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ABSTRACT

1,2-Difluorobenzene (DFB) is shown to be a useful solvent for electrochemical studies on transition metal complexes. Because DFB is non-coordinating and relatively inert chemically, it can be a useful solvent for generating and stabilizing otherwise inaccessible intermediates. The accessible potential range for electrochemical studies in DFB extends from +2.0 V to -2.2 V vs ssce.

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The criteria required of a good solvent for electrochemical studies on metal complexes or organometallic compounds include that it should: 1) be relatively easy to purify; 2) have good solvating properties both for electrolyte and the metal complexes or compounds; and 3) have a large potential "window".[1] Although these criteria are largely met by acetonitrile and other organic solvents such as DMF or DMSO, they have the ability to coordinate and often play a role as ligands in electrochemically induced substitution processes.[2] The solvents CH_2Cl_2, THF, 1,2-dimethoxyethane and propylene carbonate have a lower tendency to coordinate but all have limitations arising from restricted potential windows, poor solvating properties, or unwanted chemical reactivity.

We report here that 1,2-difluorobenzene (DFB) has some significant advantages as a solvent for electrochemical studies. It has a dielectric constant which is sufficiently high to dissolve both electrolyte and metal complex salts, it is non-coordinating, it is relatively inert chemically, and it has a wide potential window.

EXPERIMENTAL

Purification of 1,2-difluorobenzene (DFB) and electrochemical studies were carried out in a drybox (Vacuum/Amospheres). The drybox was kept under a constant flow of N_2 which acted as an atmospheric purge preventing contamination of DFB.

Materials. 1,2-difluorobenzene (Aldrich, 98% or Lancaster, 98+%) was purified by passing it through a column of activated alumina. DFB is expensive and it was collected and recycled by distillation (b.p.= 92 °C) for reuse. Tetra-n-butylammonium hexafluorophosphate (TBAH) was precipitated from water by mixing aqueous solutions containing stoichiometric amounts of tetra-n-butylammonium bromide and KPF_6 (both from Aldrich). The resulting precipitate was recrystallized twice from ethanol, dissolved in a minimum amount of acetonitrile, filtered to remove solid impurities, and precipitated by addition into ether. The resulting white solid was washed with ether, filtered, and dried *in vaccuo* at 75 °C for 24 h.

Electrochemistry. Platinum and glassy carbon button electrodes of area ~ 0.1 cm^2 were seated in teflon shrouds and cleaned by polishing with 1 μm diamond paste (Buehler). Cuvette size optically transparent electrodes (In-doped SnO_2 on glass) were purchased from Delta Technologies. Electrochemical measurements were performed by using a PAR model 173 potentiostat *in conjunction with a* PAR model 175 Universal Programmer. Electrochemical data were recorded on a Hewlett-Packard model 5017B X-Y recorder and all potentials are referenced to a saturated sodium chloride calomel reference electrode (ssce). Three compartment cells were employed where the reference and auxiliary (Pt mesh) electrodes were separated from the working compartment with fine and medium porosity frits, respectively. For controlled potential electrolysis experiments a Pt mesh served as the working electrode.

RESULTS AND DISCUSSION

Solvating Properties. 1,2-difluorobenzene is a polar molecule (μ = 2.59)[3] which has a higher dielectric constant (13.8 at 28 °C)[4] than either CH_2Cl_2 ($D_s = 8.9$)[1a] or THF ($D_s = 7.4$).[1a] The electrolyte TBAH is very soluble in DFB with a saturation limit at room temperature of ~ 1.5 M. The solvating ability of DFB toward transition metal complexes is similar to that of CH_3CN. Many neutral complexes - $M_2(CO)_{10}$ (M = Mn and Re), and Re), ferrocene, or $[Re(bpy)(CO)_3X]$ (X = Cl, Br ; bpy = 2,2'-bipyridine) - monocationic salts - $[Re(bpy)(CO)_3(CH_3CN)](PF_6)$, $[Os(bpy)_2(4\text{-vinylpyridine})Cl](PF_6)$ - and dicationic salts - $[M(bpy)_3](PF_6)_2$ (M = Fe, Ru, and Os), $[Ru^{IV}(bpy)_2(4\text{-}tert\text{-butylpyridine})(O)](PF_6)_2$ - have solubilities which are similar in CH_3CN and 1,2-difluorobenzene. The neutral compounds $[Ru(bpy)_2Cl_2]$ and $[Re(bpy)(CO)_3]_2$ are only sparingly soluble in either solvent. There are some notable differences in solubility. 1,2-Difluorobenzene will dissolve much higher concentrations of some porphyrins and phthalocyanines that are nearly or totally insoluble in acetonitrile. Ferrocene, although very soluble in DFB, leads to adsorptive behavior when oxidized to ferrocenium ion.

General Electrochemical Properties. A background cyclic voltammogram for a DFB solution 0.1 M in TBAH is shown in Fig. 1(A). The useful potential window for DFB is approximately +2.0 to -2.2 V vs ssce when the solvent is prepurified by passing it through alumina. For comparison, a chart of the electrochemical limits for a number of commonly used solvents is shown in Fig. 1(B). If the concentration of the electroactive compound is low, < ~ 0.1 mM, the background shown in Fig. 1 is not insignificant and the solvent limits become +1.8 to −2.0 V. At the anodic limit a small but discernible oxidation wave appears at E_p = +1.9 V. It arises from an impurity (< ~ 0.05 mM estimated from the peak height) that is not removed by passing the solvent through an alumina column. Removal of the impurity by fractional distillation leads to an oxidative limit of between +2.0 and +2.1 V. The cathodic limit is probably due to the reduction of DFB. The current continues to climb rapidly beyond -2.2 V. We could find no previously published information concerning the electrochemical properties of 1,2-difluorobenzene.

In order to determine the kinetic properties of the solvent, we have measured the peak to peak splitting, ΔE_p, for the $[Fe(\eta^5\text{-}Me_5C_5)_2]^{+/0}$ couple ($\eta^5\text{-}Me_5C_5$ is pentamethylcyclopentadienyl anion) as a function of scan rate and of electrolyte concentration. The results are summarized in the Table. At 0.1 M TBAH concentration and a sweep rate of 200 mV/s, the peak to peak splitting of 340 mV is far larger than the ideal value of 60 mV. Similar data were obtained for the $[Fe(bpy)_3]^{3+/2+}$ couple. With the use of IR compensation, ΔE_p could be reduced to ~ 120 mV for both couples. As shown by the data in the Table, at high electrolyte concentrations and slow scan rates, ΔE_p reaches 90 mV. The reductive shift in $E_{1/2}$ with increasing electrolyte concentrations is due to junction potential effects at the reference/solution interface in addition to ionic strength effects on the activity coefficients for $[Fe(\eta^5\text{-}Me_5C_5)_2]^{+/0}$.

For ligand based reductions the peak to peak splittings are considerably less. For example, the bipyridine-based reduction for the couple $[Re(bpy)(CO)_3Cl]^{0/-}$ in 0.2 M TBAH/DFB has ΔE_p = 110 mV at 200 mV/s sweep rate with no IR compensation. This peak splitting is much smaller than ΔE_p = 280 mV which is observed for $[Fe(\eta^5\text{-}Me_5C_5)_2]^{+/0}$ under the same conditions (Table). It is known that heterogeneous electron transfer rates can be solvent dependent[5] and the observations reported here are illustrative in this regard.

Electrogeneration of Reactive Intermediates. One of the most appealing features of 1,2-difluorobenzene as a solvent is its lack of coordinating ability. In our work, examples of the value of this property have come from a series of electrochemical studies on the reduction of $[Re^I(bpy)(CO)_3L]^{n+}$ ($L = Cl^-, Br^-, CF_3SO_3^-$, n=0; and $L = CH_3CN$, n=1). A clear understanding of the electrochemistry of these Re(I) complexes in CH_3CN has been developed.[6] Following a one electron bipyridine-based reduction, dissociative loss of L occurs to give a highly reactive metal-based radicals, e.g., reactions 1 and 2. We

$$[Re^I(bpy)(CO)_3(CH_3CN)]^+ \underset{}{\overset{-1.20\text{ V}}{\rightleftharpoons}} [Re^I(b\bar{p}y)(CO)_3(CH_3CN)]^\circ \qquad (1)$$

$$[Re^I(b\bar{p}y)(CO)_3(CH_3CN)]^\circ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Re^\circ(bpy)(CO)_3] + CH_3CN \qquad (2)$$

found that these electrogenerated metal radicals were reactive in common non-coordinating solvents. In the case of CH_2Cl_2 this complex was found to be an active electrocatalyst for dehalogenation.[7]

Cyclic voltammograms of $[Re(bpy)(CO)_3(CH_3CN)]^+$ in DFB and CH_3CN are shown in Fig 2. In DFB (Fig. 2(A)) at 200 mV/s, the first reduction of $[Re(bpy)(CO)_3(CH_3CN)]^+$ is irreversible because of rapid loss of the acetonitrile ligand, reaction 2, to form the metal-based radical $[Re(bpy)(CO)_3]^o$ followed by coupling to give the dimer, $[Re(bpy)(CO)_3]_2$, reaction 3.[6] In CH_3CN (Fig. 2(B)) the first reduction

$$2\,[Re^o(bpy)(CO)_3] \longrightarrow [Re(bpy)(CO)_3]_2 \qquad (3)$$

of $[Re(bpy)(CO)_3(CH_3CN)]^+$ is reversible (at concentrations < 0.5 m$\underline{M}$) because the high concentration of solvent suppresses the formation of the metal-based radical.

In DFB, the $[Re(bpy)(CO)_3]_2$ that forms on the initial reductive sweep (Fig. 2(A)) has a nearly reversible one electron oxidation at $E_{1/2} = -0.10$ V ($i_{p,a}/i_{p,c} = 0.75$). There is another irreversible one electron oxidation at $E_{p,a} = +0.25$ V. These data match those for an authentic sample of the dimer. The first oxidation is fully reversible with ($i_{p,a}/i_{p,c} = 1$) at a sweep rate of 1 V/s. In CH_3CN at a sweep rate of 200 mV/s, only one irreversible dimer-based oxidation is observed. It occurs at $E_{p,a} = -0.12$ V to give $[Re(bpy)(CO)_3(CH_3CN)]^+$ (Fig. 2 (C)). The difference in behavior is striking. In CH_3CN, the 1-electron Re-Re bonded cation, $[Re(bpy)(CO)_3]_2^+$, must be unstable with regard to solvolysis, reaction 4. A major factor in the instability of the cation is the

$$[Re(bpy)(CO)_3]_2^{\,+} + 2\,CH_3CN \longrightarrow [Re(bpy)(CO)_3(CH_3CN)]^+ + [Re(bpy)(CO)_3(CH_3CN)]^o \qquad (4)$$

formation of the Re(I) nitrile bond which occurs at the expense of the relatively weak Re-Re half-bond. In DFB, which is relatively non-coordinating, the once oxidized compound is sufficiently stable to persist on this cyclic voltammetry time scale and it is possible to establish the redox potential of the M-M bonded $[Re(bpy)(CO)_3]_2^{0/+}$ couple.

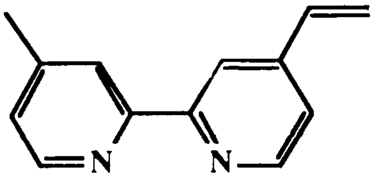
Another application where the use of DFB is has been revealing is in the observation of the direct electrochemical reoxidation of the anion, $[Re(bpy)(CO)_3]^-$. A cyclic voltammogram of $[Re(bpy)(CO)_3Cl]$ is shown in Fig. 3(A). At 200 mV/s, $[Re(bpy)(CO)_3Cl]$ has a fully reversible one electron reduction at $E_{1/2}$= -1.37 V which is followed by a second irreversible reduction at $E_{p,c}$ = -1.85 V. At the second reduction, Cl^- loss is rapid to give $[Re(bpy)(CO)_3]^-$.[6] At a scan rate of 200 mV/s the reoxidation of this anion occurs at $E_{p,a}$= -1.09 V. Controlled potential electrolysis of $[Re^I(bpy)(CO)_3Cl]$ at E_{app} = -1.7 V, which is at the foot of the second wave, occurs with n = 2 to give $[Re(bpy)(CO)_3]^-$. The anion is dark purple (λ_{max} = 560 nm) and stable in DFB. <u>The anion is not stable for extended periods in CH_3CN, DMF, or THF</u>. Following the electrolysis a voltammogram starting at -2.0 V shows the reoxidation of the electrogenerated anion at $E_{p,a}$ = -1.09 V and almost no trace of the $[Re(bpy)(CO)_3Cl]$-based couples.

Before the controlled electrolysis experiment, the scan rate dependence was investigated for reoxidation of the anion relative to the oxidation of $[Re(bpy)(CO)_3Cl]^-$ as an internal standard. Since the $[Re(bpy)(CO)_3Cl]^{0/-}$ couple is kinetically facile, the difference was taken as a means of correcting uncompensated resistance effects. As can be seen in the plot in Fig. 3(B), the difference in peak potentials shifts by 54 mV per tenfold increase in scan rate. This is near the theoretical value of ~ 60 mV for a couple that undergoes slow heterogeneous electron transfer. In CH_3CN, the reoxidation of the anion is catalyzed by the $[Re(bpy)(CO)_3(CH_3CN)]^{+/0}$ couple, which undergoes rapid heterogeneous electron transfer, reaction 5.[6] Because of the electron transfer catalysis,

$$[Re(bpy)(CO)_3(CH_3CN)]^+ + [Re(bpy)(CO)_3]^- \xrightarrow{CH_3CN} 2\,[Re(bpy)(CO)_3(CH_3CN)]^\bullet \qquad (5)$$

reoxidation of the anion in CH_3CN is independent of scan rate and always occurs at -1.15 V which obscures the direct oxidation of the anion at the electrode. The electrode oxidation of the anion in DFB is not observed when $[Re(bpy)(CO)_3(CH_3CN)]^+$ is reduced twice in a cyclic voltammetric sweep, because, on the cyclic voltammetry time-scale, there is still enough of the unreduced form diffusing from the bulk solution to the electrode to mediate the oxidation of the anion.

Electropolymerization. As a further application of DFB as a solvent for electrochemical studies, we have investigated the reductive electropolymerization of complexes containing 4-methyl-4'-vinyl-2,2-bipyridine (vbpy) as a ligand. Acetonitrile has typically been the solvent of choice in such proceedures[8,9] but we find that DFB is an excellent solvent as well.

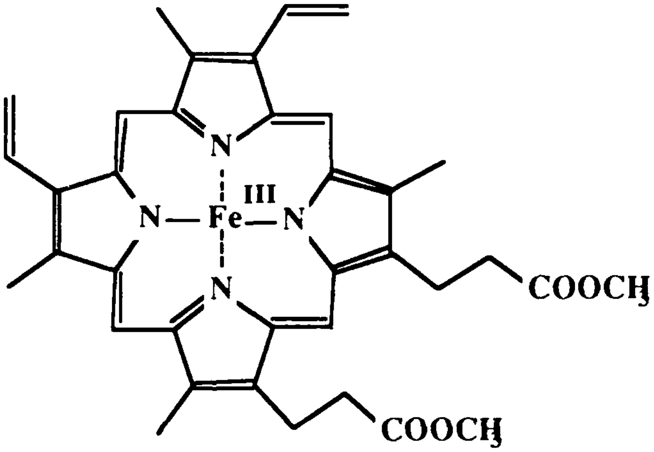


vbpy

As examples, we have studied the reductive electropolymerization of $[Fe(vbpy)_3]^{2+}$ and $[Re(vbpy)(CO)_3Cl]$, both of which have been studied previously in CH_3CN.[8,9] The rate of electropolymerization of $[Fe(vbpy)_3]^{2+}$ in DFB, Fig. 4(A), is comparable to that in CH_3CN as judged by the growth of the film-based couples. Cyclic voltammetric traces of a poly-$[Fe(vbpy)_3]^{3+/2+}$ film in DFB and CH_3CN are shown in Fig. 4(B). At a sweep rate of 50 mV/s, the peak to peak splitting for the Fe(III/II) couple is 200 mV in DFB while it is only 35 mV in CH_3CN showing that charge propagation through the film is considerably slower in DFB. Large peak splittings and slow charge transport could arise from poor solvent swelling which hinders counterion transport through the films. However, there may also be a contribution from slow heterogeneous electron transfer at the metal electrode/poly-[Fe(vbpy)$_3$]$^{3+/2+}$ interface given the slow heterogeneous kinetics of the [Fe(bpy)$_3$]$^{3+/2+}$ solution couple.

The electropolymerization of [Re(vbpy)(CO)$_3$Cl] and the electrochemical properties of the resulting films in CH_3CN are discussed in detail elsewhere.[9] 1,2-Difluorobenzene is also a useful solvent for preparing poly-[Re(vbpy)(CO)$_3$Cl]. It offers the advantages that films grown in DFB are much more stable toward reductive cycling, and that polymerization onto optically transparent In-doped SnO_2 electrodes yields much more uniform coverages at a considerably enhanced rate.

1,2-Difluorobenzene is also a useful solvent for oxidative electropolymerizations. We have studied the oxidative electropolymerization of Fe(PPIX-dme)Cl (PPIX-dme = protoporphyrin IX-dimethyl ester) on carbon, Pt, and In-doped SnO_2 electrodes by cycling the potential between 0.0 and +1.3 V at a sweep rate of 100 mV/s in 0.1 M TBAH/DFB.



Fe(PPIX-dme)$^+$

Electropolymerization proceeds more rapidly and reproducibly in DFB than in DMF, CH_2Cl_2, or CH_3CN.[10] Films with surfaces coverages x10 greater can be grown in DFB. This porphyrin also undergoes slow reductive electropolymerization in DFB by scanning between 0.0 V and -1.6 V, but only in DFB.[11]

CONCLUSIONS.

1,2-Difluorobenzene is an effective non-coordinating solvent for electrochemical studies. It posesses good solvation properties and an electrochemical window that extends from +2.0 to -2.2 V. Its inertness, chemically, and its weak coordinating abilities make it an excellent solvent in which to study unstable intermediates and to carry out sensitive reactions such as electropolymerizations.

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REFERENCES

1...(a) Lund, H. in "Organic Electrochemistry", pp 161-233, Baizer, M., Lund, H., Eds. Marcel Dekker, Inc., New York, 1983.

(b) Fry, A. J. and Britton, W. E. in "Laboratory Techniques in Electroanalytical Chemistry", pp 367-382, Kissinger, P. T., Heineman, W. R., Eds. Marcel Dekker, Inc., New York, 1984.

(c) Mann, C. K. in "Electroanalytical Chemistry", Vol. 3, pp 57-134, Bard, A. J., Ed. Marcel Dekker, Inc., New York, 1969.

2....... Pickett, C. J. in "Comprehensive Coordination Chemistry", Vol. 1, p 493, Wilkinson, G., Ed., Pergammon Press, New York, 1987.

3....... Doraiswamy, S.; Sharman, S. D. *J. Mol. Structure* **1983**, *102*, 81.

4....... Mansingh, A.; McLay, D. B. *J. Chem. Phys.* **1971** *54*, 3322.

5....... Hupp, J. T.; Liu, H. Y.; Farmer, J. K.; Gennett, T.; Weaver, M. J. *J. Electroanal, Interfacial Electrochem.* **1984**, *168*, 313.

6...(a) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Comm.* **1985**, 1414.

(b) Sullivan, B. P.; Bruce, M. R. M.; O'Toole, T. R.; Bolinger, C. M.; Megehee, E.; Thorp, H.; Meyer, T. J. In *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; ACS Symposium Series No. 363; American Chemical Society; Washington, D. C. **1988**; pp 52-90.

(c) O'Toole, T. R.; Sullivan, B. P.; Bruce, M. R.; Meyer, T. J. manuscript in preparation.

7....... O'Toole, T. R.; Meyer, T. J.; Sullivan, B. P. *Organometallics*, submitted.

8...(a) Abruna, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 56.

(b) Denisevich, P.; Abruna, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1982**, *21*, 2153.

(c) Sullivan, B. P.; Meyer, T. J.; Caspar, J. V. *Inorg. Chem.* **1987**, *26*, 4145.

9...(a) O'Toole, T. R.; Margerum, L. D.; Westmoreland, T. D.; Vining, W. J.; Murray, R. W.; Meyer, T. J. *J. Chem. Soc., Chem. Comm.* **1985**, 1416.

(b) O'Toole, T. R.; Sullivan, B. P.; Bruce, M. R.; Margerum, L. D.; Murray, R. W.; Meyer, T. J. *J. Electroanal. Chem., Interfacial Electrochem.*, in press.

10..... Dong, S.; Jiang, R. *J. Inorg. Biochem.* **1987**, *30*, 189.

11..... Younathan, J. N.; Wood, K.; Rhodes, M.; Meyer, T. J. manuscript in preparation.

12..... "Electrochemical Methods" Bard, A. J., Faulkner, L. R., eds.,Wiley, New York, 1980.

TABLE. The peak to peak splitting ($\Delta E_p = E_{p,a} - E_{p,c}$) in cyclic voltammograms of $[Fe(\eta^5\text{-}Me_5C_5)_2]^{+/o}$ in DFB.[a, b]

	ΔE_p (= $E_{p,a} - E_{p,c}$),mV			
	[TBAH], M ($E_{1/2}$ vs ssce)			
scan rate (mV/s)	0.1 (-0.036 V)	0.2 (-0.059 V)	0.5 (-0.087 V)	1.0 (-0.108 V)
20	140	130	110	90
50	185	165	145	115
100	245	215	180	140
200	320	280	240	190

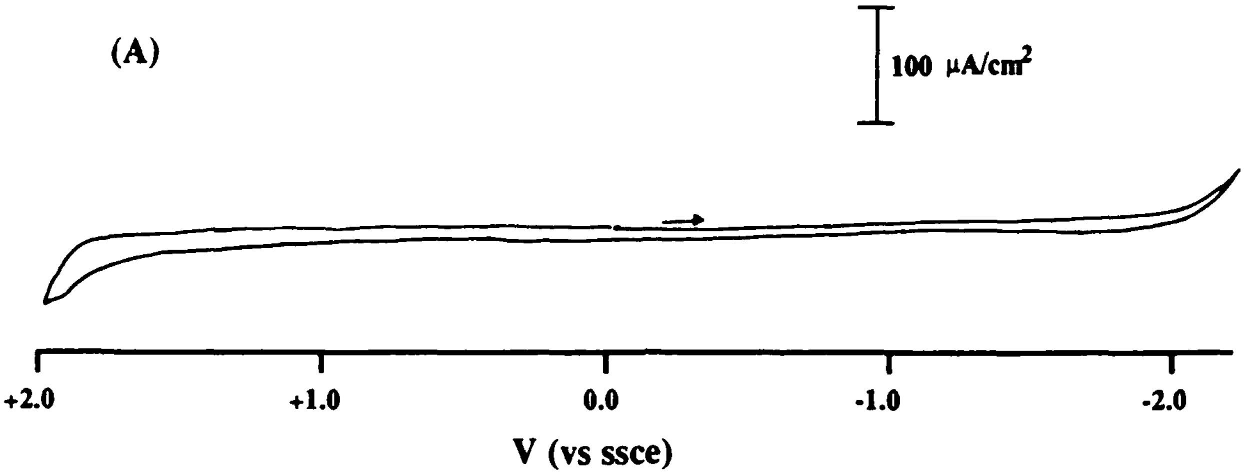
[a] $\eta^5\text{-}Me_5C_5$ = pentamethylcyclopentadienyl anion; TBAH = tetra-*n*-butylammonium hexafluorophosphate; DFB = 1,2-difluorobenzene.

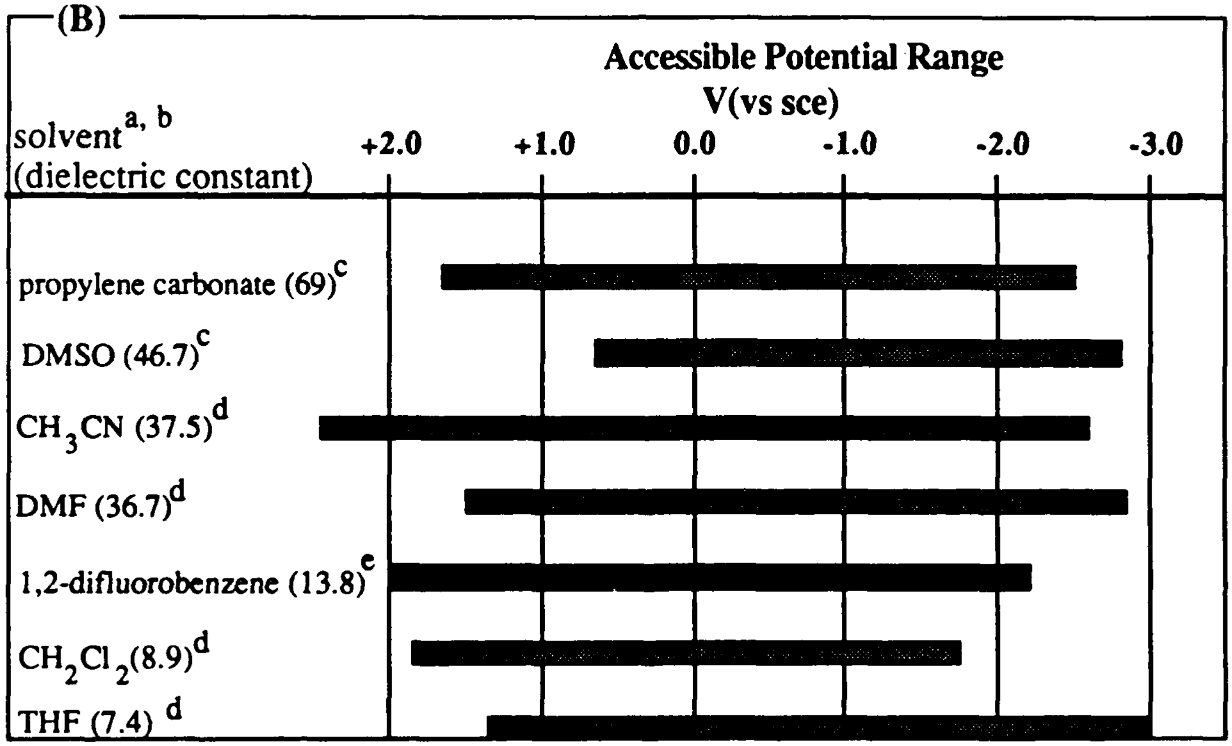
[b] without IR compensation.

FIGURE 1

(A) A background cyclic voltammogram for 0.1 M TBAH/DFB at a 0.1 cm^2 Pt electrode at sweep rate of 200 mV/s.

(B) A chart illustrating the electrochemical windows for some solvents that are commonly used in electrochemical studies.





[a] The definition of a solvent limit is somewhat dependent upon the details of the experiment. The limits shown above are illustrative for a Pt electrode in solutions containing 0.1 M concentrations of tetraalkylammonium salts of the anions ClO_4^-, BF_4^-, or PF_6^-.

[b] DMSO = dimethylsulfoxide; DMF = N,N'-dimethylformamide; THF = tetrahydrofuran.

[c] Reference 1(a)

[d] Reference 10

[e] This work.

FIGURE 2

(A) A cyclic voltammogram of a solution 0.4 mM in $[Re(bpy)(CO)_3(CH_3CN)]^+$ in 0.1 M TBAH/DFB at a sweep rate of 200 mV/s. The dotted line (·········) is the voltammogram obtained upon scan reversal at 0.0 V following a reductive scan. The waves at $E_{1/2} = -0.12$ V and $E_{p,a} = +0.25$ V are due to $[Re(bpy)(CO)_3]_2$ which is formed during the reduction.

(B) A cyclic voltammogram of a solution 0.4 mM in $[Re(bpy)(CO)_3(CH_3CN)]^+$ in 0.1 M TBAH/CH_3CN at a sweep rate of 200 mV/s.

(C) A cyclic voltammogram illustrating the irreversible oxidation ($E_{p,a} = -0.12$ V) of $[Re(bpy)(CO)_3]_2$ formed by a reductive scan at 200 mV/s in a solution ~ 1mM in $[Re(bpy)(CO)_3(CH_3CN)]^+$ in 0.1 M TBAH/CH_3CN. The reductive portion of the scan is not shown for clarity.

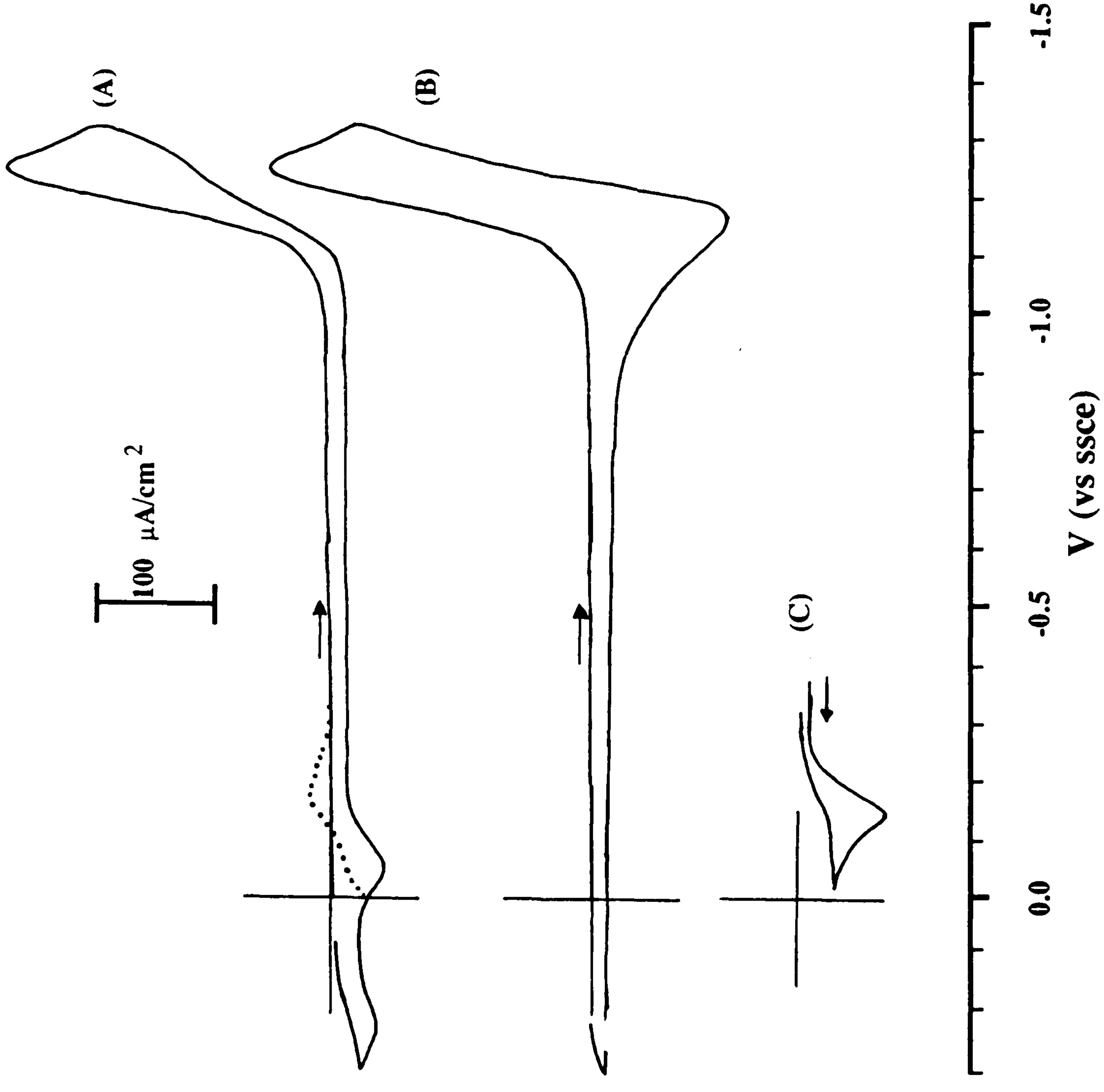

(A)
(B)
(C)
100 μA/cm^2
0.0
-0.5
-1.0
-1.5
V (vs ssce)

FIGURE 3

(A) Cyclic voltammograms of a solution 0.5 m<u>M</u> in [Re(bpy)$(CO)_3$Cl] in 0.2 <u>M</u> TBAH/DFB at 200 mV/s cycled between 0.0 and -1.5 V (#1, - - -) and between 0.0 and -2.2 V (#2, ——). Also shown is an oxidative sweep starting at -2.0 V (#3, ·····) following a controlled potential electrolysis of [Re(bpy)$(CO)_3$Cl] at -1.7 V (n = 2).

(B) The shift in the oxidative peak potential for the anion, [Re(bpy)$(CO)_3]^-$, relative to that for oxidation of [Re(bpy)$(CO)_3$Cl$]^-$ ($\Delta E_{p,a}$) versus the log of the scan rate, ν. The scan rates used ranged from 0.05 to 10 V/s. The slope of the line is 0.054 V/decade.

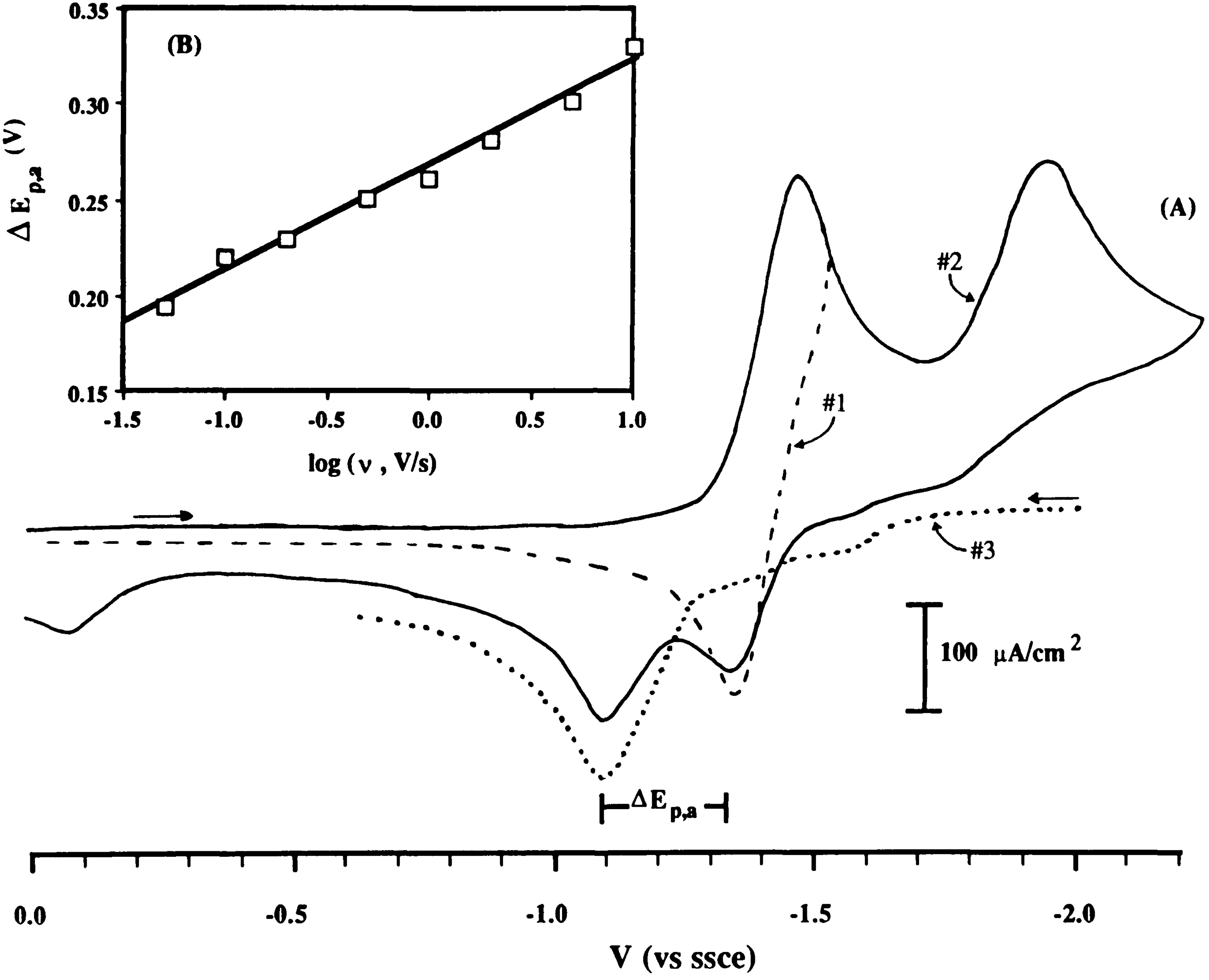
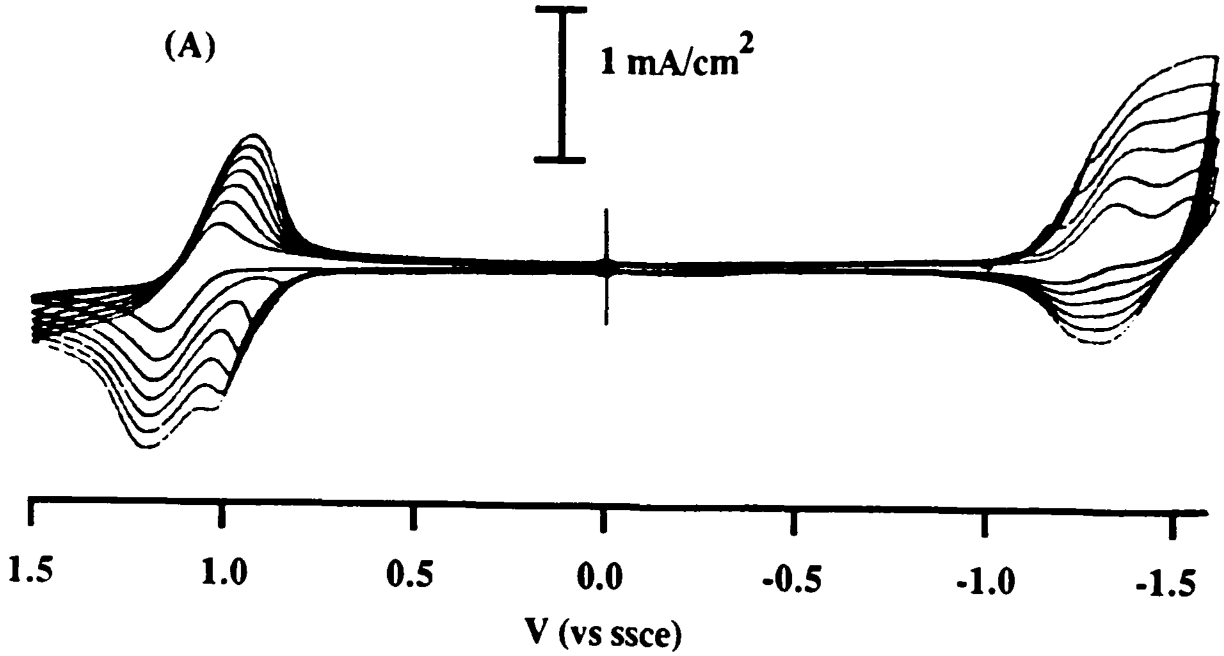
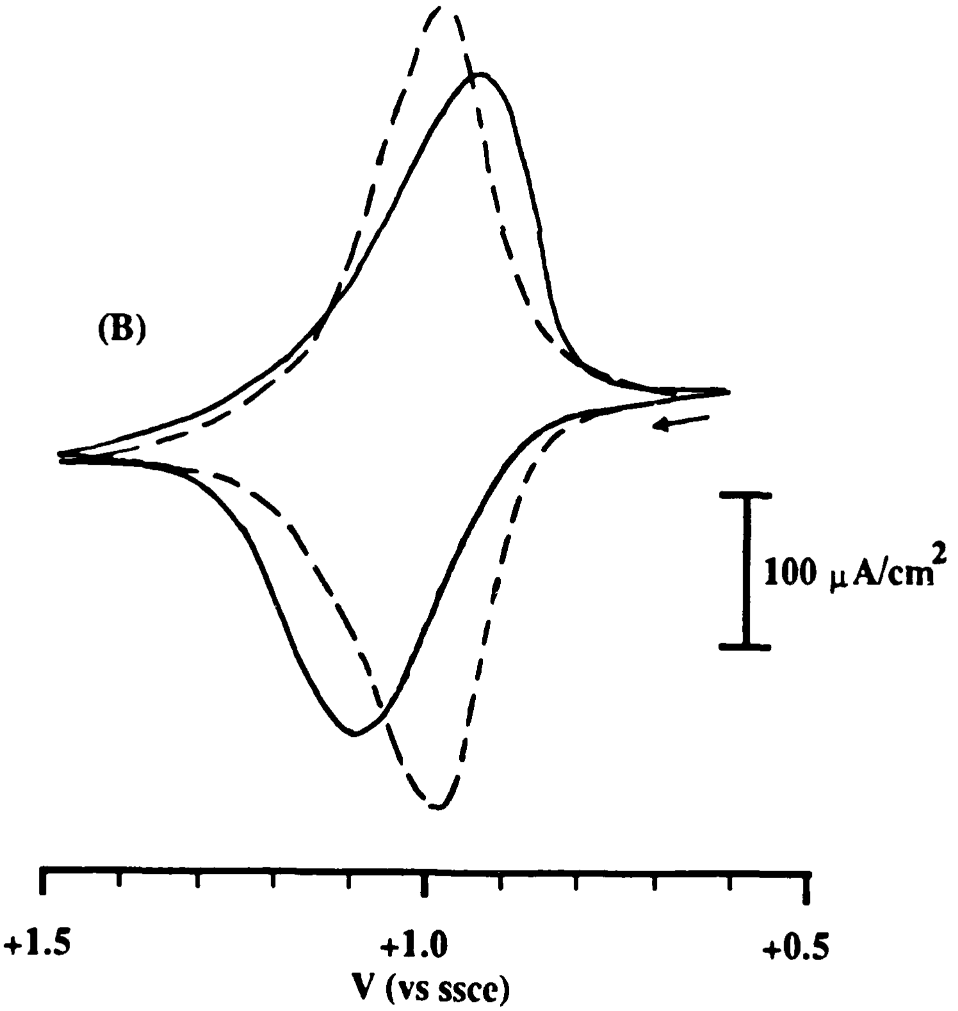

(B)
0.35
0.30
0.25
0.20
0.15
$\Delta E_{p,a}$ (V)
-1.5
-1.0
-0.5
0.0
0.5
1.0
log (ν , V/s)
(A)
#2
#1
#3
100 μA/cm^2
$\Delta E_{p,a}$
0.0
-0.5
-1.0
-1.5
-2.0
V (vs ssce)

FIGURE 4

(A) Consecutive cyclic voltammetric traces for $[Fe(vbpy)_3]^{2+}$ in 0.1 M TBAH/DFB at a 0.1 cm^2 Pt electrode at a sweep rate of 100 mV/s illustrating polymeric film growth by electropolymerization.

(B) Cyclic voltammograms of the Fe(III/II) couple in the poly-$[Fe(vbpy)_3]^{2+}$ film from (A) at 50 mV/s when immersed in 0.1 M TBAH solutions of DFB (————) and CH_3CN (- - - - -).


(A)
1 mA/cm^2
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
V (vs ssce)


(B)
100 μA/cm^2
+1.5
+1.0
+0.5
V (vs ssce)