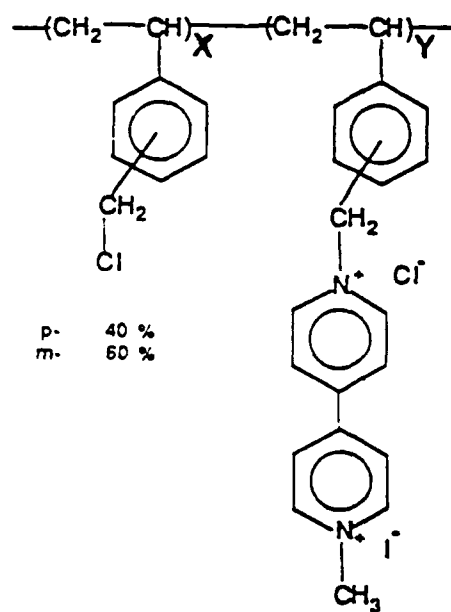
Studies of polymeric films on electrodes have been carried out to investigate the mechanism of mass and charge transport in polymeric layers, to characterize their redox properties, and for possible applications (e.g., displays, electrocatalysis).¹ Several investigations concerned the morphology of polymer films, the changes that occur upon oxidation and reduction, and how these changes affect film properties.² The present study concerns the effect of oxidation and reduction of films of redox active polymeric surfactants. Polymeric surfactants, or polysoaps, have been studied extensively (e.g., in their application in the catalysis of chemical reactions).^{3,4} Related investigations of the electrochemistry of redox species incorporated in the micelles,⁵ and of vesicles with electroactive head groups^{6a-c} have also been carried out. For example, Saji et al.,⁷ studied the formation and disruption of micelles by control of redox states of the (monomeric) surfactant ferrocene tail groups. However, no detailed study of the morphology of electroactive polymeric surfactants has been made. In this article, we report studies of the polymeric surfactant, I, PCMS-VC₁₆, containing long-chain viologen side groups. Other polymers containing viologen (V^{2+}) groups have been studied previously, because these groups show reversible electrochemical reactions and large spectral changes upon reduction.⁸ In these polymers, the charge of the viologen groups can be switched reversibly between V^{2+} (oxidized form) and V^+ (reduced form) electrochemically. The change in the structure of the polymer coatings was monitored by electrochemical, spectroscopic, and electron microscopic methods.

EXPERIMENTAL SECTION

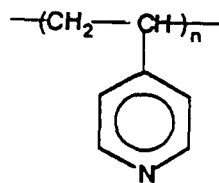
Materials. 4-Vinylpyridine (Polyscience, Inc., Warrington, PA) and

PCMS-VC₁₆

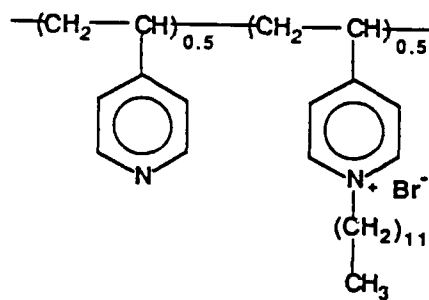
PCMS-MV



PVP



III

PVP- C_{12} 

IV

chloromethylstyrene (60% meta, 40% ortho) (Aldrich, Milwaukee, WI) were distilled under reduced pressure. Poly(4-vinylpyridine), PVP, III, was synthesized by bulk polymerization of 4-vinylpyridine initiated by benzoyl peroxide (Polyscience, Inc.) at 50° C.⁹ It was purified by reprecipitation of the nitromethane solution with excess toluene. The molecular weight was 4.9×10^5 (viscometry).¹⁰ Quaternization of poly(4-vinylpyridine) with dodecyl bromide (Aldrich) was carried out in degassed 1:1 nitromethane-nitroethane at 50° C.³ The extent of quaternization was 50% (NMR). This product is designated here PVP-C₁₂, IV. Poly(chloromethylstyrene) was synthesized¹¹ by radical chain polymerization in degassed benzene using AIBN (Polysciences, Inc.) as the initiator. It was purified by the precipitation of a benzene solution with MeOH. The average molecular weight was 8×10^4 (GPC).

N-(n-hexadecyl)-4-(4'-pyridyl)pyridinium bromide was synthesized and characterized according to reference 12. ¹NMR(DMSO-d₆), (ppm): 0.88 (t, 3H, -CH₃), 1.1 - 2.3 (m, 28H, -CH₂-), 4.7 (t, 2H, N-CH₂); aromatic H-8.13 (d, 2H), 8.73 (d, 2H), 8.96 (d, 2H), 9.33 (d, 2H).

PCMS-VC₁₆, I.- N-hexadecyl-4-(4'-pyridyl)pyridinium bromide and poly(chloromethylstyrene) were heated at 80° C in dry degassed N,N-dimethylformamide (DMF) for 48 h. The precipitate was collected, washed, and redissolved in warm MeOH. The MeOH solution was added dropwise to rapidly stirred dioxane and the resulting cloudy mixture was centrifuged. The precipitate was washed with dioxane, then acetone. A yellow powder was obtained by another reprecipitation of a MeOH solution with dioxane. The result of elemental analysis indicated that 40% of the chloromethylstyrene groups were functionalized with viologen groups. Elemental analysis for PCMS-V₁₆ (40%), 1dioxane/monomer unit: Found: C,66.8; H,8.05; N,3.32. Calcd: C,66.4; H,8.05; N,3.25.

PCMS-MV, II, was synthesized according to the procedure for a similar polymer.^{12a} Elemental analysis indicated that the extent of substitution was 42%. PCMS-MV (42%), 1 dioxane/monomer unit: Found: C, 56.2; H, 5.74; N, 4.05. Calcd: C, 56.3; H, 5.66; N, 3.93.

Apparatus. Electron spin resonance (ESR) measurements (X band) were made with a Varian E-9 spectrometer (100 kHz field modulation) equipped with a TE₁₀₂ dual-sample cavity. The ESR-electrochemical cell was a specially designed 1 mm thick flat ESR cell¹³ suitable for both electrochemical and ESR studies. Visible absorption measurements were obtained with transparent SnO₂ (PPG Glass) electrodes and an HP-8450A spectrometer. Electrochemical measurements were performed with a PAR model 175 universal programmer, a model 173 potentiostat, and a model 179 digital coulometer (Princeton Applied Research Corp., Princeton, NJ). Current-time curves were recorded on a X-Y recorder or a Norland Model 3001 digital oscilloscope. Transmission electron micrographs were obtained on a JEOL 1200 EX STEM equipped with a Tracor 5500 energy dispersive spectroscopy. The working electrode used in voltammetric experiments was a glassy carbon electrode with an area of 0.07 cm² (Bioanalytical Systems, West Lafayette, IN). The SnO₂ electrode was prepared by attaching a Cu wire to the conducting SnO₂ surface with silver paint and covering the contact with a nonconducting epoxy cement. The working electrode for the ESR experiment was a 0.3 x 0.6 cm Pt flag. The counter electrode was a Pt wire and the reference electrode was a saturated calomel electrode (SCE), except in the simultaneous electrochemical-ESR (SEESR) experiment where an Ag/AgCl electrode was used as both the counter and reference electrode. Viscometry was performed with a Bausch and Lomb Viscomatic-1 viscometer.

Procedures. The electrodes were prepared by covering the conducting substrates (C, Pt, SnO₂) with an aliquots of the polymer solution (0.25%

w/v); solvents were MeOH for PCMS-VC₁₆, PVP, and PVP-C₁₂, and DMF for PCMS-MV. Before every experiment the potential of the electrode was held at a positive value to oxidize any bromide in the polymer to bromate, and iodide to iodate. Both bromate and iodate are replaced by chloride from the supporting electrolyte solution very rapidly.^{12a} Samples for transmission electron microscopy were prepared by coating a thin polymer film on a carbon-coated copper grid. The films were then stained with a 2% aqueous uranyl acetate solution.

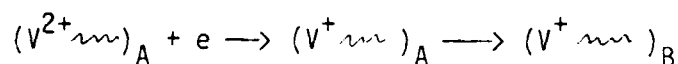
RESULTS AND DISCUSSION

Electrochemical Experiments--PCMS-VC₁₆ is a polymeric surfactant. The long-chain viologen groups are the charged pendent groups. Since the doubly charged viologen group can be reduced reversibly to the singly charged cation radical, this provides the opportunity to investigate the effects of charge on the morphology of the film of a polymeric surfactant. The cyclic voltammograms (CV) of a PCMS-VC₁₆ coating on a glassy carbon electrode are shown in Figure 1. In Figure 1a, the initial potential was -0.1 V, where all the viologen groups were in the V²⁺, oxidized, form. On the other hand, in Figure 1b, the initial potential was -0.6 V, where they were in the V⁺, reduced, form. In both cases, the coated electrode was held at the initial potential for 30 min before the potential scan. Note that the shape of the CV waves depends upon the initial potential. In both cases the waves are those of a surface-confined species with the viologen groups being completely reduced (or oxidized) during each cathodic (or anodic) scan. Under these conditions, the shape and the width at half-height ($\Delta E_{1/2}$) provides information about the extent of interaction between the reduced groups.¹⁴ In Figure 1b, the width at half-height is 75 mV and 120 mV for the anodic and cathodic wave, respectively, while it is 95 mV and 120 mV,

respectively, for Figure 1a. The width at half-height for an ideal surface wave with $n=1$ and noninteracting redox groups is 90 mV. Attractive interaction decreases the width and repulsive interaction increase it. In aqueous solution $\Delta E_{1/2}$ is usually larger than 90 mV for charged redox pendent groups or redox complexes incorporated in polyelectrolyte coatings.¹⁵ This is presumably due to the coulombic repulsion between the charged groups. However, if the redox groups are charged long-chain hydrocarbon groups, such as those in PCMS-VC₁₆, both hydrophobic and coulombic interactions would contribute to the overall interaction.

The distinctly different $\Delta E_{1/2}$ -values for the anodic and cathodic wave in Figure 1b indicate the morphology of the polymer in the reduced form is different from that in the oxidized form. The 75 mV width for the anodic wave in Figure 1a suggests that there are quite strong attractive interactions among the viologen groups in the reduced form so that the overall interaction is attractive. When the charge on the viologen groups is reduced ($V^{2+} + e \rightarrow V^+$), the coulombic repulsion between them is decreased and the long-chain hydrocarbon groups can approach one another. This results in significant enhancement of the hydrophobic interaction. This hydrophobic interaction (attractive) would also cause the structure of the reduced polymer in the aqueous solution to be more compact than in the oxidized form.

We schematically represent this process as:



where A and B represent more extended and more compact structures, respectively. The fact that the $\Delta E_{1/2}$ -value for the oxidation is larger (95 mV)² when the scan occurs on reversal from an initial potential where all of

the viologens are in the V^{2+} -form (Figure 1a) than it is (75 mV) when the viologen has been in the V^{+} -form for a much longer time (Figure 1b) indicates that the rate of change in polymer morphology from the A to the B form is slow on the time scale of this CV experiment. The following experiment was performed to estimate the rate of change. The coated electrode was allowed to equilibrate at -0.1 V and then the potential was scanned to -0.6 V, and held at this potential for different periods of time (τ) before it was scanned positively to obtain the anodic wave. For τ longer than 4 min, the $\Delta E_{1/2}$ was 75 mV and the shape of the wave did not depend on τ . For smaller τ -values, $\Delta E_{1/2}$ was larger and the wave shape depended on τ . Thus, the time required for the change in polymer morphology upon reduction is about 4 min.

Although the rate of change in polymer morphology is slow during reduction, the rate of change in polymer morphology upon re-oxidation is fast on the voltammetric time scale as indicated by the almost equal $\Delta E_{1/2}$ -values for the cathodic waves in Figure 1a and 1b. Different rates of change for expansion and contraction of charged polymers have been discussed previously.¹⁶ However, the present observation demonstrates for the first time that voltammetric methods can be used to study the kinetics of change in the morphology of a polymeric surfactant in aqueous solution.

The rate of charge transport through the films of PCMS-VC₁₆ was estimated by potential step chronoamperometry.¹ In this experiment, the potential was stepped either from -0.1 to -0.6 V (for measurement with the polymer initially in the oxidized form) or from -0.6 to -0.1 V (for the polymer initially in the reduced form) and the slope of the current (i) vs. $t^{-1/2}$ line for times (t) of 0.8 ms to 1.4 ms was used to determine the effective diffusion coefficient, D_{eff} . D_{eff} was $1.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for an initially oxidized form and $1.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for an initially reduced form,

respectively. The significant difference is consistent with a morphology change accompanying the redox process.

To demonstrate that the variation in $\Delta E_{1/2}$ is due to the variation in the intensity of the hydrophobic interaction among the long-chain side groups, the same experiment was carried out with another viologen polymer, PCMS-MV. As shown in Figure 2a and 2b, $\Delta E_{1/2}$ for the two pairs of waves are all in the range of 138-145 mV. This finding not only supports the structural change upon reduction of PCMS-VC₁₆, but suggests that even in the oxidized form the attractive interactions of the hydrocarbon chains partially compensates for the repulsive interactions of the V²⁺ groups. The greater stabilization of the radical cation of PCMS-VC₁₆ by the attractive, hydrophobic interaction among the charged long-chain hydrocarbon groups is also reflected in the redox potential. The redox potential of PCMS-VC₁₆ is -0.44 V, compared to that of PCMS-MV, -0.38 V vs. SCE.

Spectroscopic Study with Absorption Probe--To gain more insight into the change in polymer morphology, spectroscopy in the visible region with and without methyl orange as a absorption probe was carried out. The absorption spectrum (Figure 3) of the reduced form of PCMS-VC₁₆ film on an SnO₂ electrode shows an absorption maximum at 540 nm, indicating predominantly dimeric species in the film matrix.¹⁷ The dimerization of the cation radical head groups could contribute to some extent to the more compact aggregation of the polymer in the reduced form, but we do not believe that it is the major factor.

Absorption probes, such as methyl orange, have been used to investigate the microenvironments in polymer matrices.¹⁸ For example, Martin and coworkers have applied this techniques in several studies.^{18b-d} Methyl orange has long been used as an absorption probe to investigate the hydrophobicity of the binding sites.¹⁹ The absorbance maximum is 460 nm in

water, but is 420-430 nm in organic solvents. When it is bound to biopolymers or charged polymers, the maximum is at a shorter wavelength than 460 nm. Thus, an absorbance maximum of shorter wavelength indicates a higher hydrophobicity at the binding site. The difference spectra for methyl orange in PCMS-VC₁₆ coating on SnO₂ electrodes is shown in Figure 4. By taking the difference between the absorption spectrum of PCMS-VC₁₆ coating alone and that of PCMS-VC₁₆ coating in which methyl orange has been incorporated from a dilute solution, the contribution from the viologen groups is eliminated. Two difference spectra were taken by holding the potential of the electrode at -0.1 V (oxidized form of PCMS-VC₁₆), or at -0.6 (reduced form of PCMS-VC₁₆). That the absorption spectrum of methyl orange incorporated in the reduced form of the polymer coating is blue shifted from that incorporated in the oxidized form indicates that the environment of the binding sites of methyl orange in the reduced form of the polymer is more hydrophobic. Thus, in the reduced form of the polymer, the long-chain hydrocarbon groups approach one another and form more compact hydrophobic domains. The result here is consistent with the conclusion drawn from the variation of $\Delta E_{1/2}$ of the CV waves.

This is the first demonstration of the effect of charge on the hydrophobicity of the binding sites (or the domains) associated with a polymer in aqueous solution. Previously, Ikemi et al.,²⁰ used the shift of emission spectrum of the fluorescent probe, 8-anilino-naphthalene-1-sulfonate to study the effect of polymer concentration on the hydrophobicity of the hydrophobic domains formed by the triblock copolymer, poly(2-hydroxyethyl methacrylate) - poly(ethylene oxide - poly(2-hydroxyethyl methacrylate)). Their study and this one demonstrate the usefulness of probe molecules in the investigation of the morphology of polymers.

ESR Experiment--The ESR spectra of the reduced form of PCMS-VC₁₆ is shown in Figure 5 for (a) aqueous and (b) acetonitrile (MeCN) solutions. In MeCN (Figure 5b) the usual spectrum of polymeric radicals, namely, an approximately symmetric single line spectrum is observed. The disappearance of the hyperfine structure exhibited by the monomer in dilute solution is caused by dipolar interactions and/or electron and spin exchange reactions in systems of high concentration of radicals.²¹ The ESR spectrum in aqueous solution (Figure 5a) approaches the solid-state (or powder) spectrum²² and indicates immobile radical cation side groups in the reduced PCMS-VC₁₆. Thus, in aqueous solution the long-chain viologen radical cation side groups are embedded in very hydrophobic, only slightly swollen hydrocarbon domains. The rotational motion is severely retarded. The difference between the spectrum in aqueous and that in MeCN solution also points to the so-called hydrophobic effect--the aggregation of the amphiphilic molecules is only pronounced in those solvents with high strength of hydrogen bonding and high dielectric constant, such as water.²³

Transmission Electron Microscopy--It has long been known that the size of micelles is in the range of 15-30 Å.²⁴ We were interested in investigating the size of the hydrophobic domains formed in polymeric surfactants and the effect of the charge on the size. Because of the film-forming property of polymeric surfactants, we were able to investigate the morphology of polymeric surfactants by transmission electron microscopy (TEM). Figure 6 shows the micrographs of several charged polymers. A polymer film cast on a carbon-coated copper grid, was stained with 2% uranyl acetate solution (Figure 6a-e). The film of oxidized PCMS-VC₁₆ clearly shows continuous spherical domains, with typical domain diameters of about 200-500 Å (Figure 6a). The size of the domains is similar to those

exhibited by synthetic vesicles.⁶ However, the domains in the films of vesicles are discrete whereas in PCMS-VC₁₆, the domains are close-packed. We believe the hydrophobic domains observed in the film of PCMS-VC₁₆ are formed both inter- and intramacromolecularly by the aggregation of the long chain viologen groups.

If the film of PCMS-VC₁₆ was first reduced chemically before staining with uranyl acetate, the size of the hydrophobic domains became smaller; the typical diameters were about 100 Å (Figure 6b). This is consistent with the results of electrochemical and absorption experiments, which indicates a more compact structure for the reduced form of the polymer.

Another polymeric surfactant PVP-C₁₂, IV (see Experimental section), was also investigated for comparison. As shown in Figure 6c, hydrophobic domains were also observed. However, in this case the domains showed an elliptical rather than a spherical shape. The origin of this difference is not clear. For charged polymers that do not have long-chain hydrocarbon groups, such as PCMS-MV (Fig. 6d) and sodium polystyrenesulfonate (Fig. 6e), domain structure was not observed. This supports the view that domains observed in the polymeric surfactant film are formed by the aggregation of long-chain hydrocarbon groups.

Incorporation of both inorganic and organic compounds--We are particularly interested in the incorporation of organic molecules by polymeric surfactants for potential applications of such films in electrocatalysis. Conventional polyelectrolytes, such as protonated-polyvinylpyridine^{19b} are capable of incorporating inorganic compounds (as catalysts or mediators) such as Fe(CN)₆^{3-/4-} but do not incorporate organic substrates. We anticipated that the hydrophobic domains formed by PVP-C₁₂ would incorporate organic compounds and this was indeed observed. Previous studies of perfluorosulfonate (Nafion) and

perfluoro-carboxylate (Flemion)^{15,18} indicated these perfluoro polyelectrolytes can incorporate both hydrophilic and hydrophobic compounds.

Figure 7a illustrates one such experiment. A PVP-C₁₂-coated electrode was dipped in 1 mM anthraquinone- β -sulfonate (AQS) aqueous solution and then transferred to a pure supporting electrolyte solution. The much larger response (reduction and reoxidation of AQS), (solid line) obtained compared with the response (dashed line) of a 1 mM AQS solution at an uncoated electrode indicates that a large amount of AQS has been incorporated into the PVP-C₁₂ coating. When the same experiment was carried out for a protonated PVP-coated electrode, the amount of incorporation was very small (Figure 7b).

Figure 7c shows CV with the co-incorporation of Fe(CN)₆³⁻ and AQS. In this experiment an electrode with incorporated AQS, as in Figure 7a, was dipped in 1 mM Fe(CN)₆³⁻ solution, then washed and transferred to pure supporting electrolyte. Note that after incorporation of Fe(CN)₆³⁻, the response due to AQS became smaller. This indicates a smaller effective diffusion coefficient of AQS in the Fe(CN)₆³⁻ incorporated film. This is presumably caused by the crosslinking of the film by Fe(CN)₆³⁻.²⁵

The co-incorporation of an inorganic catalyst or mediator and organic substrate could be useful in the design of electrocatalytic films. Most electrocatalysis involve systems where only catalysts are incorporated (or concentrated) in the polymer coatings. Polymeric surfactants provided an environment in which both catalyst and nonpolar substrate can be concentrated. This might increase the efficiency of electrocatalysis.

CONCLUSIONS

The investigation of electroactive polymeric surfactants revealed a number of interesting properties. The film-forming property might make them more useful than micelles or even vesicles in some applications. Although

vesicles do retain their structure after solvent evaporation, they do not form good films and the domains are discrete. These polymeric surfactants can behave as bound or immobilized micelles with both hydrophobic and hydrophilic domains. Films of Nafion also exhibit segregated hydrophobic and hydrophilic domains. It would be interesting to compare their behavior with those of the polymeric surfactants. These polymeric surfactants may also be useful as model systems for electron or energy transfer reactions in organized assemblies. With stable films, investigation by the combination of electrochemical, spectroscopic, and other techniques can be easily carried out.

The effects of charge on the side groups on the morphology of polymeric surfactants have been demonstrated, and it was shown that reduction of the viologen groups leads to a more compact structure in the polymer. Studies of the morphology and properties of blends of polymeric surfactants with other polymers should also be of interest.

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REFERENCES

1. For a general review, see (a) Murray, R. W. *Acc. Chem. Res.* 1980, 13, 135; (b) Murray, R. W. "Electroanalytical Chemistry," Bard, A. J., Ed., Marcel Dekker:New York, 1984, Vol. 13; (c) Alberly, W. J.; Hillmann, A. R. *Chem. Soc. Ann. Rep. C* 1981, 377.
2. (a) Montgomery, D. D.; Anson, F. C. *J. Am. Chem. Soc.* 1985, 107, 3431; (b) Sharp, M.; Montgomery, D. D.; Anson, F. C. *J. Electroanal. Chem.* 1985, 194, 247; (c) Burgmayer, P.; Murray, R. W. *J. Am. Chem. Soc.* 1982, 104, 6139; (d) Kahata, Y.; Enna, G.-I.; Taguchi, T.; Seki, T. *J. Am. Chem. Soc.* 1985, 107, 5300.
3. (a) Strauss, U. P.; Gershfeld, N. L. *J. Am. Chem. Soc.* 1954, 58, 747; (b) Strauss, U. P.; Gershfeld, N. L. *J. Am. Chem. Soc.*, 1954, 58, 753; (c) Chiao, Y.-C.; Strauss, U. P. *Polym. Preprints* 1985, 26(1), 214; (d) Piirma, J. C.; Chang, J. C.; Daneshvar, M. *Polym. Preprints* 1985, 26(1), 219; (e) Chiou, J. J.; Piirma, I. *Polym. Preprints* 1985, 26(1), 221; (f) Ikeda, T.; Tazuke, S. *Polym. Preprints* 1985, 26(1), 226; (g) Pickelman, D. M.; Schmidt, D. L.; Wessling, R. A. *Polym. Preprints* 1985, 26(1), 230.
4. Kunitake, T. in "Polymer-Supported Reactions in Organic Synthesis, Hodge, P. and Sherrington, D. C., eds., John Wiley:New York, 1981.
5. (a) Oshawa, Y.; Shimazaki, Y.; Aoyagui, S. *J. Electroanal. Chem.* 1980, 114, 235; (b) Oshawa, Y.; Aoyagui, S. *J. Electroanal. Chem.* 1982, 136, 353; (c) Yep, P.; Kuwana, T. *J. Electrochem. Soc.* 1976, 123, 1334; (d) Meyer, G.; Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem.* 1981, 119, 417; (e) McIntire, G. L.; Chiappardi, D. M.; Casselberry, R. L.; Blount, H. N. *J. Phys. Chem.* 1982, 86, 2632; (f) McIntire, G. L.; Blount, H. N. *J. Am. Chem. Soc.* 1979, 101, 7720; (g) Kaifer, A. E.; Bard, A. J. *J. Phys. Chem.* 1985, 89, 4876.

6. (a) Kano, K.; Romero, A.; Djermouni, B.; Ache, H. J.; Fendler, J. H. J. *Am. Chem. Soc.* 1979, 101, 4030; (b) Fuhrhop, J.-H.; Bartsch, H.; Fritsch, D. *Angew. Chem., Int. Ed. Engl.*, 1981, 20 804; (c) Baumgartner, E.; Fuhrhop, J.-H. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 550; (d) Regen, S. L.; Czech, B.; Singh, A. J. *Am. Chem. Soc.* 1980, 102, 6638; (e) Kunitake, T.; Nakashima, N.; Shimomura, M.; Okakata, Y.; Ogawa, T.; Kano, K. *J. Am. Chem. Soc.* 1980, 102, 6642.

7. (a) Saji, T.; Hoshino, K.; Aoyagui, S. *J. Chem. Soc., Chem. Commun.* 1985, 865; (b) Saji, T.; Hoshino, K.; Aoyagui, S. *J. Chem. Soc., Chem. Commun.* 1985, 107, 6865.

8. (a) Mortimer, R. J.; Anson, F. C. *J. Electroanal. Chem.* 1982, 138, 325; (b) Simon, M. S.; Moore, P. J. *J. Polym. Sci.* 1975, 13, 1; (c) Bookbinder, D. C.; Wrighton, M. S. *J. Electrochem. Soc.* 1983, 130, 1087; (d) Factor, A.; Heinsohn, G. E. *J. Polym. Sci.*, 1971, 139, 289; (e) Oyama, N.; Ohsaka, T.; Yamamoto, H.; Kaneko, M. *J. Phys. Chem.* 1986, 90, 3850; (f) Gaudiello, J. G.; Ghosh, P. K.; Bard, A. J. *J. Am. Chem. Soc.* 1985, 107, 3027; (g) Abruna, H. D.; Bard, A. J. *J. Am. Chem. Soc.* 1981, 103, 6898.

9. Fitzgerald, E. B.; Fuoss, R. M. *Ind. Eng. Chem.* 1950, 42, 1603.

10. Berkowitz, J. B.; Yamin, M.; Fuoss, R. M. *J. Polym. Sci.* 1958, 28, 69.

11. Kondo, S.; Ohtsuka, T.; Ogura, K.; Tsuda, K. *J. Macromol Sci.-Chem.* 1979, A13, (6) 767.

12. (a) Tundo, P. Kippenberger, D. J.; Politi, M. J.; Klahn, P.; Fendler, J. H. *J. Am. Chem. Soc.* 1982, 104, 5352; (b) Bruinink, J.; Kregting, C. G. A.; Ponjee, J. J. *J. Electrochem. Soc.* 1977, 124, 1854.

13. Goldberg, I. B.; Bard, A. J. *J. Phys. Chem.* 1971, 75, 3281.

14. (a) Laviron, E. *J. Electroanal. Chem.* 1974, 52, 395; (b) Pearce, P. J.; Bard, A. J. *J. Electroanal. Chem.* 1980, 114, 89; (c) Brown, A. P.;

Anson, F. C. *Anal. Chem.* 1977, 49, 1589.

15. (a) Tsou, Y.-M.; Anson, F. C. *J. Electrochem. Soc.* 1984, 131, 595; (b) Oyama, N.; Anson, F. C. *Anal. Chem.* 1980, 52, 1192; (c) Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* 1983, 105, 685; (d) White, H. S.; Leddy, J.; Bard, A. J. *J. Am. Chem. Soc.* 1982, 104, 4811; (e) Martin, C. P.; Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* 1982, 104, 4817; (f) Krishnan, M.; Zhang, X.; Bard, A. J. *J. Am. Chem. Soc.* 1984, 106, 7371.

16. (a) Daum, P.; Murray, R. W. *J. Electroanal. Chem.* 1979, 103, 289; (b) Grank, J.; Park, G. S. "Diffusion in Polymers," Academic Press:New York, 1978, Ch. 3; (c) Helfferich, F. "Ion Exchangers," McGraw-Hill:New York, 1962, Ch. 5.

17. (a) Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* 1964, 86, 5524; (b) Watanabe, T.; Honda, K. *J. Phys. Chem.* 1982, 86, 2617.

18. (a) Lee, P. C.; Meisel, D. *J. Am. Chem. Soc.* 1980, 102, 5477; (b) Alvarez-Roa, E. R.; Prieto, N. E.; Martin, C. R. *Anal. Chem.* 1984, 131, 751; (c) Prieto, N. E.; Martin, C. R. *J. Electrochem. Soc.* 1984, 131, 751; (d) Szentirmay, M. N.; Prieto, N. E.; Martin, C. R. *J. Phys. Chem.*, in press.

19. (a) Klotz, I.; Royer, G. P.; Sloniewsky, A. R. *Biochem.* 1969, 8, 4752; (b) Klotz, I. M.; Shikarna, K. *Arch. Biochem. Biophys.* 1968, 123, 551.

20. Ikemi, M.; Odagiri, N.; Tanaka, S.; Shinchara, I.; Chiba, A. *Macromolecules* 1981, 14, 34.

21. Smith, I. C. P.; Butler, K. W. in "Spin Labeling, Theory and Applications," Berliner, L. J., ed., Academic Press:New York, 1976, Ch. 11.

22. Bolton, J. R., in "Biological Application of Electron Spin Resonance," Swartz, H. N., Bolton, J. R. and Borg, D. C, eds., John Wiley:New York, 1972, Ch. 1.

23. Tanford, C. "Hydrophobic Effect: Formation of Micelles and Biological Membranes," John Wiley:New York, 1973.

24. (a) Thomas, J. K. *Chem. Rev.* 1980, 80, 283; (b) Fendler, J. H. *Acc. Chem. Res.* 1976, 9, 1953.

25. Tsou, Y. M.; Anson, F. C. *J. Phys. Chem.* 1985, 89, 3818, and references therein.

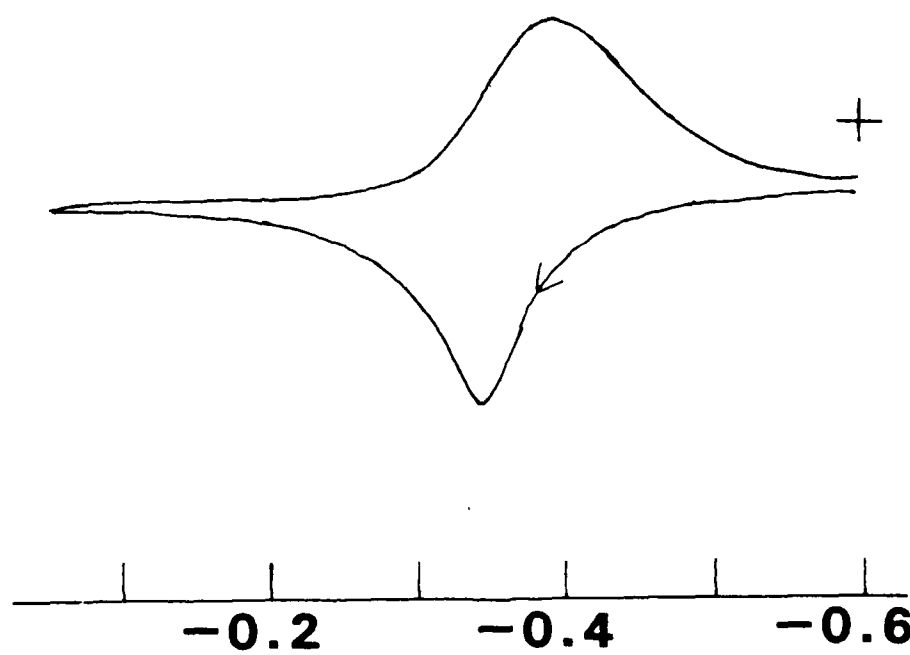
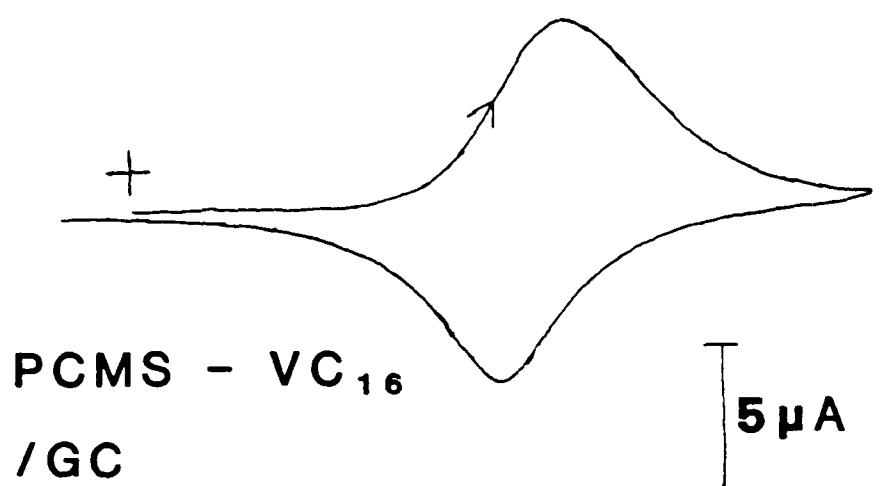
FIGURE CAPTIONS

- Figure 1 Cyclic voltammograms of $1.3 \times 10^{-8} \text{ mol cm}^{-2}$ (viologen groups) of PCMS-VC₁₆ film on a glassy carbon electrode. The electrode was (a) equilibrated at -0.1 V before potential scan, (b) equilibrated at -0.6 V before potential scan. Scan rate: 10 mV s^{-1} . Supporting electrolyte: 0.2 M KCl.
- Figure 2 Cyclic voltammograms of $2.6 \times 10^{-9} \text{ mol cm}^{-2}$ (viologen groups) of PCMS-MV film on a glassy carbon electrode. The electrode was (a) equilibrated at -0.2 V before potential scan, (b) equilibrated at -0.7 V before potential scan. Scan rate: 10 mV s^{-1} . Supporting electrolyte: 0.2 M KCl.
- Figure 3 Absorption spectrum of fully reduced $2.5 \times 10^{-7} \text{ mol cm}^{-2}$ (viologen groups) of PCMS-VC₁₆ film on SnO₂ electrode.
- Figure 4 Difference absorption spectra of methyl orange incorporated in the PCMS-VC₁₆ film of Figure 3. Solid line, PCMS-VC₁₆ film fully oxidized; dotted line, PCMS-VC₁₆ film fully reduced. Supporting electrolyte: 0.2 M KCl and 0.01 M CH₃COONa, pH=5.6.
- Figure 5 ESR spectra of fully reduced $1.4 \times 10^{-6} \text{ mol cm}^{-2}$ (viologen groups) of PCMS-VC₁₆ film on a Pt flag electrode; (a) in 0.2 M KCl aqueous solution, (b) in 0.1 M (n-C₄H₉)₄NBF₄ MeCN solution.
- Figure 6 Transmission electron micrographs of polymer films; (a) fully oxidized PCMS-VC₁₆, (b) fully reduced PCMS-VC₁₆, (c) PVP-C₁₂, (d) PCMS-MV, (e) sodium polystyrenesulfonate.

Figure 7 Cyclic voltammograms for anthroquinone- β -sulfonate (AQS); (a) dotted line, on uncoated electrode, 1 mM AQS; solid line, electrode coated with 4.6×10^{-7} mol cm^{-2} (dodecyl groups) of PVP- C_{12} , dipped in 1 mM AQS solution, and replaced in pure supporting electrolyte solution; (b) repeat of (a) but with electrode coated with 2.0×10^{-6} mol cm^{-2} (pyridine groups) of PVP; (c) electrode coated with PVP- C_{12} used to record Figure 7 (a) (solid line) after it was dipped in 1 mM $\text{Fe}(\text{CN})_6^{3-}$ solution, washed, and replaced in pure supporting electrolyte solution.

10 mv/s

H₂O/0.2M KCl



V vs. SCE

H₂O/0.2 M KCl

10 mv/s

+

PCMS - MV

/GC

0.5 μ A

+

-0.2 -0.4 -0.6

V vs. SCE

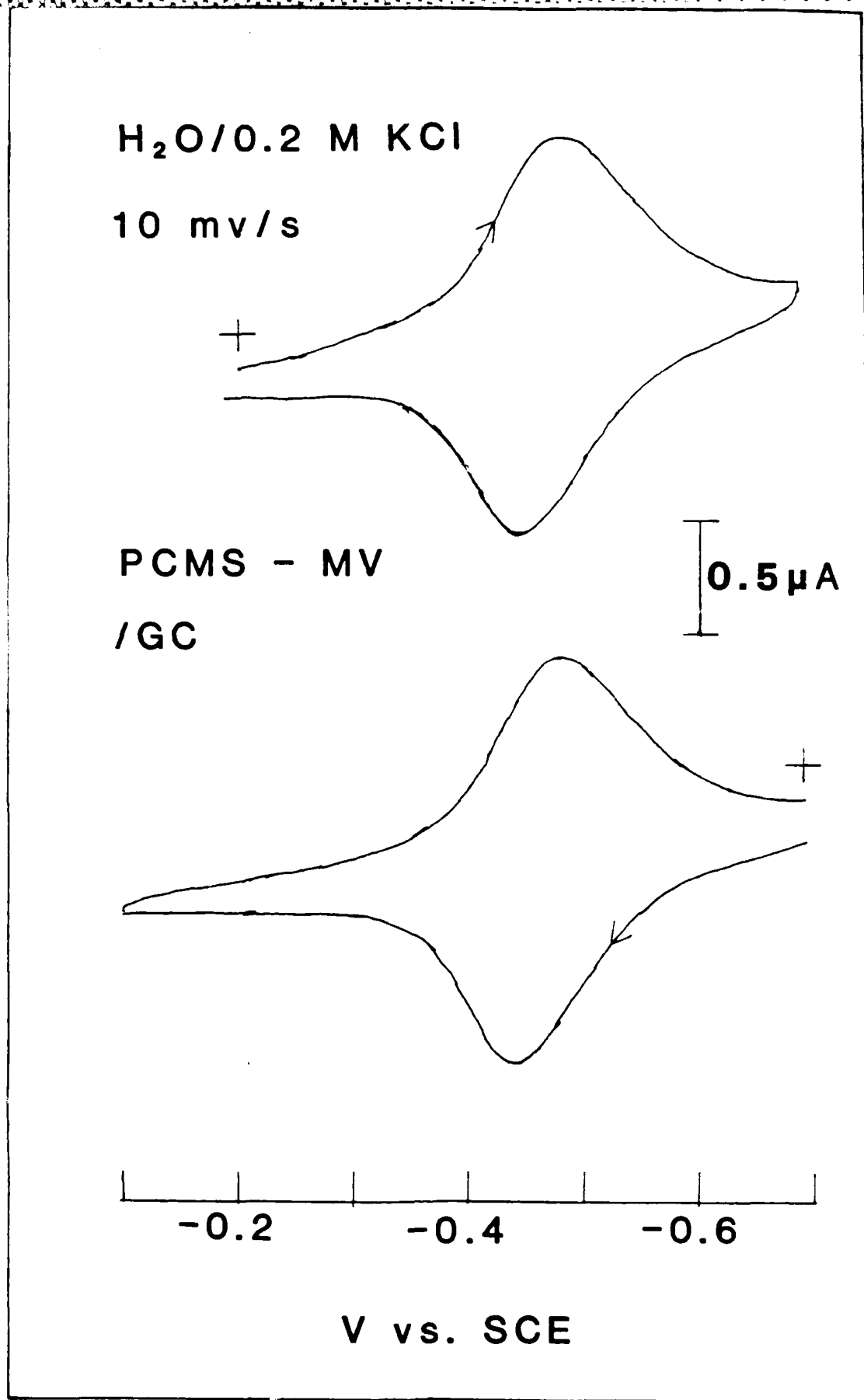
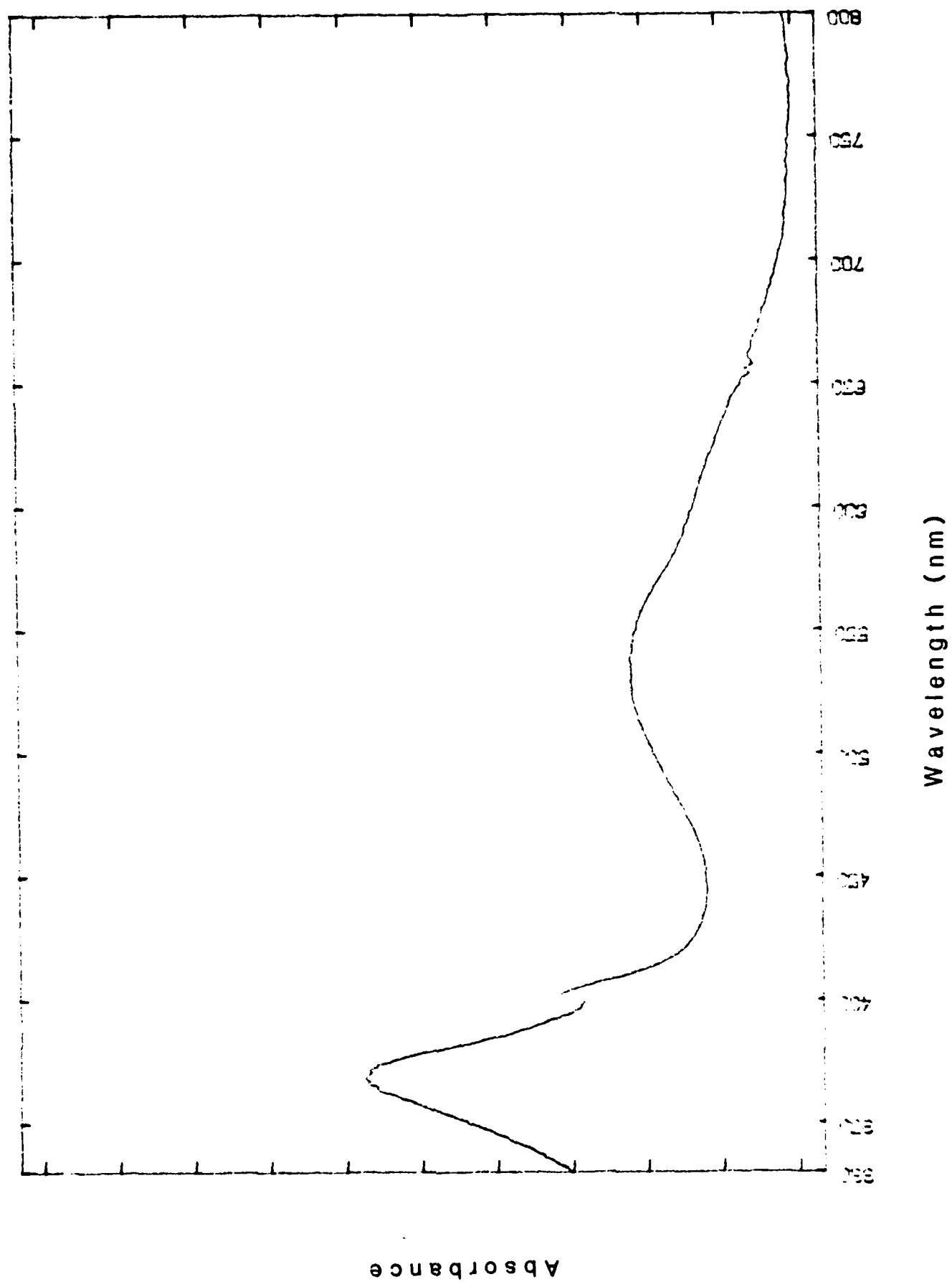


Fig. 3



Difference Spectra

Methyl Orange
in
PCMS - VC₁₆/SnO₂

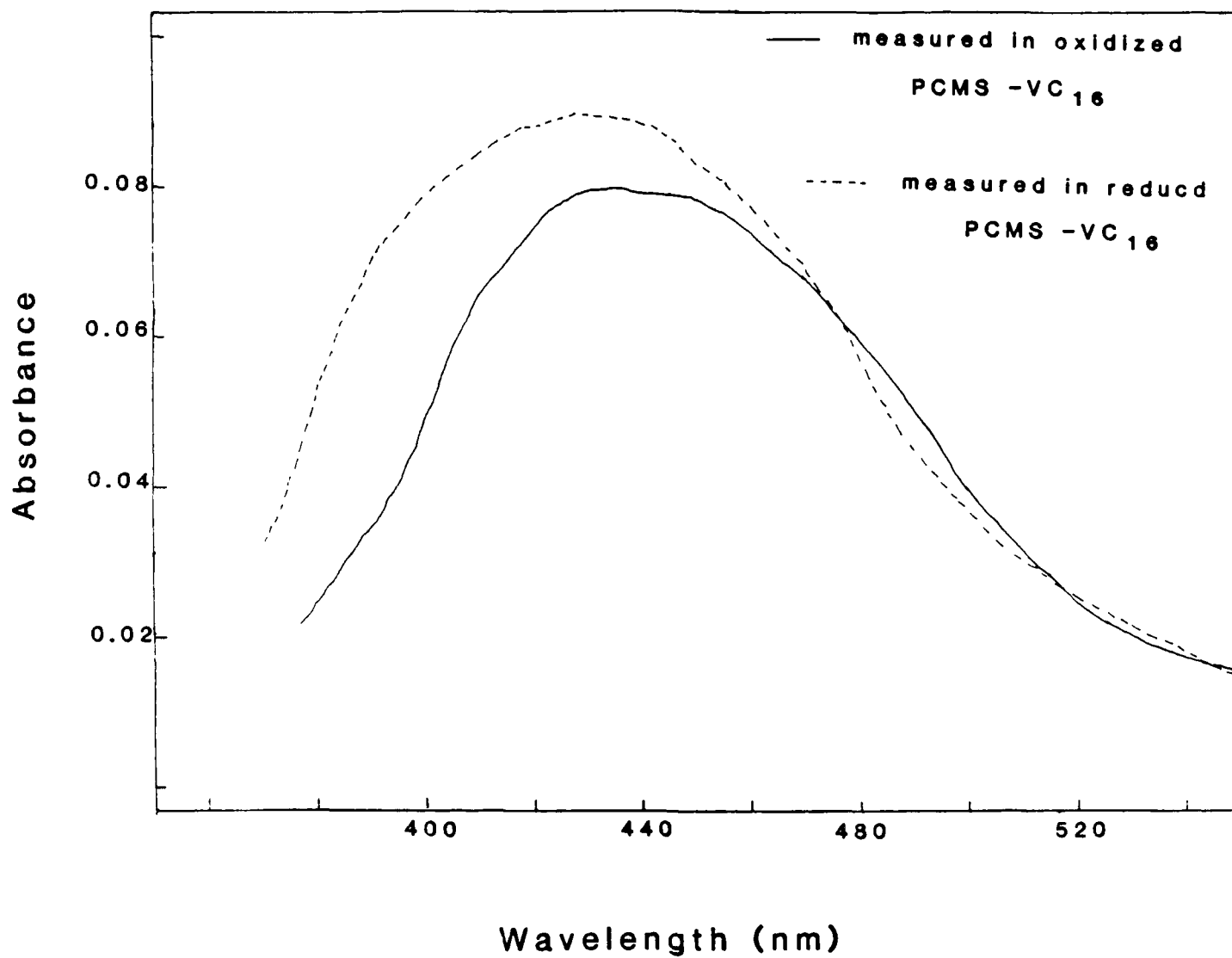
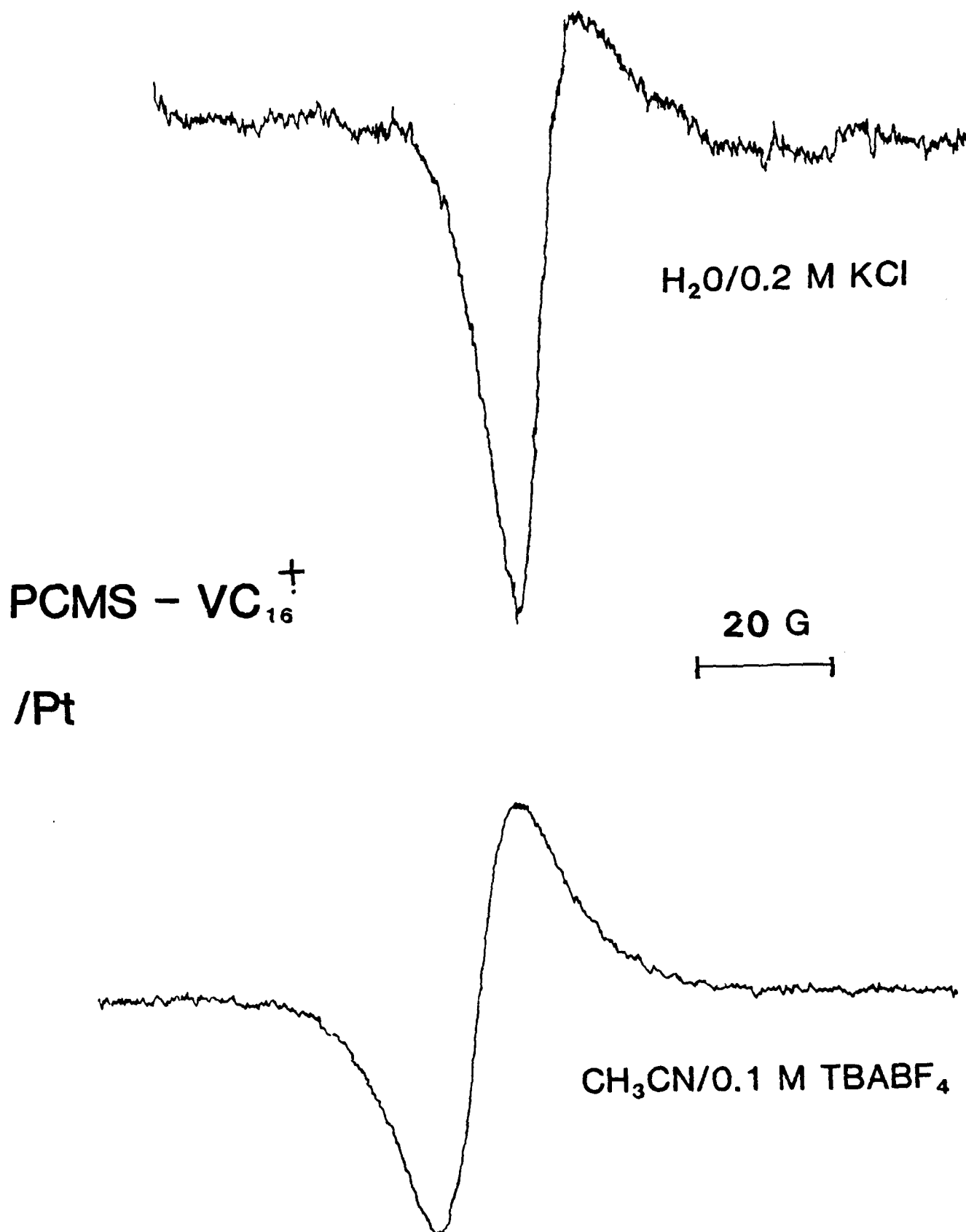


Fig 4

Fig. 5



500 Å

Fig. 6a



500 Å

Fig 6b



500 Å

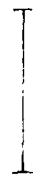


Fig 6c



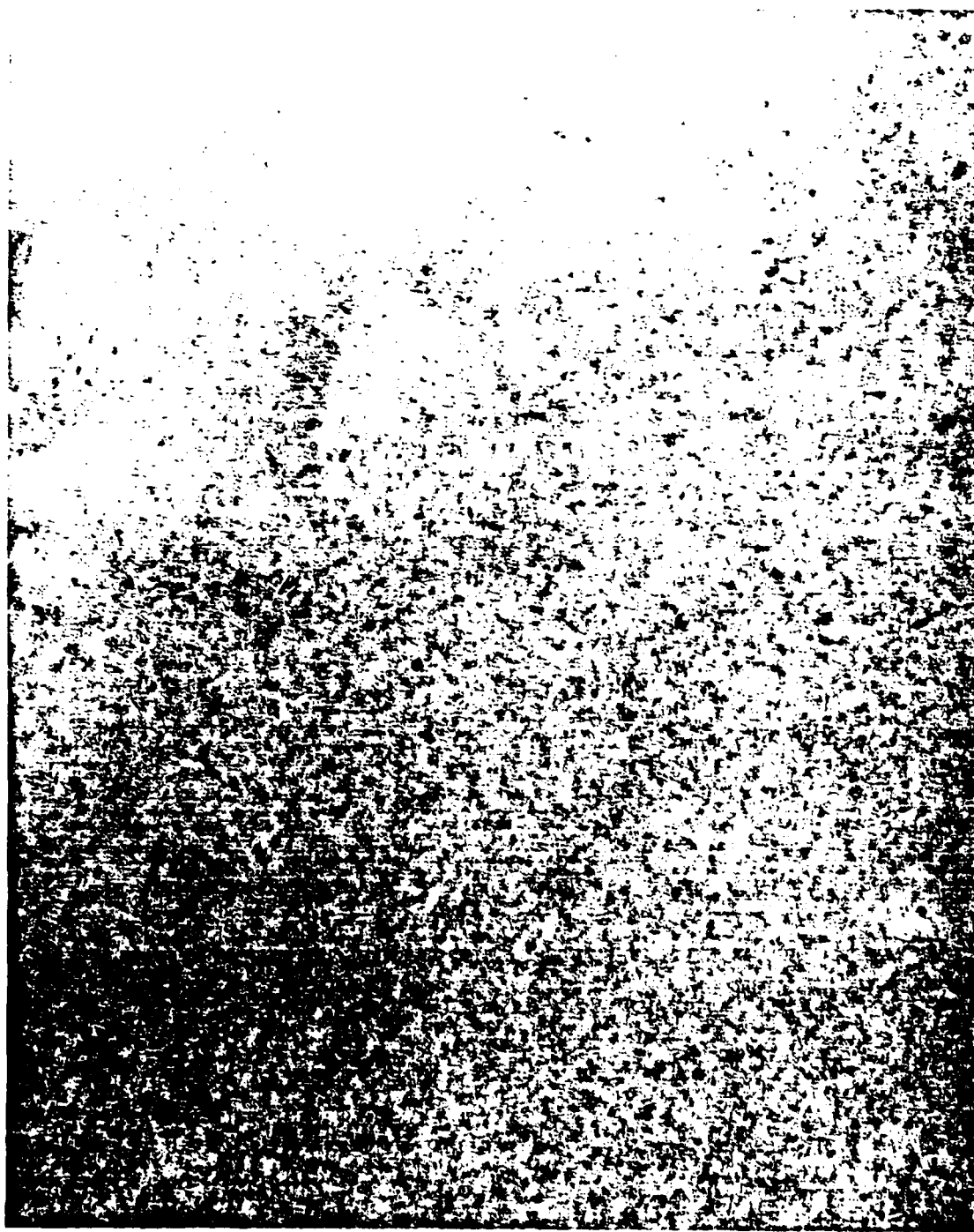


500 Å

Fig 6d

500 Å

Fig 6c



PVP - AQ-SO₃Na

/GC

(b)

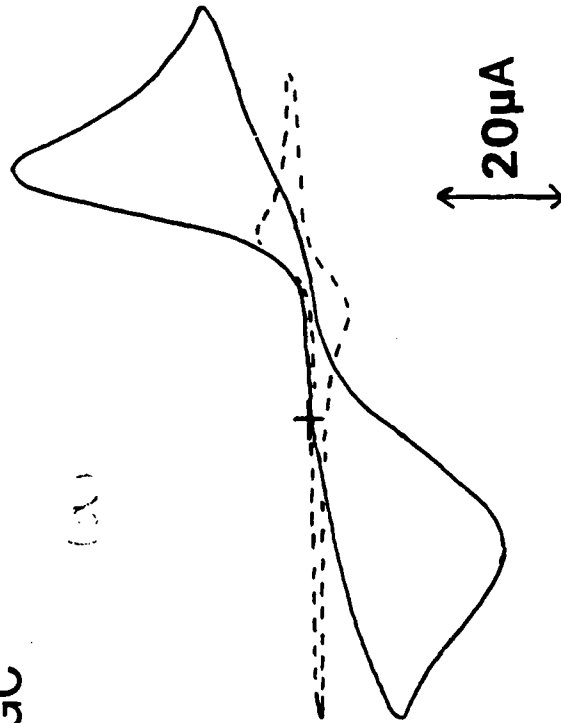
5 μ A



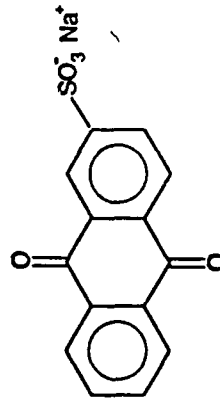
PVP - C₁₂ - AQ-SO₃Na

/GC

(a)



AQ-SO₃ Na



0.2 M CF₃CO₂Na

pH 2.6

0.0

-0.4

0.4

-0.4

V vs. SCE

Fig. 7a, 7b

Co-incorporation of $\text{Fe}(\text{CN})_6^{3-}$
and $\text{AQ-SO}_3\text{Na}$

PVP - C_{12}

/GC

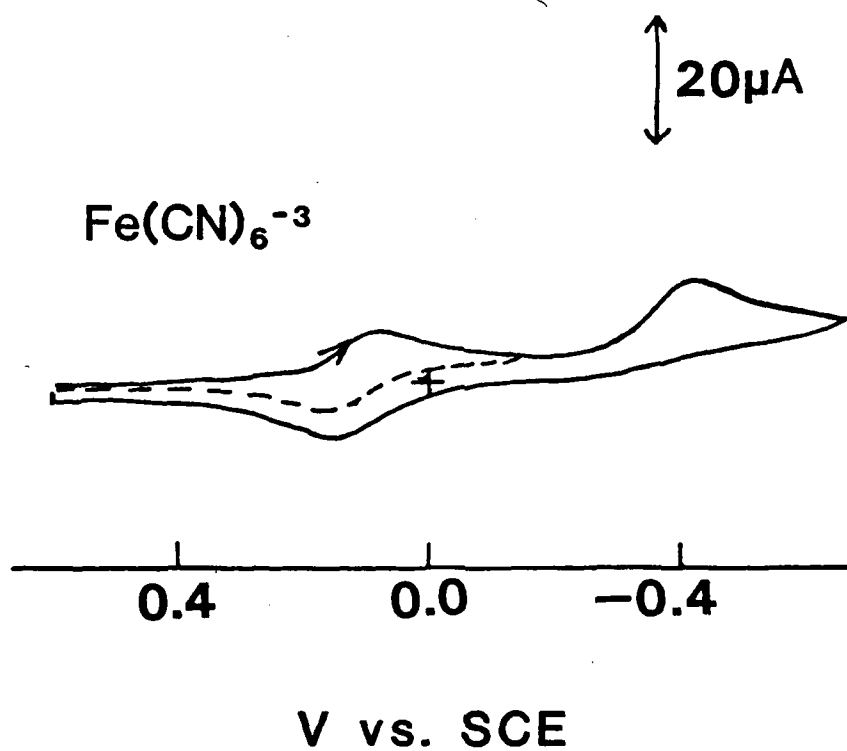


Fig. 9c

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