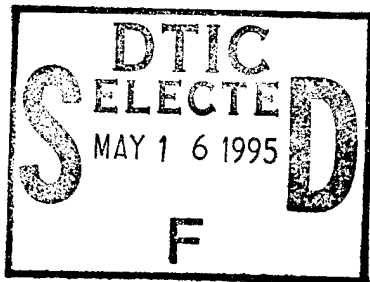


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ROTATING MICRODISK VOLTAMMETRY IN LOW IONIC  
STRENGTH SOLUTIONS

by

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# ROTATING MICRODISK VOLTAMMETRY IN LOW IONIC STRENGTH SOLUTIONS.

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**Abstract.** The influence of the supporting electrolyte concentration on the steady-state voltammetric behavior of a 12.5  $\mu\text{m}$ -radius rotating Pt disk electrode (angular velocity,  $\omega = 0$  to 378 radian/s) has been investigated for several electrochemical reactions in acetonitrile solutions. The results demonstrate that the voltammetric response is a strong function of the ratio of the supporting electrolyte and redox concentrations ( $C_{\text{elec}}/C_{\text{redox}}$ ) as well as the charge of the reactant, ( $z$ ). For the oxidation or reduction of monovalent and divalent species (e.g., [(trimethylammonio)methyl]ferrocene ( $z = +1$ ) and methylviologen ( $z = +2$ )), the observed voltammetric limiting currents are found to increase linearly with  $\omega^{1/2}$ , independent of  $C_{\text{elec}}/C_{\text{redox}}$ . Voltammetric currents corresponding to the oxidation or reduction of neutral reactants (e.g., ferrocene and nitrobenzene ( $z = 0$ )) show a more complex dependence on  $C_{\text{elec}}/C_{\text{redox}}$ . In solutions containing an appreciable quantity of supporting electrolyte,  $C_{\text{elec}}/C_{\text{redox}} > 0.1$ , mass-transport limited currents are found to increase linearly with  $\omega^{1/2}$ . However, for  $C_{\text{elec}}/C_{\text{redox}} < 0.1$ , the voltammetric currents *decrease* with increasing  $\omega$ . The unusual behavior observed for neutral species in low ionic strength solution is interpreted in terms of the rate of migration of charge-balancing electrolyte ions to the electrode surface, relative to the rate of removal of the same ions by forced convection. In low ionic strength solutions, electrolyte ions are removed by forced convection more rapidly than they are replenished by migration, resulting in a decrease in the electrical driving force for electron-transfer.

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**Introduction.** One of several advantages of using microelectrodes in electrochemical investigations is the ability to perform quantitative measurements in low ionic strength solutions<sup>1,2</sup>. For instance, a steady-state, sigmoidal-shaped voltammetric curve can be readily obtained at a stationary 10  $\mu\text{m}$ -radius Pt microdisk electrode in solutions in which the concentration of the supporting electrolyte is significantly lower than the concentration of redox-active species, i.e.,  $C_{\text{elec}}/C_{\text{redox}} \ll 1$ . This experimental capability essentially eliminates the requisite use of solutions containing a large excess concentration of an inert supporting electrolyte, and has provided new opportunities for fundamental investigations and applications of electrochemistry in low ionic strength solutions.<sup>3</sup>

The ability to perform voltammetric measurements in low ionic strength solutions using microelectrodes is a result of the transient fluxes of supporting electrolyte ions in response to the electric field created by electrogeneration of charged products. For example, consider the oxidation of 1 mM ferrocene (Fc) in an unstirred acetonitrile solution containing a small quantity ( $\sim 10 \mu\text{M}$ ) of tetrabutylammonium hexafluorophosphate ( $\text{TBA}^+\text{PF}_6^-$ ) (conditions that correspond to  $C_{\text{elec}}/C_{\text{redox}} \ll 1$ ). As initially described by Amatore et al.<sup>1</sup> and Oldham<sup>2</sup>, oxidation of Fc to the cation  $\text{Fc}^+$  (ferrocenium) results in a depletion layer surrounding the microelectrode in which the electrical charge associated with  $\text{Fc}^+$  is balanced by a local increase and decrease in the concentrations of the electrolyte anion  $\text{PF}_6^-$  and cation  $\text{TBA}^+$ , respectively. For Fc oxidation, charge compensation primarily occurs by migration of  $\text{PF}_6^-$  from the bulk solution to the electrode, resulting in the concentration of  $\text{PF}_6^-$  within the depletion layer being significantly larger than in the bulk of the solution. A consequence of this increase in ionic concentration is that the conductivity of the depletion layer is significantly higher relative to the bulk solution value, allowing voltammetric measurements to be made under conditions that are normally considered to be prohibitively resistive.

Although the near-surface electrolyte conductivity is greatly increased relative to the bulk conductivity, a significant ohmic potential loss occurs across the depletion layer during voltammetric experiment using microelectrodes. This potential loss can be expressed as the difference in the electrostatic potential between the bulk of the solution ( $\phi^S$ ) and the plane of electron transfer ( $\phi^{\text{PET}}$ , where the PET corresponds roughly to the closest

approach of the redox molecules to the surface<sup>4</sup>). Based on simple thermodynamic arguments, the quantity  $(\phi^{\text{PET}} - \phi^{\text{S}})$  can be readily related to the applied electrode potential (E) and the equilibrium surface concentrations of the electrochemical reactant and product. Thus, for the general redox reaction,  $\text{O} + \text{e} \rightleftharpoons \text{R}$ ,

$$(E - E^{\circ}) - (\phi^{\text{PET}} - \phi^{\text{S}}) = \left(\frac{RT}{nF}\right)\ln(C_{\text{O}}/C_{\text{R}}) \quad (1)$$

where  $C_{\text{O}}$  and  $C_{\text{R}}$  represent the concentrations of O and R at the PET. Eq. (1) is simply the Nernst equation written to take into account the effect of the electrostatic potential at the PET on the chemical potentials of O and R. It has been theoretically<sup>1</sup> and experimentally<sup>3c</sup> demonstrated that  $(\phi^{\text{PET}} - \phi^{\text{S}})$  increases at a rate of  $RT/nF$  ( $\sim 59/n$  mV at room temperature) per decade decrease in  $C_{\text{elec}}/C_{\text{redox}}$ . For the steady-state voltammetric oxidation of Fc, the effect is manifested in a shift in the voltammetric half-wave potential ( $E_{1/2}$ ) to more positive potentials in lower ionic strength solutions. In the total absence of a supporting electrolyte (including ionic impurities), the theoretical description of this problem indicates that the electrostatic potential drop within the depletion layer is sufficiently large to prevent the faradaic reaction from occurring at a significant rate. Thus, all electrochemical studies employing microelectrodes appear to require a finite concentration of supporting electrolyte<sup>5</sup>.

In this report, we describe steady-state voltammetric experiments in low ionic strength solutions using a *rotating* microdisk electrode (RMDE). As in experiments using a conventional-size rotating disk electrode (RDE), rotation of a microelectrode results in an increase in the convective diffusional flux of the electroactive component to the electrode surface. Although a rigorous theoretical description of diffusional-convective transport to a RMDE does not currently exist, the hydrodynamic velocity profiles for a rotating disk are independent of the electrode size (assuming the electrode is shrouded in a larger insulating plane), suggesting that voltammetric limiting currents,  $i_{\text{lim}}$ , for a RMDE will have a similar dependence on rotation rate as that predicted for a RDE. Indeed, Mallouk et al.<sup>6</sup> have previously investigated the response of a 12.5  $\mu\text{m}$ -radius Pt RMDE in aqueous solutions containing 1 M KCl as supporting electrolyte. These authors reported that  $i_{\text{lim}}$  for

$\text{Fe}(\text{CN})_6^{4-}$  oxidation increased linearly with the square root of the angular velocity of the electrode,  $\omega^{1/2}$ , for large values of  $\omega$ . An analogous linear relationship between  $i_{\text{lim}}$  and  $\omega^{1/2}$  is predicted by the well-known Levich equation for a conventional-size RDE<sup>7</sup>.

In addition to increasing the convective-diffusional flux of the reactant to the electrode surface, fluid flow induced by rotation of the electrode also increases the rate at which product ions are removed from the surface. Thus, for a RMDE employed in low ionic strength solutions, it may be anticipated that the structure of the depletion layer that comprises the product, reactant, and charge-compensating electrolyte ions will be significantly altered relative to the depletion layer structure in an unstirred solution. The situation is schematically depicted in Fig. 1, in which the oxidation of a neutral reactant (e.g., Fc) in a low ionic strength solution ( $C_{\text{elec}}/C_{\text{redox}} \ll 1$ ) is considered again. As described above, in the absence of electrode rotation, the electrochemical generation of a charged product ( $\text{Fc}^+$ ) causes in the migration of charge-compensating anions ( $\text{PF}_6^-$ ) toward the electrode surface, resulting in an increase in the concentration of ions ( $\text{Fc}^+$  and  $\text{PF}_6^-$ ) within the depletion layer. Fluid convection induced by rotation of the electrode (shown by arrows in Fig. 1a) will tend to transport these ions away from the surface. Evidently, the steady-state concentration of the ions within the depletion layer will depend on the rate of migration of  $\text{PF}_6^-$  to the surface, relative to the rate of convective transport of  $\text{PF}_6^-$  away from the surface.

At sufficiently high rotation rates, the convective transport of electrogenerated and charge-compensating ions away from the electrode surface is anticipated to occur at a much larger rate than migration of  $\text{PF}_6^-$  from the bulk solution to the electrode. Consequently, the concentration of  $\text{PF}_6^-$  in the depletion layer is expected to decrease, asymptotically approaching the bulk solution  $\text{PF}_6^-$  concentration as the rotation rate is increased. However, as described above, the accumulation of charge-compensating ions within the depletion layer is necessary in order to observe a voltammetric response in low ionic strength solutions. Thus, the decrease in ion concentration resulting from electrode rotation will cause a decrease in the depletion layer conductivity, thereby increasing the potential drop ( $\phi^{\text{PET}} - \phi^{\text{S}}$ ) across the depletion layer, Fig. 1b. This physical scenario raises the interesting question of

whether it is possible for an electrochemical reaction to occur at a RMDE in very low ionic strength solutions.

In the current work, we have examined the influence of rotation rate on the voltammetric response of a 12.5  $\mu\text{m}$ -radius Pt RMDE for several electrochemical reactions. Our results indicate that fluid convection causes a increase in the potential drop ( $\phi^{\text{PET}} - \phi^{\text{S}}$ ) in low ionic strength solutions, resulting, for some reactions, in a dramatic decrease in the voltammetric current as the rotation rate is increased. The voltammetric response of the RMDE, however, is strongly dependent on the electric charge of the reactant ( $z$ ) as well as the ratio  $C_{\text{elec}}/C_{\text{redox}}$ . The results suggest that the use of microelectrode voltammetry in analytical applications involving flowing systems (e.g., detectors in chromatography<sup>8</sup>) or as models of chemistry occurring on dispersed semiconductor or metal particles<sup>9</sup>, may be complicated by the complex dependence of the reaction driving force on fluid convection.

#### Experimental.

*Chemicals.* Ferrocene (Fc) was sublimed twice under vacuum. [(Trimethylammonio)methyl]ferrocene (TMAFc<sup>+</sup>) hexafluorophosphate and methylviologen (MV<sup>2+</sup>) hexafluorophosphate were prepared by metathesis of the corresponding halide salt (TMAFcI and MVCl<sub>2</sub>) with ammonium hexafluorophosphate. Acetonitrile (CH<sub>3</sub>CN, HPLC Grade) was used as received. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was recrystallized from ethanol. Nitrobenzene (NB) was stored over molecular sieves.

*Rotating Microdisk and Electrochemical Apparatus.* The Pt microdisk electrode was constructed by sealing a 12.5  $\mu\text{m}$ -radius Pt wire in 8-mm diameter glass tube. The position of the disk relative to the axis of rotation in RMDE experiments is critical in determining the fluid velocity profiles effecting mass-transfer rates. In these experiments, we have attempted to center the disk at the center of the glass tube (corresponding approximately to the axis of rotation). Analysis of the voltammetric response (*vide infra*) suggests that the disk is located  $\sim 250$   $\mu\text{m}$  from the rotation axis. The electrode was polished using 0.02  $\mu\text{m}$  Al<sub>2</sub>O<sub>3</sub>, rinsed with water, and sonicated in water for 4 minutes to remove polishing debris. The radius of the microelectrode was measured to be  $r_0 = 14.9$   $\mu\text{m}$  as computed based on the voltammetric

limiting current for Fc oxidation in acetonitrile and the literature value for the diffusion coefficient of Fc ( $2.4 \times 10^{-5} \text{ cm}^2/\text{s}$ )<sup>10</sup>.

A commercial rotating disk apparatus (Pine Instrument Co., Model No. PIR) was used to rotate the microelectrode at angular velocities between 0 and 378 rad/s. A standard three-electrode cell (~30 mL) containing a Ag/AgO<sub>x</sub> reference electrode, and Pt wire counter electrode was employed throughout. Voltammograms were recorded using a BAS CV 27 potentiostat. The current was low-pass filtered to reduce noise originating at the electrical contact made to the shaft of the rotating electrode. All voltammetric data were recorded at a scan rate of 10 mV/s.

### Results and Discussion.

To our knowledge, no exact theoretical treatment exists that describes convective-diffusive transport to a RMDE. In principle, a description of the RMDE response can be obtained from the simultaneous solution of the differential equations governing momentum and mass transport to a rotating microdisk. Smyrl and Newman considered a similar problem involving radial diffusion at the edges of a conventional-size RDE<sup>11</sup>. They obtained a relationship describing the dependence of the voltammetric current on rotation rate for situations in which the depletion layer thickness is considerably smaller than the electrode dimension. In this limit, radial diffusion at the edge of the RDE accounts for a small percentage (~1%) of the total flux. However, as will be shown below, radial diffusion represents a significant fraction of the total flux to a microdisk, even at relatively large rotation rates.

The electrochemical responses of a stationary microdisk (area  $\sim 2 \times 10^{-6} \text{ cm}^2$ ) and a rotating disk of conventional size (area  $\sim 0.5 \text{ cm}^2$ ) have relatively simple and well-known descriptions. It is useful to consider these latter two cases in some detail in order to gain insight into the magnitude of the effects that fluid convection might have on the behavior of a RMDE.

In the presence of an excess concentration of a supporting electrolyte ( $C_{\text{elec}}/C_{\text{redox}} \gg 1$ ), molecular diffusion of the reactant from the bulk solution to the surface of a stationary

microdisk electrode produces a true steady-state limiting current density ( $i_{lim}/A$ ) that can be expressed as<sup>12</sup>

$$\frac{i_{lim}}{A} = \frac{4nFD C^*}{\pi r_o} \quad (2)$$

where  $A$  is the electrode area,  $D$  is the diffusion coefficient,  $C^*$  is the concentration of the reactant in the bulk of the solution, and  $r_o$  is the electrode radius. For a microdisk electrode, the diffusional flux converges towards the surface in a quasi-radial fashion. Eq. (2) demonstrates clearly that the current density at a stationary microdisk increases as the electrode size is decreased.

The analogous expression for a large rotating disk electrode is given by the Levich equation,

$$\frac{i_{lim}}{A} = 0.620nFD^{2/3}\omega^{1/2}\nu^{-1/6}C^* \quad (3)$$

where  $\omega$  is the angular velocity (rad/s) and  $\nu$  is the kinematic viscosity. Eq. (3) is derived based on the assumption of an infinitely large planar electrode, without interference from radial diffusion at the electrode edges. Eq. (3) indicates that the current density is independent of the electrode size.

The dependencies of  $i_{lim}/A$  on electrode size (eq. (2)) and angular velocity (eq. (3)) for stationary and rotating disks, respectively, suggests that the magnitude of current enhancement resulting from rotation of a microdisk will depend strongly on  $r_o$  as well as  $\omega$ . For instance,  $i_{lim}/A$  resulting from radial diffusion (eq. (2)) will dominate the total flux to a microdisk if  $r_o$  is sufficiently small. In this situation, rotation of a microelectrode is not expected to have a significant effect of the current. Conversely, for a sufficiently large value of  $r_o$ , radial diffusion (eq. (2)) will be negligibly small, and the convective-diffusive flux described by eq. (3) will dominate the response of the electrode, resulting in a linear dependence of current on  $\omega^{1/2}$ .

Mass-transfer coefficients ( $m$ ) for a 10  $\mu\text{m}$ -radius stationary disk and a RDE are plotted in Fig. 2a. The magnitude of  $\omega$  at which comparable fluxes are predicted to result

from radial diffusion (at a stationary disk) and linear convection-diffusion (at a rotated disk) can be estimated from this plot. Values of  $m$  are determined from the usual definition<sup>13</sup>

$$\frac{i_{\text{lim}}}{A} = nFmC^* \quad (4)$$

yielding  $m_{\text{stationary}} = 4D/\pi r_0$  and  $m_{\text{rde}} = 0.620D^{2/3}\omega^{1/2\nu-1/6}$  (by inspection of eqs. (2), (3) and (4)). The results plotted in Fig. 2a suggest that  $i_{\text{lim}}$  at a stationary 10  $\mu\text{m}$ -radius electrode is equivalent to that of a RDE (of equivalent size) rotated at  $\omega = 400$  rad/s. Furthermore, since the convective-diffusive flux increases very rapidly with increasing  $\omega$ ,  $m_{\text{rde}}$  is comparable to  $m_{\text{stationary}}$  for all angular velocities within the normal working range employed in RDE experiments (10 - 1000 rad/s).

The effect of rotation on the concentration profiles of the redox species and electrolyte ions at a microelectrode will be considered in more detail in a later section. Here, we briefly examine the approximate thicknesses of the depletion layer at stationary and rotating microdisks. Fig. 2b show normalized reactant concentration profiles,  $C(z)/C^*$ , normal to the electrode surface for a stationary 10- $\mu\text{m}$  radius and for a RDE at different values of  $\omega$ . For the RDE, the concentration profile within the depletion layer is uniform across the electrode surface. For a stationary disk, the convergent flux of reactant dictates that the reactant concentration increases as one moves in a radial direction away from the center of the disk into the solution. Thus, for the purpose of comparing the depletion layer thicknesses, the profile of  $C(z)/C^*$  for the stationary disk is computed normal to the surface at the center of the electrode.  $C(z)/C^*$  for the stationary microdisk is given by<sup>12</sup>

$$\frac{C(z)}{C^*} = 1 - \tan^{-1} \frac{2^{1/2} r_0}{[(z^2 - r_0^2) + ((z^2 - r_0^2)^2 + 4z^2 r_0^2)^{1/2}]^{1/2}} \quad (5)$$

and the corresponding equation for a RDE is<sup>13</sup>:

$$\frac{C(z)}{C^*} = \frac{(3B)^{-1/3}}{0.8934} \int_0^z \exp\left(\frac{-z^3}{3B}\right) dz \quad (6)$$

where  $B = D\nu^{1/2} / 0.51\omega^{3/2}$ .

Inspection of Fig. 2b shows that the thickness of the depletion layer surrounding a microdisk is expected to be a relatively strong function of  $\omega$ . However, the depletion layer thicknesses for the stationary 10  $\mu\text{m}$ -radius electrode and a RDE are comparable for all reasonable values of  $\omega$ . The similar magnitudes of the depletion layer thicknesses suggest that rotation will have a significant effect on the concentration profiles of the various species that comprise the depletion layer. For  $\omega \gg 100$  rad/s, convection will reduce the thickness of the depletion layer to a value significantly smaller than predicted for a stationary disk. In this limit, the concentration profiles are approximated by the theoretical description of convective diffusional transport to a conventional size RDE. On the other hand, at low rotation rates, e.g.,  $\omega \ll 100$  rad/s, the depletion layer for the RDE is predicted to be much larger than that of the stationary microdisk, as shown in Fig. 2b. In this limit, the concentration profiles are approximated by the theoretical description of diffusional transport to a stationary disk. At intermediate rotation rates, convective diffusional transport and radial molecular diffusion will make approximately equal contributions to the transport of the reactant.

The qualitative description presented above allows several predictions to be made about the behavior of a RMDE. First, rotation of a 10  $\mu\text{m}$ -radius electrode over a reasonable range of  $\omega$  should result in a significant enhancement of  $i_{lim}$ . This is verified by the experimental data presented below. Second, from the definition of the mass-transport coefficient for a stationary disk ( $m_{stationary} = 4D/\pi r_0$ ), it is clear that the effect of rotation will be less influential as the electrode radius decreases. For instance, for  $r_0 = 0.1$   $\mu\text{m}$ ,  $m_{stationary} = 1.3$  cm/s, which is  $\sim 100$  times larger than  $m_{rde}$  for all reasonable values of  $\omega$  (see Fig. 2a). For such a small electrode, rotation should have an insignificant effect on the voltammetric currents.

We note that the above discussion is limited to situations where the microdisk is centered directly on the axis of rotation. As will be discussed below,  $m_{rde}$  can be significantly larger when the electrode is not centered exactly at the rotation axis, since the fluid velocity tangential to the surface of a rotating disk is dependent on the radial position (*vide infra*). The above discussion is also limited to situations where an excess amount of

an electrolyte is present in the bulk of the solution ( $C_{\text{elec}}/C_{\text{redox}} \gg 1$ ), such that migration of ions is negligibly small compared to diffusive and convective transport. As shown below, a rather dramatic decrease in  $i_{\text{lim}}$  is observed at a RMDE for some electrochemical reactions when this condition is not fulfilled.

In a related problem, Tait et al. have investigated the effect of fluid convection on  $i_{\text{lim}}$  at microdisks inside a narrow channel<sup>14</sup>. Finite difference simulations were used to compute the convective diffusive flux assuming a parabolic flow distribution within the channel. These studies were limited to solutions containing an excess concentration of supporting electrolyte ( $C_{\text{elec}}/C_{\text{redox}} \gg 1$ ).

#### *RMDE Voltammetry of Charged Redox-Active Molecules.*

The voltammetric response of the 12.5  $\mu\text{m}$ -radius Pt RMDE was initially examined as a function of the supporting electrolyte concentration in  $\text{CH}_3\text{CN}$  solutions containing either 1mM TMAFc<sup>+</sup> or  $\text{MV}^{2+}$  as the redox-active species. As shown in Fig. 3(a) and (b), sigmoidal-shaped voltammograms were obtained in both the presence and absence of a supporting electrolyte (10 mM TBAPF<sub>6</sub>) for angular velocities,  $\omega$ , between 0 and 378 rad/s. We observed that rotation of the microelectrode significantly enhances the mass-transport limiting currents corresponding to the 1-e<sup>-</sup> oxidation of TMAFc<sup>+</sup> and the 1-e<sup>-</sup> reduction of  $\text{MV}^{2+}$ , in agreement with the behavior of the RMDE reported by Mallouk et al.<sup>6</sup> However, the absolute value of the voltammetric current (at constant  $\omega$ ) is dependent on the concentration of the supporting electrolyte. For instance, the limiting current measured for  $\text{MV}^{2+}$  reduction is approximately 25% larger in the absence of a supporting electrolyte than in solutions containing 10 mM TBAPF<sub>6</sub> (Fig. 3(b)). To account for this difference, we recall the analysis of Amatore et al.<sup>1</sup> of coupled migrational and diffusional fluxes to a stationary microelectrode. In the presence of an excess supporting electrolyte ( $C_{\text{elec}}/C_{\text{redox}} \gg 1$ ), the electric field in the solution is negligibly small and the steady-state voltammetric current is expected to be controlled solely by diffusion of the reactant to the surface. For this condition, the current at a stationary electrode is given by eq. (2), which, for convenience, can be written as

$$i_{lim}^{xs} = 4nFDr_oC_{redox} \quad (7)$$

In solutions in which the concentration of supporting electrolyte is less than that of the redox species ( $C_{elec}/C_{redox} \ll 1$ ), significant electric fields exist within the depletion layer and transport of the charged species  $MV^{2+}$  and  $TMAFc^+$  to the electrode surface are controlled by both diffusion and migration. For a spherical microelectrode, Amatore et al. have shown that for such situations  $i_{lim}$  is given by<sup>1</sup>

$$\frac{i_{lim}}{i_{lim}^{xs}} = 1 \pm z \left\{ 1 + \beta \left[ \ln(1 - \beta^{-1}) \right] \right\} \quad (8)$$

where  $\beta = (1 + |z|)(1 - z/n)$ . In eq. (8),  $n$  is positive for reductions and negative for oxidations. The sign ( $\pm$ ) is taken as positive when  $n < z$  and negative when  $n > z$ .

For  $MV^{2+}$  reduction,  $z = 2$  and  $n = 1$ , yielding a theoretical  $i_{lim}/i_{lim}^{xs} = 1.27$ . The corresponding experimental value is equal to 1.25 (computed from the ratio of the limiting currents for  $\omega = 0$ , Fig. 3(b)). Similarly,  $z = 1$  and  $n = -1$  for  $TMAFc^+$  oxidation, yielding  $i_{lim}/i_{lim}^{xs} = 0.85$ . The corresponding experimental value is 0.85. It is apparent that eq. (8) yields excellent predictions of the influence of migration at a stationary microdisk. Unfortunately, no analogous analytical expression exists that allows computation of the current at a RMDE in the absence of an electrolyte (conditions where the flux results from combined convection, diffusion, and migration). Experimentally, we find that the ratio of limiting currents ( $i_{lim}/i_{lim}^{xs}$ ) for  $MV^{2+}$  reduction remains nearly constant over the range of  $\omega$  accessible in this study (decreasing slightly from 1.25 at  $\omega = 0$  to 1.22 at  $\omega = 378$  rad/s), although there is no apparent *a priori* reason for this ratio to remain constant. On the other hand,  $i_{lim}/i_{lim}^{xs}$  for  $TMAFc^+$  oxidation increases from 0.85 at  $\omega = 0$  to 1.04 at  $\omega = 378$  rad/s.

Fig. 4 shows plots of  $i_{lim}$  on the square root of the angular velocity ( $\omega^{1/2}$ ) for  $MV^{2+}$  reduction, in the presence and absence of 10 mM TBAPF<sub>6</sub>. The nonlinear dependence of  $i_{lim}$  on  $\omega^{1/2}$  at low  $\omega$  is essentially identical to that reported by Mallouk et al.<sup>6</sup> for  $Fe(CN)_6^{4-}$  oxidation in a 1M KCl solution using a 12.5  $\mu$ m-radius Pt RMDE. At  $\omega^{1/2} > 5$  (rad/s)<sup>1/2</sup>, the limiting current increases linearly with  $\omega^{1/2}$ , indicating that convective

diffusion is the predominate mode of transport of the reactant to the surface. However, extrapolation of this linear region to  $\omega = 0$  yields a nonzero intercept, demonstrating that radial diffusion also contributes significantly to the flux over the investigated range of  $\omega$ . The fact that the extrapolated intercept is smaller than the measured value of  $i_{lim}$  at  $\omega = 0$  suggests that the contribution of the radial diffusion is smaller when the electrode is rotating.

The slope of the linear region of the plot of  $i_{lim}$  vs.  $\omega^{1/2}$  ( $= 1.54 \text{ nA}/(\text{rad/s})$ ) is  $\sim 2.7$  times larger than that predicted by the Levich equation. We believe that this is due to the microdisk being positioned slightly off the center axis of rotation (Fig. 5). For such a geometry, Chin and Litt<sup>15</sup> and Mohr and Newman<sup>16</sup> have demonstrated (ignoring the contribution of radial diffusion) that the current at a RDE will be given by

$$\frac{i_{lim}}{A} = 0.64nFD^{2/3}\omega^{1/2}v^{-1/6}C^*\epsilon^{1/3} \quad (9)$$

where  $\epsilon$  (the so-called eccentricity factor) is defined as the ratio of the distance between the axis of rotation and the center of the disk ( $R$ ) relative to the radius of the microdisk ( $r_0$ ).

$$\epsilon = R / r_0.$$

Eq. (9), which is applicable in the limit  $R \gg r_0$ , indicates that the voltammetric current increases as the cube-root of the displacement of the electrode from the axis of rotation. Physically, this results from the dependence of the tangential fluid velocity on the radial distance  $r$  from the center of the electrode. For a rotating disk, both the angular ( $v_\phi$ ) and radial ( $v_r$ ) fluid velocities are proportional to the position  $r$ . Thus, the rate at which the reactant is transported to the electrode surface (by tangential convective flow) will increase if the electrode is located off of the rotation axis (i.e.,  $R \neq 0$ ).

From the data in Fig. 4, and using  $D = 1.35 \times 10^{-5} \text{ cm}^2/\text{s}$  for  $MV^{2+}$ , we compute  $\epsilon = 20.4$ , corresponding to  $R \sim 300 \text{ }\mu\text{m}$ . Similar values  $R$  were determined from voltammetric measurements using different redox systems; for instance, for Fc oxidation,  $R$  was measured to be  $210 \text{ }\mu\text{m}$ . Given the cubic dependence of  $R$  on measured values of  $i_{lim}$ , the agreement between these values appears quite reasonable.

### *RMDE Voltammetry of Neutral Redox-Active Molecules.*

In the preceding section we have shown that the voltammetric behavior of a RMDE in solutions containing charged redox species ( $z = +1$  or  $+2$ ) is adequately described (albeit qualitatively) by extension of existing theories of mass transport at stationary and rotating disks. We now consider the oxidation and reduction of neutral ( $z = 0$ ) reactants at a RMDE. Fig 6 shows the voltammetric responses of the RMDE corresponding to the  $1\text{-e}^-$  reduction of nitrobenzene (NB) and the  $1\text{-e}^-$  oxidation of Fc. In the presence of an appreciable quantity of electrolyte, we observe that the voltammetric behavior for these two redox systems is qualitatively similar to that previously discussed for  $\text{MV}^{2+}$  and  $\text{TMAFc}^+$ . For instance, Fig 6a shows that  $i_{\text{lim}}$  for the reduction of 20 mM NB increases with increasing rotation rate in  $\text{CH}_3\text{CN}$  solutions containing 100 mM  $\text{TBAPF}_6$ . A similar behavior is observed for oxidation of 2 mM Fc in the presence of 0.2 mM  $\text{TBAPF}_6$ . In each case, a plot of  $i_{\text{lim}}$  vs.  $\omega^{1/2}$  exhibits linear behavior at high angular velocities. The slope of the linear region of the  $i_{\text{lim}}$  vs.  $\omega^{1/2}$  curves yields  $\epsilon$  and  $R$  values that are in reasonable agreement with the corresponding values determined for the  $\text{MV}^{2+}$  system.

When the ratio  $C_{\text{elec}}/C_{\text{redox}}$  is decreased below a critical value, the voltammetric current at the RMDE is observed to decrease with increasing rotation rate. Fig. 6b, for instance, shows that a 10-fold decrease in the electrolyte concentration (from 0.2 mM to 0.02 mM  $\text{TBAPF}_6$ ) results in a dramatic change in the voltammetric response for Fc oxidation. The  $i$ - $V$  curves no longer have a sigmoidal shape, but are drawn out, suggestive of either a kinetic or ohmic potential limitation that is dependent upon both the angular velocity and  $C_{\text{elec}}/C_{\text{redox}}$ .

The results of a number of voltammetric experiments for Fc oxidation are summarized in Fig. 7 as plots of  $i/i_{\text{lim}}^{25}$  vs.  $C_{\text{elec}}/C_{\text{redox}}$  for different angular velocities. Here,  $i$  is the voltammetric current measured at 1.05 V vs.  $\text{Ag}_x\text{O}$  (note:  $i$  is used rather than  $i_{\text{lim}}$ , since a true limiting current is not obtained at small  $C_{\text{elec}}/C_{\text{redox}}$ ). In these experiments, the concentration of Fc was held constant at 2 mM and the concentration of  $\text{TBAPF}_6$  was varied from 2  $\mu\text{M}$  to 20 mM.  $i_{\text{lim}}^{25}$  was taken as the value of the limiting current at  $C_{\text{elec}}/C_{\text{redox}} = 10$  for computing  $i/i_{\text{lim}}^{25}$  at each specific rotation rate.

The data in Fig. 7 clearly demonstrate that there is a precipitous decrease in current for all non-zero values of  $\omega$  when  $C_{\text{elec}}/C_{\text{redox}} < 0.1$ . Voltammetric data were also obtained for the reduction of NB in  $\text{CH}_3\text{CN}$  solution in which  $C_{\text{elec}}/C_{\text{redox}}$  was held constant at 0.01, and the concentration of NB was varied from 20 mM to 1M. The dependence of  $i/i_{\text{lim}}^{\text{st}}$  on  $\omega$  for these data (not shown) was essentially identical to that shown in Fig. 7 and, more importantly, was found to be independent of the absolute concentration of NB. Based on these data sets, we conclude that the unusual decrease in voltammetric currents is only a function of  $C_{\text{elec}}/C_{\text{redox}}$  and  $\omega$ , and is not a function of the absolute concentrations of either  $C_{\text{elec}}$  or  $C_{\text{redox}}$ .

In considering the above behavior, we note that the heterogeneous rate constants for the oxidation of Fc and the reduction of NB in  $\text{CH}_3\text{CN}$  are sufficiently large that the effects of slow electron-transfer should be negligible in slow-scan RMDE experiments. Thus, following the arguments presented in the *Introduction*, the decrease in voltammetric currents upon rotation of the electrode must result from an increase in the potential drop between the microdisk surface and the bulk solution ( $\phi^{\text{PET}} - \phi^{\text{S}}$ ). This dependence results from the charge-compensating ions being convected away from the rotating electrode surface. From Fig. 7, it is apparent that even relatively low rotation rates result in rapid convective transport of charge-compensating ions away from the electrode surface.

The effect of electrode rotation is examined in more detail by considering the individual components of the fluid velocity ( $v_\phi$ ,  $v_r$ , and  $v_z$ , where the cylindrical coordinate system is defined in Fig. 5). The magnitudes of these velocities are computed from the following approximate expressions derived by Levich<sup>7</sup>:

$$\begin{aligned} v_\phi &\approx r\omega[1 + b\xi + (1/3)a\xi^3] \\ v_r &\approx r\omega[a\xi - (1/2)\xi^2 - (1/3)b\xi^3] \\ v_z &\approx (\omega v)^{1/2}[-a\xi + (1/3)\xi^3] \end{aligned} \tag{10}$$

where  $\xi$  is defined as  $z(\omega/v)^{1/2}$ , and the constants  $a$  and  $b$  are equal to 0.510 and -0.616, respectively. Fig. 5b shows  $v_\phi$ ,  $v_r$ , and  $v_z$  computed using the following parameters (corresponding to the experimental parameters of the current work):  $\omega = 200 \text{ rad/s}$ ,  $v =$

0.00452 cm<sup>2</sup>/s, and  $r (\equiv R) \sim 250 \mu\text{m}$ . In examining these curves, a key point is to recall is that the fluid flow effects the driving force for electron-transfer via the disruption of the depletion layer structure; fluid flow beyond the depletion layer region should have very little influence on depletion layer structure. Thus, in order to define an appropriate length scale for considering the effects of convection, the dimensionless concentration profile for a neutral reactant at a stationary microdisk is also plotted in Fig. 5b (using the experimentally-determined value of  $r_0 = 14.9 \mu\text{m}$  and eq. 5).

Inspection of the plots of  $v_\phi$ ,  $v_r$ , and  $v_z$  suggests that the significant velocity components are those associated with flow tangential to the electrode surface (i.e.,  $v_r$  and  $v_\phi$ ). This follows from  $v_z$  being negligibly small within the depletion layer (i.e., for  $z < 25 \mu\text{m}$ ) in comparison to either  $v_r$  or  $v_\phi$ . Thus, the fluid velocity at any point within the depletion layer can be approximated by  $v = (v_r^2 + v_\phi^2)^{1/2}$ . The net relative fluid velocity,  $v_{\text{net}}$ , which is defined here as the difference between the fluid velocity at some distance  $z$  from the electrode surface and the velocity of the electrode is the critical parameter in determining the rate at which ions are removed from the depletion layer. This parameter is given by  $v_{\text{net}} = (v_r^2 + (v_\phi - \omega R)^2)^{1/2}$ . For  $z = 10 \mu\text{m}$ , we compute  $v_{\text{net}} \sim 0.9 \text{ cm/s}$ . Thus, assuming that the potential drop in the depletion layer is altered whenever charge balancing ions are moved ca. 1 radius from the electrode surface, the timescale on which rotation alters the depletion layer structure can be estimated as  $|r_0/v_{\text{net}}|$ . For  $r_0 = 14.9 \mu\text{m}$ ,  $t_{\text{expt}}$  is equal to  $\sim 2 \text{ ms}$ . For larger values of  $z$ , the corresponding timescale to alter the depletion layer decreases; however, as noted above, any effect of convection on the concentration profiles at distances far from the surface is expected to have an inconsequential effect on the potential and ion distributions near the surface. On the other hand,  $v_{\text{net}}$  decreases rapidly at very small values of  $z$  ( $< 1 \mu\text{m}$ ). Thus, although our choice of  $z = 10 \mu\text{m}$  in computing  $t_{\text{expt}}$  is rather arbitrary, any value of  $z$  within the depletion layer that is not too small or large will yield a comparable value of  $t_{\text{expt}}$ .

When the time required for migration of electrolyte ions from the bulk of the solution to the electrode is longer than  $t_{\text{expt}}$ , the ion profiles that define the depletion layer structure (which is necessary to perform voltammetry in low ionic strength solutions) can no longer be

established. Consequently, the solution resistivity and  $(\phi^{\text{PET}} - \phi^{\text{S}})$  become sufficiently large that the reaction will not be driven at the normal convective-diffusion controlled rate.

Recent computer simulations<sup>17</sup> of the chronoamperometric response of microspherical electrodes indicate the time required for the potential and ion distribution to be established following a potential step is on the order of  $\sim 10^{-1}$  s for the oxidation of a neutral redox species at a 10  $\mu\text{m}$ -radius electrode when  $C_{\text{elec}}/C_{\text{redox}} = 10^{-2}$ . The corresponding value for the oxidation of a charged reactant ( $z = +1$ ) is  $10^{-5}$  s. Since the value of  $t_{\text{expt}}$  computed for the RMDE (2 ms) is intermediate between these cases, it follows that a highly conductive depletion layer can be established at a RMDE in low ionic strength solutions for the reduction (or oxidation) of a charged species, but not for a neutral species.

**Conclusion.** The voltammetric response of a Pt RMDE is dependent on the charge of the electroactive reactant and the ratio  $C_{\text{elec}}/C_{\text{redox}}$ . For charged species,  $z \neq 0$ , the observed dependence of  $i_{\text{lim}}$  on  $\omega$  and  $C_{\text{elec}}/C_{\text{redox}}$  appears to be interpretable in terms of existing mathematical treatments of fluid convection and ion migration, albeit only in a qualitative fashion. A rigorous description of the behavior of a rotating microelectrode that takes into account the comparable magnitude of radial diffusion and convective diffusion, as well as the eccentricity factor, is yet established.

RDME voltammetric currents corresponding to the oxidation or reduction of a neutral redox species have a much more complex dependence on  $C_{\text{elec}}/C_{\text{redox}}$ . In low ionic strength solutions, the voltammetric currents have been shown to decrease with increasing  $\omega$  whenever  $C_{\text{elec}}/C_{\text{redox}} \ll 0.01$ . This behavior results from electrolyte ions being removed from the depletion layer by forced convection more rapidly than they are replenished by migration. We have qualitatively shown that this competition of transport paths results in a decrease in the electrical driving force for electron-transfer.

The complex nature of RMDE behavior on the parameters  $z$ ,  $C_{\text{elec}}/C_{\text{redox}}$ ,  $\epsilon$ , and  $\omega$  can be expected to apply to other electrochemical systems involving forced convection. For instance, there has been recent interest in the use of microelectrodes as on-line detectors in chromatography, since the use of a microelectrode eliminates the need of a large excess concentration of supporting electrolyte.<sup>8</sup> Such an application may involve flow of the

carrier fluid pass a small microelectrode, which, as shown here for a RMDE, can alter the potential distribution near the electrode surface. The degree to which the potential distribution is altered will be determined largely by the analyte charge ( $z$ ), thus making it difficult to obtain a useful relationship between the detector signal and analyte concentration. The present results are also relevant to the use of microelectrodes as models for electrochemical reactions that occur on small metal particles dispersed in a solution (by rapid stirring or gas sparging).<sup>9</sup> In these situations, it seems altogether reasonable that increased convection may have a significant and adverse effect on reaction rates, in clear opposition to conventional wisdom.

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- $E_{1/2}$  for Fc oxidation in  $\text{CH}_3\text{CN}$  is shifted positive by 209 mV from  $E^0(\text{Fc}/\text{Fc}^+)$ . This shift corresponds to an ionic impurity concentration of 80 nM (ref. (3c)).
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### Figure Captions.

1. Schematic diagram of the (a) ion and (b) potential distributions at a stationary ( $\omega = 0$ ) and rotating ( $\omega > 0$ ) microdisk electrode.  $\phi_{\text{PET}}$  is the electrostatic potential (vs. bulk solution) at the plane of electron transfer.
2. (a) Mass-transfer coefficients for stationary and rotating disk electrodes. (b) Dimensionless reactant concentration profiles for stationary and rotating disks. The mass-transfer coefficient and concentration profile for the stationary disk are independent of  $\omega$  and are computed assuming a  $10 \mu\text{m}$ -radius disk. The concentration profile for the stationary disk is computed along the direction normal to the electrode surface directly above the center of the disk, eq. (5).
3. Voltammetric response of a Pt RMDE (radius  $\sim 14.9 \mu\text{m}$ ) for (a) the  $1\text{-e}^-$  oxidation of  $1 \text{ mM TMAFc}^+$  and (b) the  $1\text{-e}^-$  reduction of  $1 \text{ mM MV}^{2+}$  in  $\text{CH}_3\text{CN}$ . Voltammetric curves were obtained in the presence and absence of supporting electrolyte ( $10 \text{ mM TBAPF}_6$ ) as indicated in the figures. Scan rate:  $10 \text{ mV/s}$ .
4. Dependence of limiting current,  $i_{\text{lim}}$ , on angular velocity for the reduction of  $\text{MV}^{2+}$  in the absence and presence of a supporting electrolyte.
5. (top) Schematic diagram of a rotating microdisk offset from the axis of rotation by a distance  $R$ .  
(bottom) Velocity profiles normal to the surface of an offset RMDE ( $R = 250 \mu\text{m}$ ).  $C(z)/C^*$  is the dimensionless concentration reactant profile for a  $14.9 \mu\text{m}$ -radius stationary disk, computed assuming that transport occurs only by molecular diffusion, eq. (5).
6. Voltammetric response of a Pt RMDE (radius  $\sim 14.9 \mu\text{m}$ ) for (a) the  $1\text{-e}^-$  reduction of  $20 \text{ mM NB}$  and (b) the  $1\text{-e}^-$  oxidation of  $2 \text{ mM Fc}$  in  $\text{CH}_3\text{CN}$  as a function of the supporting electrolyte ( $\text{TBAPF}_6$ ) concentration (indicated on the figure). Scan rate:  $10 \text{ mV/s}$ .
7. Plot of normalized steady-state current  $i/i_{\text{lim}}^{\text{xs}}$  as a function of  $\log(C_{\text{elec}}/C_{\text{redox}})$  for the oxidation of  $2 \text{ mM ferrocene}$  in acetonitrile.  $i_{\text{lim}}^{\text{xs}}$  is the limiting current measured at  $\log(C_{\text{elec}}/C_{\text{redox}}) = 1$  for each rotation rate,  $\omega$ . The four data sets correspond to  $\omega = 0, 42, 167, \text{ and } 378 \text{ rad/s}$ . The supporting electrolyte is  $\text{TBAPF}_6$ .

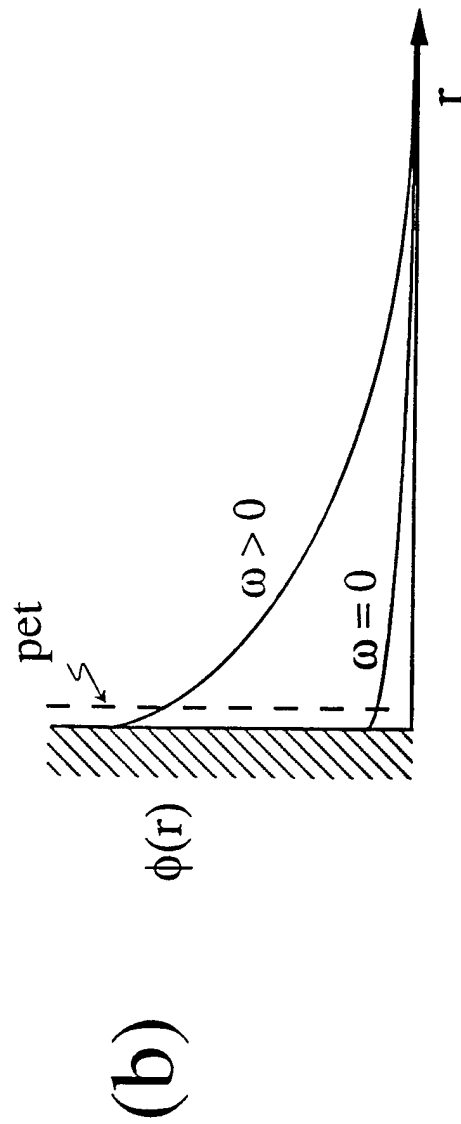
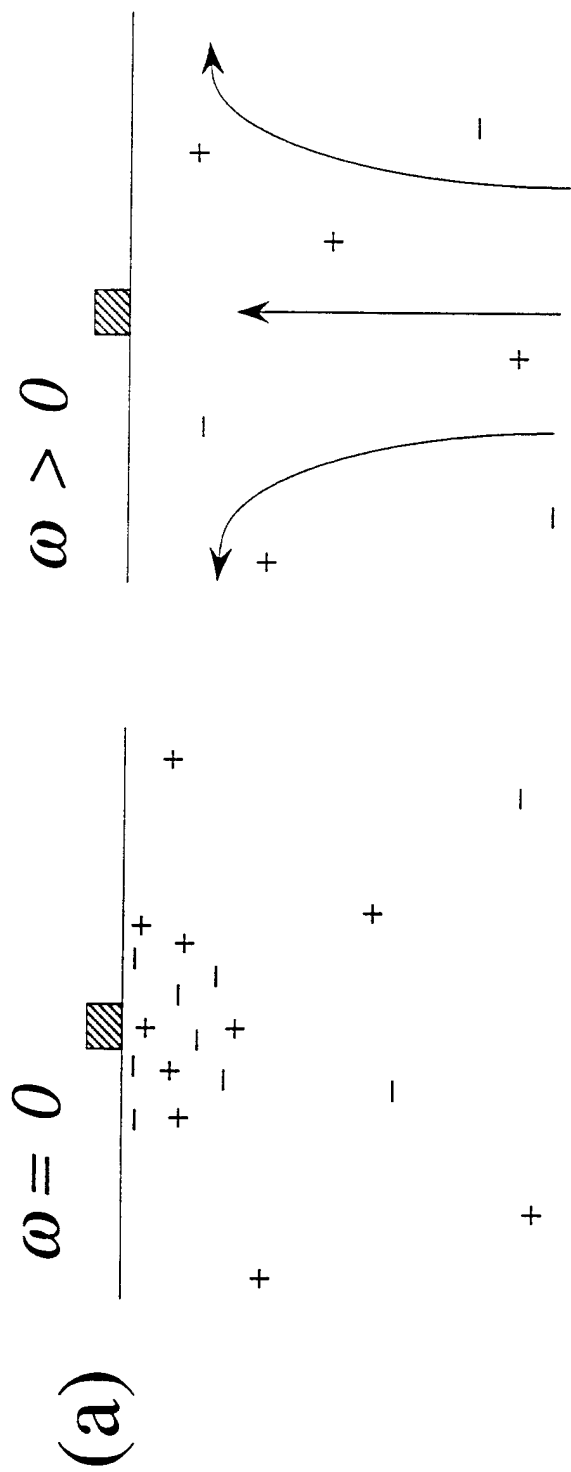


FIGURE 1

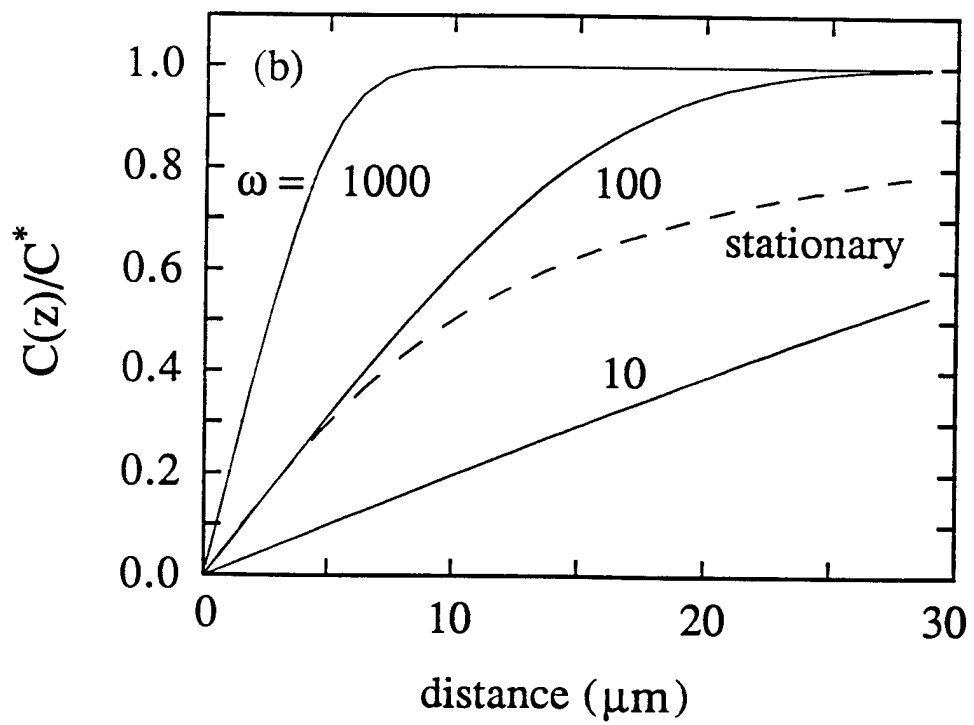
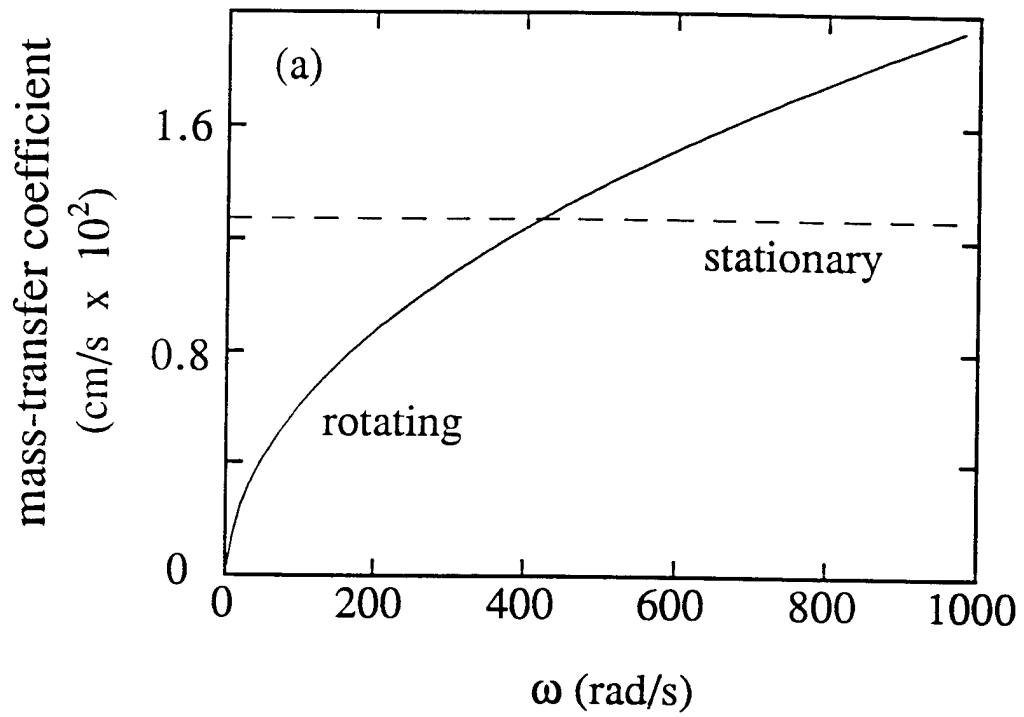


FIGURE 2

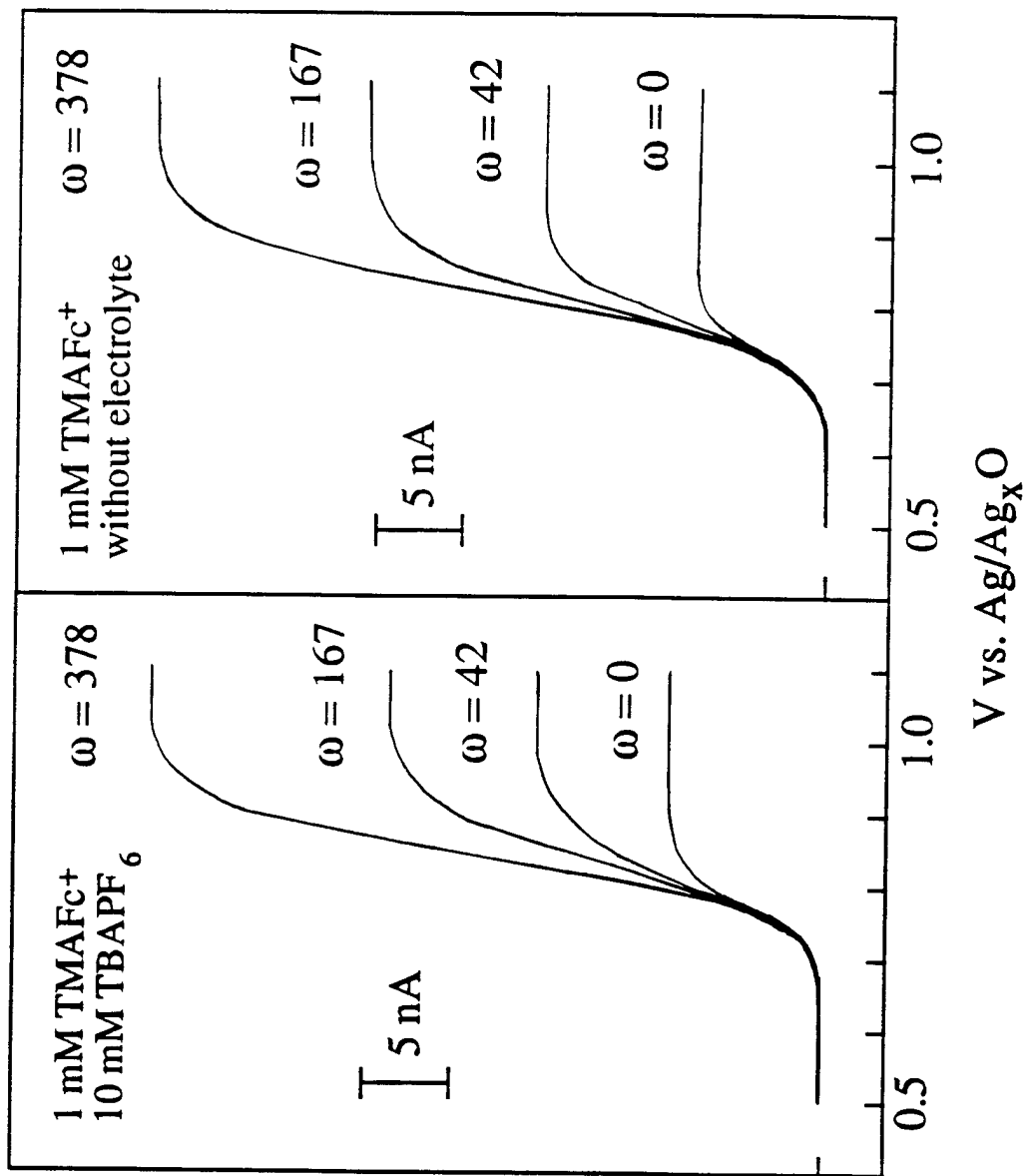


Figure 3a

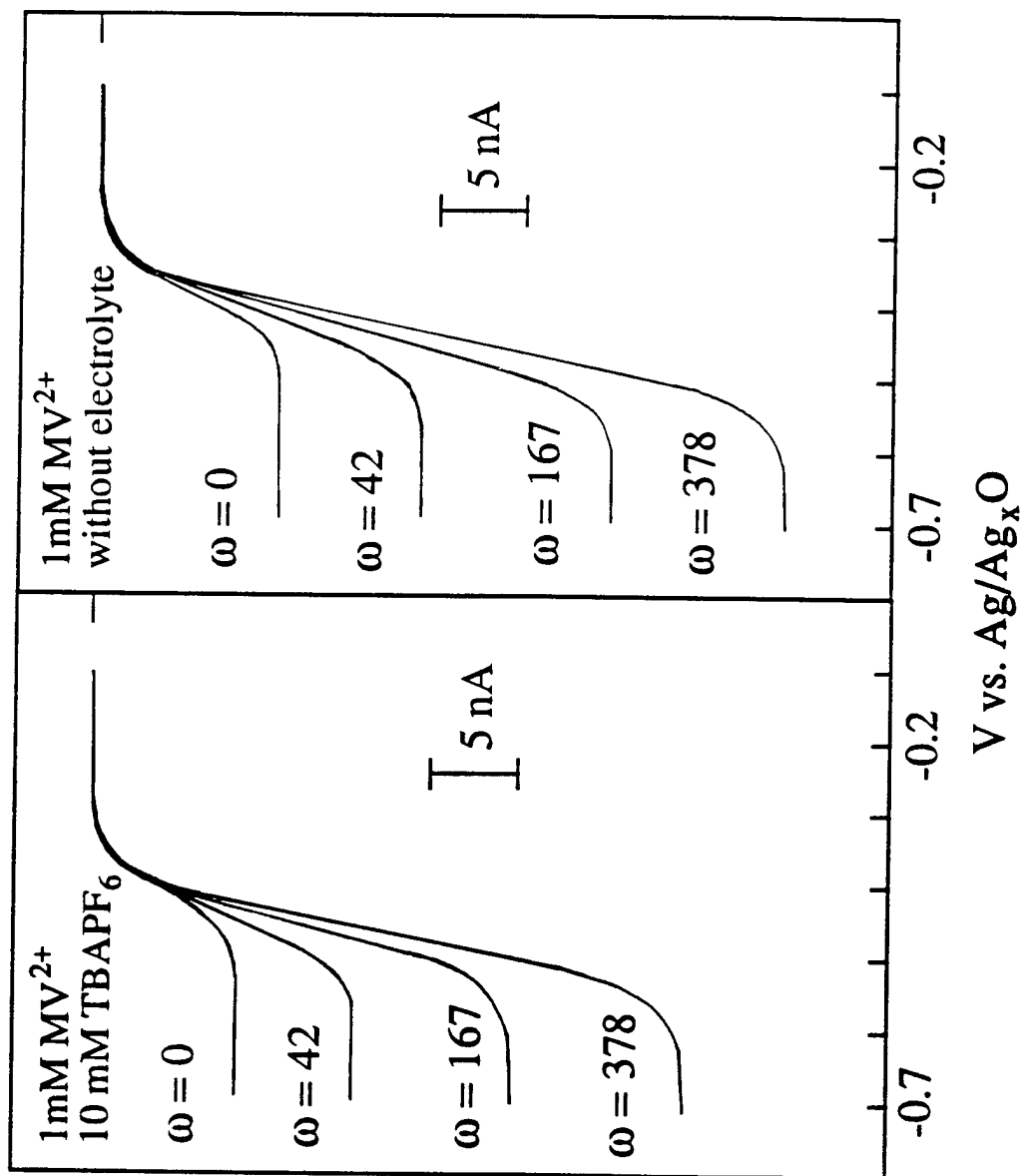


Figure 3b

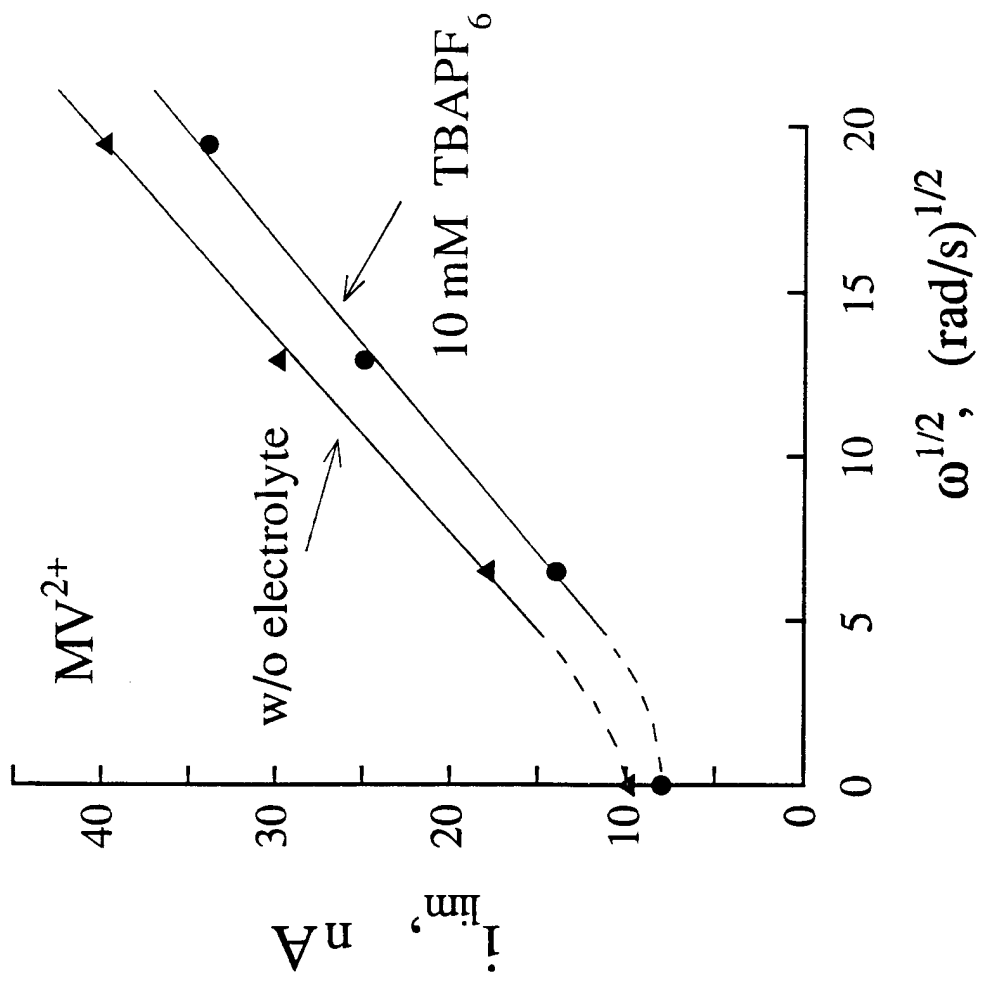


Figure 4

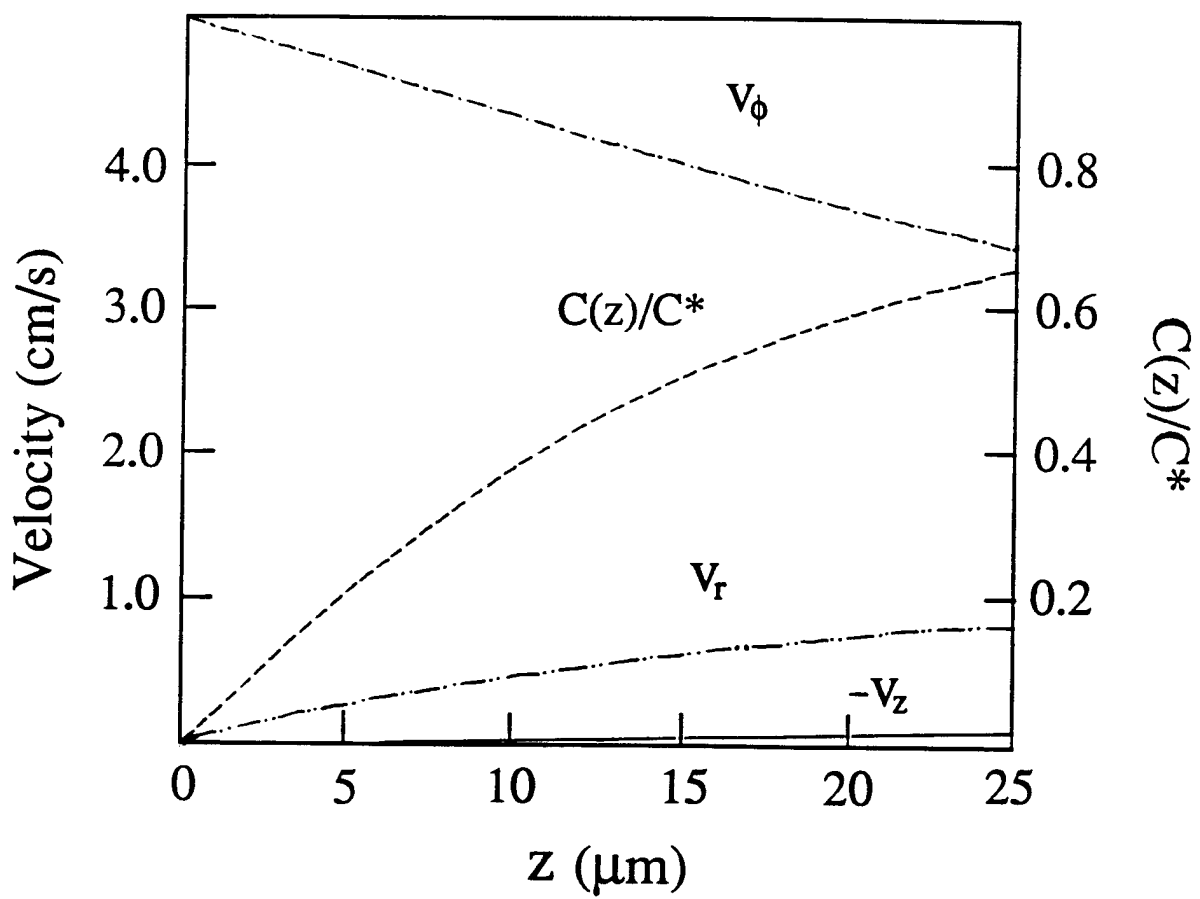
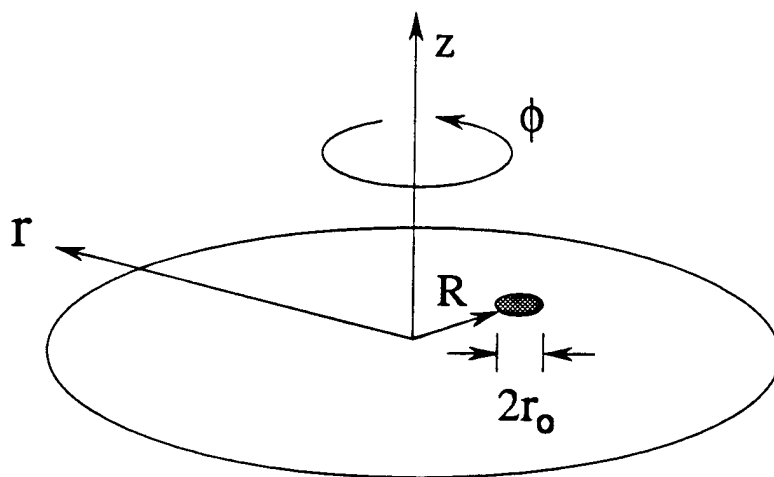


FIGURE 5



FIGURE 6a

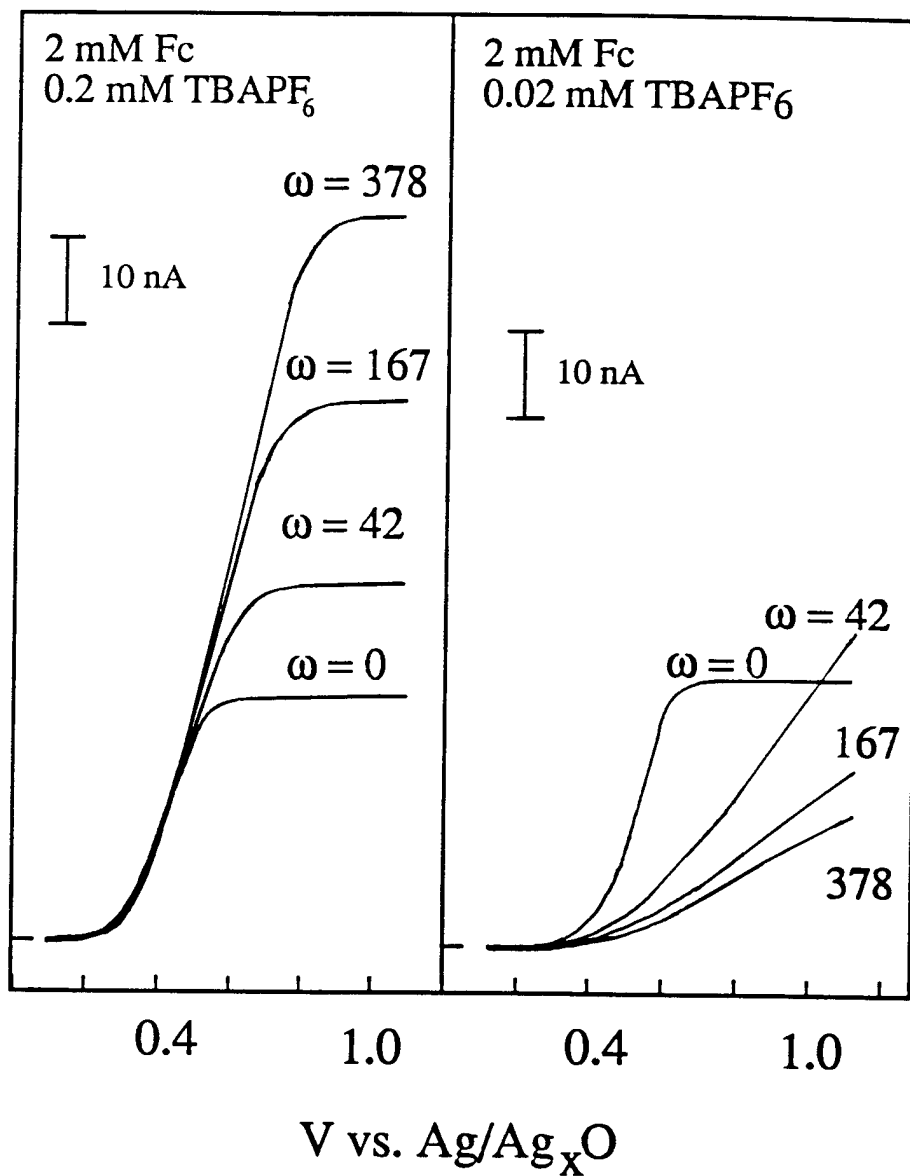


FIGURE 6b

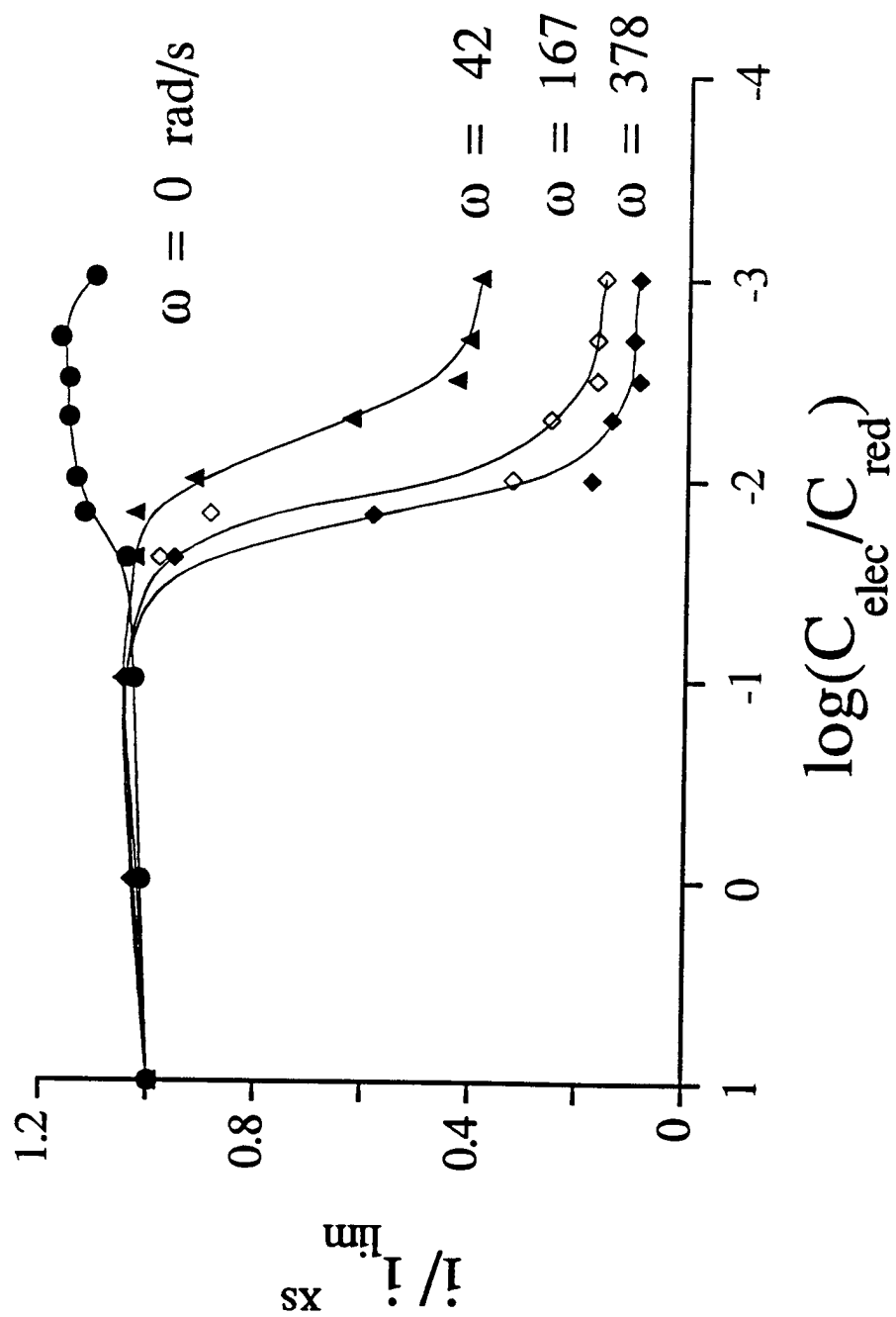


FIGURE 7