OFFICE OF NAVAL RESEARCH

Contract N00014-94-1-0323

R&T Code 413v001

Technical Report No. 7

INFLUENCE OF MAGNETIC FIELDS ON THE VOLTAMMETRIC RESPONSE OF MICROELECTRODES IN HIGHLY CONCENTRATED ORGANIC REDOX SOLUTIONS

by

Jeonghee Lee, Xiaoping Gao, Laurie D. A. Hardy
and Henry S. White

Submitted for publication

Journal of the Electrochemical Society

University of Utah
Department of Chemistry
Salt Lake City, UT 84112

April 31, 1995

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
3/31/95

3. REPORT TYPE AND DATES COVERED
Interim 6/94 - 12/94

4. TITLE AND SUBTITLE
Influence of Magnetic Fields on the Voltammetric Response of Microelectrodes in Highly Concentrated Organic Redox Solutions

5. FUNDING NUMBERS
N0014-94-1-0323

R & T Code 413V001

6. AUTHOR(S)
Jeonghee Lee, Xiaoping Gao, Laurie D. A. Hardy, and Henry S. White

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
Henry Eyring Building
University of Utah
Salt Lake City, Utah 84112

8. PERFORMING ORGANIZATION REPORT NUMBER
7

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Arlington, Virginia

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unclassified/Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The voltammetric response of Au and Pt microdisk electrodes (6.4, 12.5, and 25 μm) in concentrated solutions of organic redox species (nitrobenzene, acetophenone and benzophenone) has been measured as a function of the orientation and magnitude of an externally applied magnetic field (0 - 1 Tesla). A magnetic field effect on voltammetric currents is observed for redox concentrations greater than ~0.01 M, and is a strong function of the orientation of the field. Large enhancements (+100%) or diminishments (-15%) of limiting currents can be induced by application of the magnetic field. The observed phenomena are discussed in terms of magnetic field-induced transport of electrogenerated products.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
Unclassified	Unclassified	Unclassified	

NSN 7540-01-280-5500

[illegible]

INFLUENCE OF MAGNETIC FIELDS ON THE VOLTAMMETRIC RESPONSE OF MICROELECTRODES IN HIGHLY CONCENTRATED ORGANIC REDOX SOLUTIONS

Jeonghee Lee, Xiaoping Gao, Laurie D. A. Hardy, and Henry S. White*
Department of Chemistry, University of Utah, Salt Lake City, UT 84412

Abstract. The voltammetric response of Au and Pt microdisk electrodes (6.4, 12.5, and 25 µm) in concentrated solutions of organic redox species (nitrobenzene, acetophenone and benzophenone) has been measured as a function of the orientation and magnitude of an externally applied magnetic field (0 - 1 Tesla). A magnetic field effect on voltammetric currents is observed for redox concentrations greater than ~0.01 M, and is a strong function of the orientation of the field. Large enhancements (+100%) or diminishments (-15%) of limiting currents can be induced by application of the magnetic field. The observed phenomena are discussed in terms of magnetic field-induced transport of electrogenerated products.

* Address correspondence to this author.

Submitted to J. Electrochemical Society, Nov., 1994; revised, March, 1995.

Introduction. We report preliminary applications of microelectrode techniques for investigating the effects of an external magnetic field on electrochemical phenomena. Previous investigations of magnetic field effects in electrochemistry have focused on observations of field-induced convective flow, described by magnetohydrodynamic (MHD) theory.[1-3] MHD effects are sufficiently large when employing electrodes of conventional size (e.g., ~0.1 cm^2) that they appear likely to mask all other potentially interesting phenomena, e.g., the dependence of rates of coupled homogenous reactions on the external field. The use of electrodes having characteristic dimensions on the order of micrometers or less (i.e., microelectrodes or ultramicroelectrodes) appears to offer several interesting and potentially significant advantages in studying magnetic field effects. First, because of the greatly reduced dimensions of the depletion layer surrounding the microelectrode, the effects of convective fluid flow (either density driven or magnetic field driven) is significantly reduced. Consequently, it is much more likely that other magnetic field-related phenomena can be observed. Second, since the magnetic force, $\vec{F}$, that induces MHD convective flow is equal to the cross-product of the current and magnetic field vectors, i.e., $\vec{F} = \vec{i} \times \vec{B}$, the large reduction in the faradaic current ($\vec{i}$) associated with measurements using microelectrodes should also result in an additional reduction in obscuring effects of convective flow. In addition, because of the convergent flux of redox species to a microelectrode, the observed current is approximately proportional to the electrode dimensions (e.g., radius of a microdisk).[4] Thus, by varying the electrode size, it is possible to study magnetic effects over a wide range of current magnitudes. Third, the effect of the magnetic field on ion transport is strongly coupled to electric fields engendered by the diffusional fluxes of charged species. In prior investigations of MHD phenomena in electrochemistry, the coupling of the electric and magnetic field on transport phenomena[5] has generally been ignored, even though the majority of these studies have been performed in solutions which do not contain an excess quantity of supporting electrolyte. However, during the past decade, it has been established that quantitative electrochemical investigations can be performed using microelectrodes in solutions containing very low concentrations of supporting electrolyte.[6] Thus, microelectrode techniques should allow quantitative investigations of coupled magnetic and electric field effects. Fourth, quantitative electrochemical investigations of solutions containing high concentrations of redox-active species are possible using microelectrodes, including measurements in the absence of an inert solvent.[7] It is thus possible to explore magnetic-field phenomena over a wide range of solution conditions that are inaccessible using electrodes of macroscopic dimensions. Finally, microelectrode techniques may offer a number of advantages in experimental design for studying magnetic field effects. For instance, in spite of the expected dependence of the force of the orientation between $\vec{i}$ and $\vec{B}$, only a very few studies have investigated this relationship.[8,9] We show below that microelectrode techniques allow the angular dependency to be measured with relative ease.

In preliminary experiments, we have investigated the electrochemical reductions of several organic species (e.g., nitrobenzene, NB) using Pt and Au microdisk electrodes. Since the organic reactants in our studies are uncharged and diamagnetic, the molecular transport of these species is not anticipated to be directly influenced by an external magnetic field. However, we observed large enhancement or diminishment of faradaic currents associated with the reduction of these compounds, the magnitude and direction of the effect dependent upon the redox concentration and the orientation of the field with respect to the electrode surface. The results suggest that microelectrode techniques may be very useful for quantitative investigations of magnetic-field effects in electrochemistry.

Experimental. Au (6.4 μm radius) and Pt (12.5 and 25 μm radius) microdisk electrodes were constructed by sealing Au or Pt wire in glass tube. Electrodes were polished using 0.1 μm Al_2O_3, rinsed with H_2O, and sonicated in H_2O for ~2 minutes to remove polishing debris. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was recrystallized and dried. All other chemicals were used as received.

A GMW Associates Model 5403 electromagnet was used to apply a uniform magnetic filed across the electrochemical cell, Fig. 1. A three-electrode cell (Ag/Ag_xO quasi-reference electrode, Pt wire counter electrode, and Au or Pt microelectrode) was placed between the poles (7.6 cm diameter, ~ 2 cm gap) of the electromagnet. The field strength was adjusted between 0 and 1 Tesla (T) by varying the current through the electromagnet. Field strengths were measured using a gauss meter (F.W. Bell, Model 4048). In order to study the dependence of the orientation of the field with respect to the electrode surface, microelectrodes were constructed with a 90° bend in the glass tubing, such that rotation of the electrode in the cell resulted in a change in the angle θ between the field, $\vec{B}$, and the electrode surface normal, $\hat{n}$ (Fig. 1).

Results and Discussion. Fig. 2 shows the voltammetric response (20 mV/s) of a 25 µm radius-Pt disk electrode in an acetonitrile solution containing 1 M NB and 0.1 M ($TBAPF_6$). The set of curves corresponds to applied magnetic fields ($\theta = 90^\circ$) of 0.0, 0.2, 0.4, 0.6, and 0.8 Tesla (T). The sigmoidal-shaped voltammogram results from the 1-e^- reduction of NB to the corresponding radical anion ($NB + e^- \rightarrow NB^-$). For this reaction, as well as for the 1-e^- reductions of acetophenone and benzophenone, the limiting current (i_{lim}) is enhanced by application of a magnetic field at $\theta = 90^\circ$, while the current on the rising part of the wave is relatively insensitive to the external field. The relative enhancement of i_{lim} at $\theta = 90^\circ$ is shown in the inset of Fig. 2 as a plot of $(i_B - i_o)/i_o$ vs $|B|$, where i_o and i_B are the measured limiting currents (i_{lim}) in the absence and presence of the field. The observed hysteresis on the rising part of the voltammetric wave is due to slow transient migration of charge-balancing counterions from the bulk solution to the depletion layer. This hysteresis is frequently apparent in slow-scan voltammograms obtained in highly concentrated redox solutions[8], and is not a function of the magnetic field.

Fig. 3 shows the dependence of i_{lim} for NB reduction on the angle θ at a constant magnetic strength of 0.7 Tesla. Maxima in $(i_B - i_o)/i_o$ are observed at $\theta = 90$ and 270° (i.e., the surface normal $\hat{n}$ is perpendicular to $\vec{B}$) which correspond to an ~100% increase in i_{lim}. Conversely, the limiting current is suppressed by ~15% at $\theta = 0$ and 180°, producing minima in $(i_B - i_o)/i_o$ at these angles. We find that the angular dependence follows the relationship: $(i_B - i_o)/i_o \sim \alpha|\sin\theta| - \beta$, where the values of α and β are dependent on redox concentration, electrode radius, and electrolyte concentration. A similar functional dependence of i_{lim} on θ is observed for acetophenone and benzophenone reductions at microdisk electrodes.

At $\theta = 90°$, an enhancement of the limiting current is observed for NB concentrations (C_{NB}) > 0.01 M (for $|B| \sim 1$ T). Below $C_{NB} = 0.01$M, the enhancement is less that 1%. We find that the largest field-dependent enhancement (or diminishment) in current occurs at $C_{NB} \sim 2$M. When C_{NB} is increased above 2M, $(i_B - i_o)/i_o$ rapidly decreases again. The maximum field-induced enhancements for acetophenone and benzophenone reduction also occur at intermediate redox concentrations. In previous investigations, we have shown that i_{lim} for NB reduction at 12.5 μm Pt disks increases with increasing concentration up to $C_{NB} \sim 2$M.[10] Above this value, the current decreases with increasing NB concentration for reasons that are not understood. Thus, the dependence of $(i_B - i_o)/i_o$ on C_{NB} parallels that of i_o on C_{NB}, indicating that the magnetic effect is roughly proportional to the current. We have also investigated the dependence of the field-induced enhancement on the electrode radius using Au (radius $r_o = 6.4$ μm) and Pt (12.5 and 25 μm) disks. For NB, benzophenone, and acetophenone, we observe that $(i_B - i_o)/i_o$ scales with absolute current, rather than the current density (the latter increases by ~4 times as the electrode radius is decreased from 25 to 6.4 μm).

In order to understand the origin of the magnetic field effect, we first note that the limiting current for the reduction of a neutral species at a microdisk electrode is given by eq. (1), independent of the electrolyte concentration.[11]

$$i_{lim} = 4nFDC^{*}r_{o} \qquad (1)$$

Here, n = the number of electrons transferred per molecule (n = 1 for NB), F is Faraday's constant, D is the diffusion coefficient for the redox species, C^{*} is the bulk concentration, and r_o is the electrode radius. Since the redox molecules we have examined are neutral and diamagnetic, there should be no direct effect of the magnetic field on the transport of these species to the electrode surface. Therefore, we attribute the magnetic effect to the interaction of the current-carrying ions with the magnetic field. Our experiments suggest that this interaction must indirectly effect the diffusional flux of NB to the surface. For the steady-state conditions reported in Fig. 2, the current is carried by the coupled diffusion/migration of the electrogenerated radical anion, NB^{-}, in a nearly radial direction from the surface.[6,12] In addition to this consideration, it is important to note that electroneutrality in the depletion layer is maintained by transient migration of the electrolyte cation TBA^{+} towards the electrode (at steady-state, the flux of TBA^{+} is zero). Since the bulk solution concentration of NB is much larger that of $TBAPF_6$ in our experiments, there will be a large increase in the total ion concentration within the depletion layer, relative to that in the bulk. For example, in solutions containing 2M NB and 0.1 M $TBAPF_6$, the surface concentration of ions is ~4M (= $C_{NB^-} + C_{TBA^+}$) at potentials corresponding to the limiting current plateau, which is ~20x larger than the bulk ion concentration ($C_{TBA^+} + C_{PF_6^-} = 0.2$ M). Thus, as previously discussed in detail,[7] it is reasonable to assume that the increased ion concentration in the depletion layer results in an increase in the solution viscosity near the surface.

When a magnetic field is applied, the force acting on the charge carriers ($\vec{F} = \vec{i} \times \vec{B}$) will alter the nearly radially-outward flux of NB^{-}. For a microdisk, the net current vector, $\vec{i}_{net}$, is normal to the electrode surface, even though the current carrying ions are transported radially outward . Thus, when the electrode is oriented at 90 or 270° with respect to $\vec{B}$, the field will tend to increase the flux of NB^{-} in the direction parallel to the electrode surface (see lower half of Fig. 3, and note that, by convention, the current vector for an electrochemical reduction is directed towards the electrode surface). At 90°, there will be a downward force on the current carrying ions (i.e., in the direction of the gravitational field). Conversely, when the direction of the field is 270°, there will be an upward acting force on the ions. In either case, the field-driven flux is expected to reduce the concentration of product anions and charge balancing cations within the depletion layer, resulting in a decrease in the near surface solution viscosity. The expected result of this effect is an increase in the diffusional transport of NB to the surface. We observe that the maxima in $(i_B-i_o)/i_o$ at 90 and 270° have nearly identical magnitudes, indicating that density-driven convective flow is insignificant relative to the effect of the magnetic field.

At 0 and 180°, $(i_B-i_o)/i_o$ is negative indicating that the magnetic force induces a diminishment of the current. Based on the above arguments, the *net force* acting on the current-carrying ions is zero since $\vec{i}$ and $\vec{B}$ are parallel. However, because the flux is radially outward, there will be a torsional force acting on each ion, resulting in a cyclotron-like motion of the ions as they are transported away from the surface (Fig. 3). Because of this motion, the residence time of the ions near the surface will increase, thereby resulting in an increase in the near surface solution viscosity and a concurrent decrease in the faradaic current.

Although the above arguments are supported by the experimental data, it is not possible to eliminate the possibility that the observed phenomena is due to the onset of magnetic-field-induced fluid convection, as frequently observed with macroscopic electrodes. However, the diminishment of the current at $\theta = 0°$ and $180°$ is not consistent with convective flow, which would be expected to increase the rate of transport of NB to the surface (similar to the expected effects of rotating the electrode). In addition, it has been experimentally observed that the magnetic-field enhancement at macroscopic electrodes is proportional to $\vec{B}^{1/3}C^{*4/3}$, in agreement with predictions from classical MHD theory. We observe that the field-induced enhancement is nearly linearly proportional to

$\vec{B}$ at low fields, and that the enhancement is largest at intermediate concentrations. Neither of these observations are consistent with MHD-based theory of convective flow.[1,2]

Because of the divergent outward flux of the product ions, the magnetic force within the depletion layer is nonuniform, decreasing with distance away from the electrode surface. An estimate of the magnetic force at the surface can be obtained from the relationship $\vec{F} = \vec{i} \times \vec{B}$. Using $\vec{B} = 0.7$ Tesla, $\vec{i}_{net} \sim 20\ \mu A$ (in the absence of the field, Fig. 2), and $\theta = 90^o$, we compute the magnetic force per unit length at the electrode surface to be 1.4×10^{-5} N/m.

In concluding, we note that it is possible to perform quantitative voltammetric measurements with microelectrodes having radii on the dimensions of nanometers[13,14] (3 orders of magnitude less than the size of the electrodes employed in the current study). We anticipate that fluid convection can be entirely eliminated using electrodes of such dimensions. Future work in this area may greatly expand the application of electroanalytical methods in investigations of magnetic-field phenomena in chemistry.

Acknowledgment. The authors gratefully acknowledge support of the Office of Naval Research and National Science Foundation/Electric Power Research Institute Program.

References.

1. T. Z. Fahidy, *J. Appl. Electrochem.*, **13**, 553 (1983).
2. O. Aaboubi, J. P. Chopart, J. Douglade, A. Olivier, C. Gabrielli, and B. Tribollet, *J. Electrochem. Soc.*, **137**, 1796 (1990).
3. I. Mogi, G. Kido, and Y. Nakagawa, *Bull. Chem. Soc. Jpn.*, **63**, 1871 (1990).
4. A. Russell, K. Repka, T. Dibble, J. Ghoroghchian, J . J. Smith, M. Fleischmann, C. H. Pitt, and S. Pons, *Anal. Chem.*, **58**, 2961 (1986).
5. E. Tronel-Peyroz and A. Olivier, *Phys. Chem. Hydrodyn.*, **3**, 251 (1982).
6. C. P. Smith and H. S. White, *Anal. Chem.*, **65**, 3343 (1993), and references therein.
7. R. B. Morris, K. F. Fischer, and H. S. White, *J. Phys. Chem.* **92**, 5306 (1988).

---

8. M. S. Quraishi and T. Z. Fahidy, *Electrochimca Acta*, **25**, 591 (1980).
9. Z. H. Gu and T. Z. Fahidy, *J. Electrochem. Soc.*, **134**, 2241 (1987).
10. R. A. Malmsten, C. P. Smith, and H. S. White, *J. Electroanal. Chem.* **215**, 223 (1986).
11. Y. Saito, *Rev. Polarogr.*, **15**, 177 (1968).
12. K. B. Oldham, *J. Electroanal. Chem.*, **250**, 1 (1988).
13. R. B. Morris, D. J. Franta, and H. S. White, J. Phys. Chem., **91**, 3559 (1987).
14. B. D. Pendley and H. D. Abruna, *Anal. Chem.*, **62**, 782 (1990).

Figures.

1. Experimental set-up for measuring voltammetric response of a microelectrode as a function of magnetic field strength and orientation. The angel θ is defined by the surface normal ($\hat{n}$) and the field $\vec{B}$.
2. Voltammetric response of 25 μm-radius Pt disk electrode as a function of magnetic field ($\theta = 90°$). [NB] = 1M, [$TBAPF_6$] = 0.1 M. Scan rate = 20 mV/s. Inset shows the dependence of the normalized current enhancement $(i_B - i_o)/i_o$ on the magnetic field. i_B is the measured limiting current with an applied magnetic field; i_o is the limiting current in the absence of the field.
3. (*Top*) Dependence of steady-state limiting current for NB reduction on the orientation of the electrode (25 μm-radius Pt electrode) with respect to magnetic field (see Fig. 1 for definition of θ). Magnetic field = 0.7 Tesla. Concentrations of redox species and electrolyte: [NB] = 1M and [$TBAPF_6$] = 0.1 M. (*Bottom*) Schematic diagram of the *top view* of the cell showing the electrode orientation relative to the magnetic field. Positive current (carried by the radial-outward flux of electrogenerated anions) is shown as dashed lines pointed inwards towards the electrode surface. The magnetic force, $\vec{F}$, is oriented downward (along the direction of the gravitational field) at 90^o and upward at 270^o. At 0^o and 180^o, there is a torsional force on the radially-outward diffusing and migration of electrogenerated anions, resulting in a cyclotron-like motion. In all cases, the net current vector ($\vec{i}_{net}$, not shown) is normal to the electrode surface.

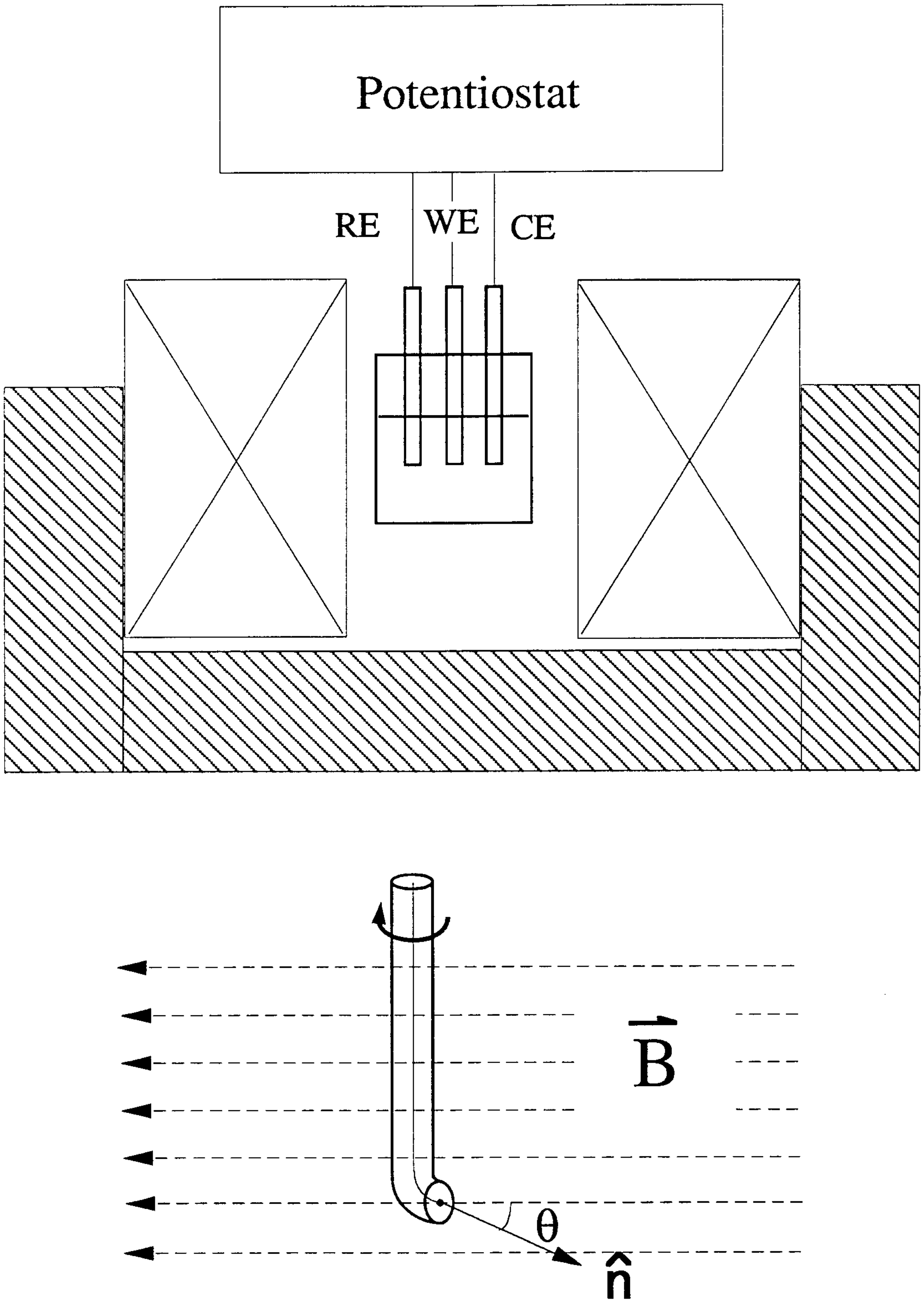


Fig 1

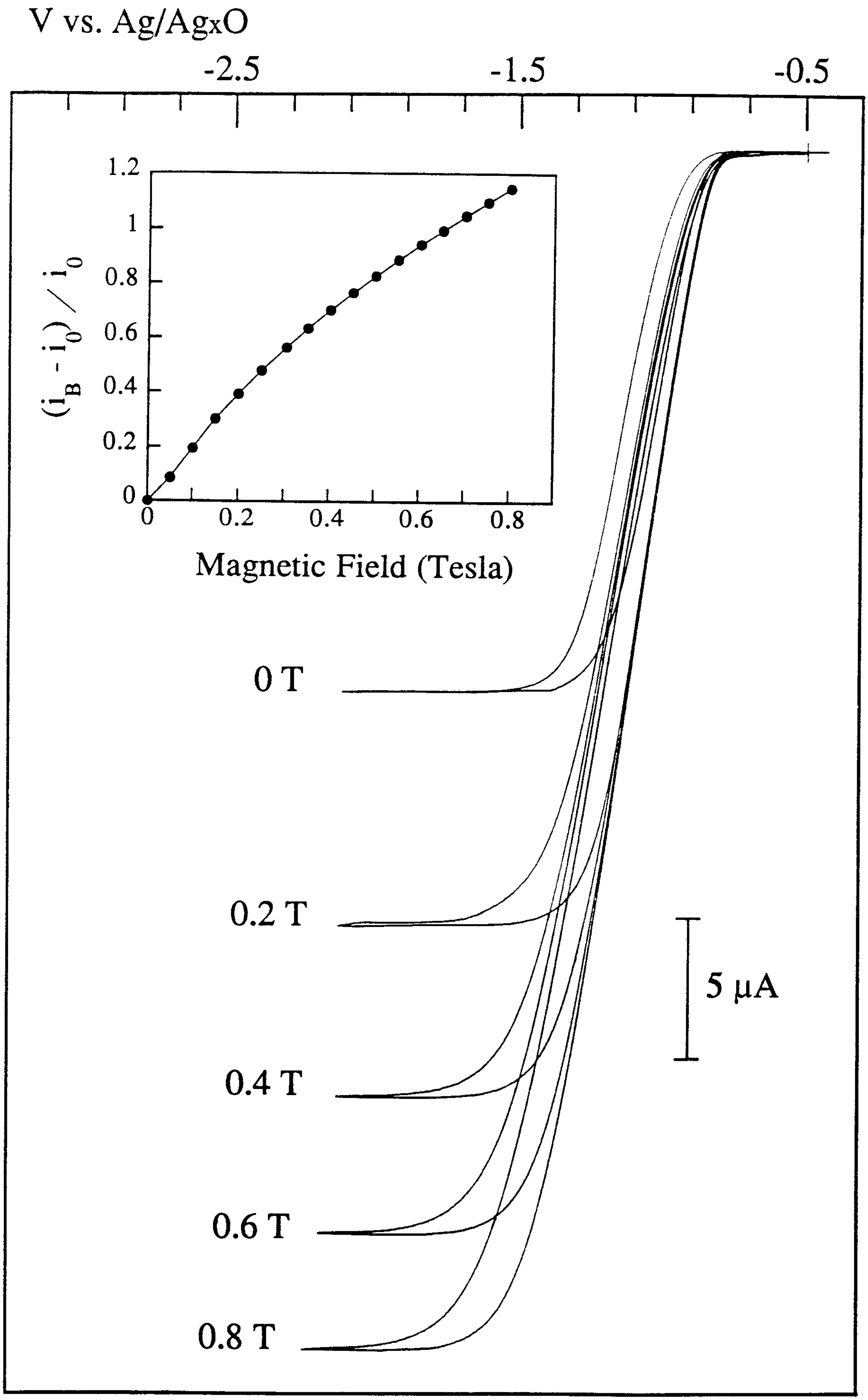
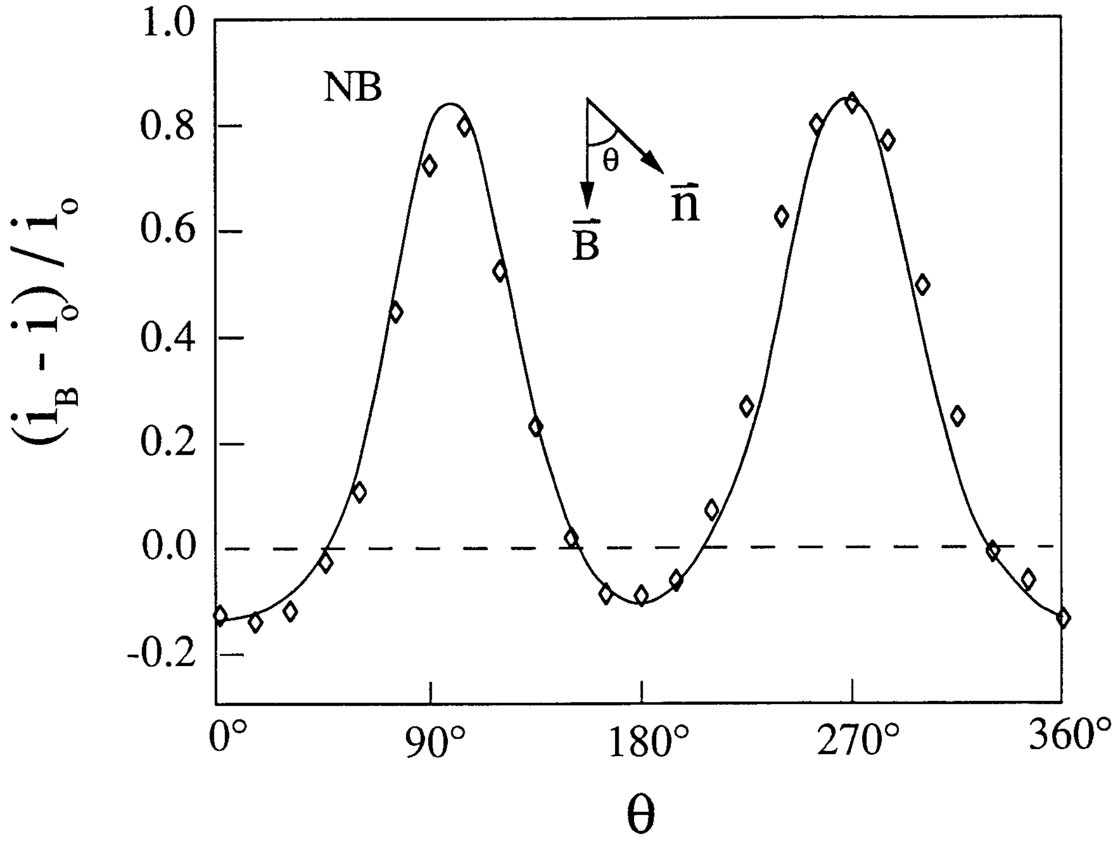

V vs. Ag/AgxO
-2.5
-1.5
-0.5
1.2
1
0.8
0.6
0.4
0.2
0
$(i_B - i_0) / i_0$
0
0.2
0.4
0.6
0.8
Magnetic Field (Tesla)
0 T
0.2 T
0.4 T
0.6 T
0.8 T
5 μA

Fig 2


NB
$\vec{B}$
θ
$\vec{n}$
$(i_B - i_o)/i_o$
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
0°
90°
180°
270°
360°
θ

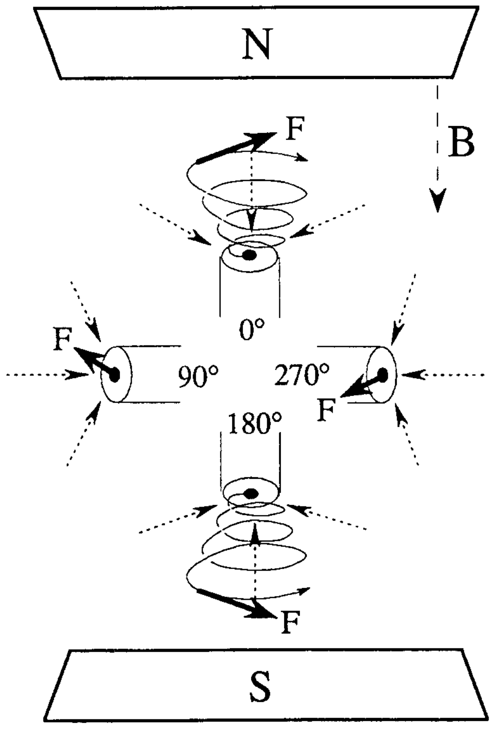

N
B
F
0°
F
90°
270°
F
180°
F
S

Fig 3

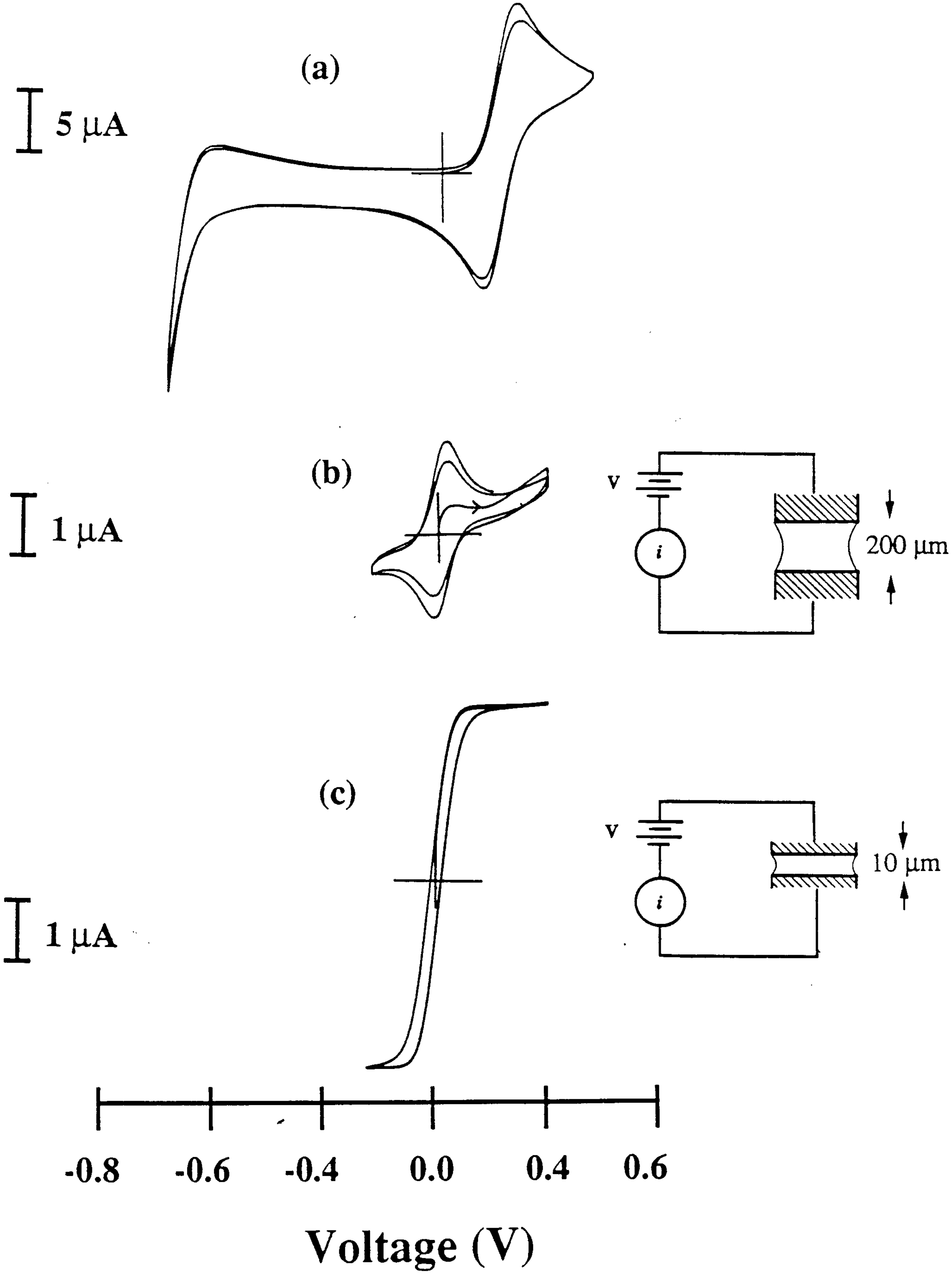


Fig 6

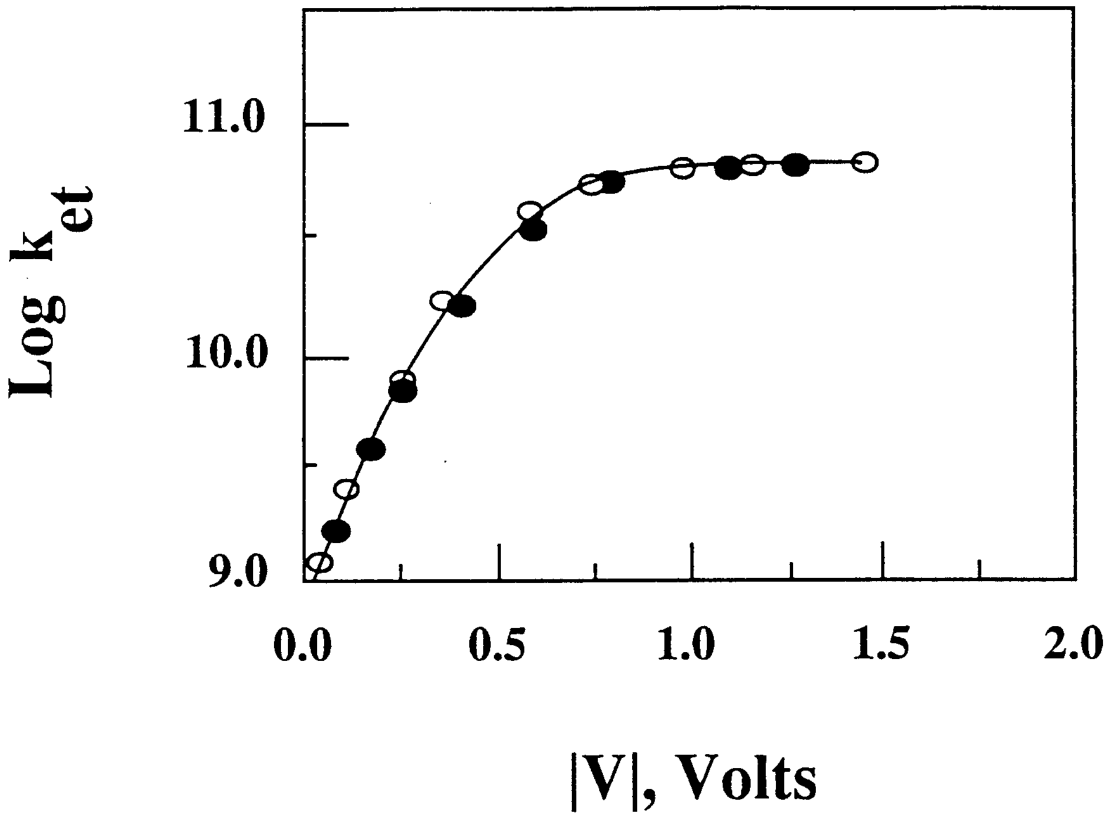


Fig. 7