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A voltammetric study of electron conduction in nitrobenzene(NB)toluene solutions is presented. Analysis of steady-state mass-transport limited currents corresponding to the first and second one-electron reductions of NB (to the radical anion, NB⁻, and dianion, NB⁻², respectively) indicates that electrogeneration of NB⁻² is suppressed to negligible values in concentrated NB solutions as a result of the increased flux of electrons away from the electrode surface via the self-exchange electron-transfer mechanism,

NB⁻ + NB $\xrightleftharpoons{k_{et}}$ NB + NB⁻. Comparison of experimental and computer-simulated fluxes yields

$k_{et} \sim 8.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. Current densities of magnitude greater than 0.5 A/cm^2 can be attributed to the self-exchange electron-transfer reaction.

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ELECTRON CONDUCTION IN ORGANIC SOLUTIONS

by

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ELECTRON CONDUCTION IN ORGANIC SOLUTIONS

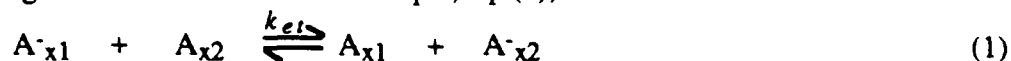
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ABSTRACT. A voltammetric study of electron conduction in nitrobenzene(NB)/toluene solutions is presented. Analysis of steady-state mass-transport limited currents corresponding to the first and second one-electron reductions of NB (to the radical anion, NB^- , and dianion, NB^{2-} , respectively) indicates that electrogeneration of NB^{2-} is suppressed to negligible values in concentrated NB solutions as a result of the increased flux of electrons away from the electrode surface via the self-exchange electron-transfer mechanism, $\text{NB}^- + \text{NB} \xrightleftharpoons{k_{\text{et}}} \text{NB} + \text{NB}^-$. Comparison of experimental and computer-simulated fluxes yields $k_{\text{et}} \sim 8.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. Current densities of magnitude greater than 0.5 A/cm^2 can be attributed to the self-exchange electron-transfer reaction.

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INTRODUCTION. Electrical conduction in nonmetallic liquids occurs by diffusion, migration, and convection of charged species. As early as 1966, it was proposed by Levich¹ that in addition to these mechanisms, self-exchange electron-transfer reactions involving a reversible electroactive couple, eq. (1),



can enhance the apparent transport of A and A⁻ in a potential gradient. Eq. (1) results in the apparent interchange of species A and A⁻ between physical positions x₁ and x₂. This type of charge transport has been the focus of numerous investigations during the past decade concerned with thin films containing fixed-site redox centers^{2,3}. In these systems, transport occurring by "electron-hopping" has been shown to be equivalent to diffusion-migration of the immobilized redox centers with an apparent diffusivity, D_{app}, described by

$$D_{app} = D_{phys} + D_{et} \quad (2)$$

In eq. (2), D_{phys} is the physical diffusivity of A and A⁻, while D_{et} contains the contribution from the self-exchange reaction. According to the theories of Dahms⁴ and Ruff⁵, D_{et} = k_{et}λ²(C_A + C_{A⁻})/6, where C_A and C_{A⁻} are the local concentrations of A and A⁻, respectively, and λ = |x₁ - x₂|.

In this preliminary report, we describe a new steady-state voltammetric method using microelectrodes that allows a direct evaluation of the contributions of electron-hopping to the flux of an electroactive species and the measurement of the self-exchange rate constant, k_{et}. Although there have been two reported attempts^{5a,b,e} to measure k_{et} in homogeneous monomeric solutions using the Dahms-Ruff model and eq (2), the results of these previous studies suggest that the contribution of electron-hopping to the measured flux is very small. Our present experimental and numerical results demonstrate that electron transfer between nitrobenzene (NB) and the nitrobenzene radical anion (NB⁻) can increase the apparent fluxes of these species by more than a factor of two in NB/toluene solutions.

EXPERIMENTAL. Pt microdisk (12.5 μm radius) electrodes were constructed as described in previous reports⁶. A single-compartment 5 ml electrochemical cell equipped with a Ag wire quasi-reference electrode and a Pt wire counter electrode was employed throughout these studies. Voltammograms were obtained using a Princeton Applied Research Corp. Model 173 Potentiostat and a Model 175 Universal Programmer. Solution viscosities were measured using a capillary viscometer (Gilmont Instruments, size No. 1). Digital simulations of the flux employed a finite-difference methodology with a 1-D spherical expanding space grid⁷ and were performed on an HP 375 CH work station. Nitrobenzene (A.C.S. grade, Aldrich) and toluene (spectroscopic grade, Fisher) were used as received. Tetra-n-butylammonium perchlorate (Kodak) was recrystallized twice from acetone/ether and dried under vacuum.

RESULTS AND DISCUSSION. Fig. 1 shows the steady-state voltammetric responses of a 12.5 μm radius Pt microdisk electrode in toluene solutions containing 3.9 - 8.7 M NB and 0.5 M tetra-n-butylammonium perchlorate (TBAP) as supporting electrolyte. The voltammogram recorded in the 8.7 M NB solution shows two reduction waves with half-wave potentials⁸, $E_{1/2}$, at ~ -1.3 and ~ -3.2 V vs the Ag quasi-reference electrode that correspond to the sequential one-electron reductions of NB to the radical anion, $\text{NB}^\cdot$ (eq. (3)) and dianion, NB^{2-} (eq. (4)).



Two qualitative features of the voltammograms deserve comment. First, as previously reported⁶, the magnitude of the limiting current of the first reduction wave, i_1 , decreases slightly as the concentration of NB is increased from 3.9 to 8.7 M (from 5.9 μA to 4.1 μA

in Fig. 1). Assuming that the transport-limited current reflects the diffusional flux of NB to the electrode, i_1 is given as⁹

$$i_1 = 4nFD C_{\text{redox}} r_0, \quad (5)$$

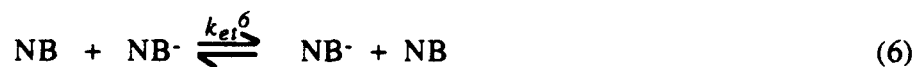
where n is the number of electrons transferred per molecule, F is Faraday's constant, r_0 is the electrode radius, and D and C_{redox} are the diffusivity and concentration, respectively, of the redox species in the bulk solution far from the electrode surface. From i_1 and eq. (5), the apparent diffusivity of NB decreases from $3.1 \times 10^{-6} \text{ cm}^2/\text{s}$ at 3.9 M to $0.98 \times 10^{-6} \text{ cm}^2/\text{s}$ at 8.7 M. The absolute viscosity, η , of the same solutions, measured with a capillary viscometer, monotonically increases from 2.4 to 4.6 cp over the same concentration range. Thus, assuming η is inversely proportional to D , the surprisingly weak dependence of i_{lim} on C_{redox} can be accounted for (within 50%) by the increase in bulk solution viscosity.

The second qualitative feature of the voltammograms in Fig. 1 that is of interest in the present report is that the limiting current of the second reduction wave, i_2 , decreases to a very small value ($i_2 \sim 0.05i_1$) as the concentration of NB is increased from 3.9 to 8.7 M. (Note: i_2 is measured with respect to the limiting current plateau of the first reduction wave.) While i_2 should also be affected by variations in solution viscosity, the relative magnitudes of the first and second waves, i_2/i_1 , should be independent of physical properties of the solution. Since i_2 is proportional to the rate at which NB^{-2} is electrogenerated, the voltammograms suggest that relative reaction flux of eq. (4) decreases with increasing NB concentrations.

The solution resistance of the NB/toluene (TBAP) solutions becomes prohibitively large as the concentration of NB is reduced below 3 M, preventing quantitative measurement of limiting currents in dilute NB solutions. However, for comparison to the voltammetric response obtained in concentrated NB solutions (Fig. 1), the reduction of NB

at a Pt microdisk in dry and O₂-free acetonitrile solutions containing ≤ 10 mM NB and excess TBAP (> 0.1 M) results in two voltammetric waves that are of equal height ($i_2/i_1 \sim 1$) and that are proportional to the bulk solution concentration and diffusivity of NB (eq. (5)). These results suggest that in dilute solutions, both eq(3) and eq(4) are diffusion controlled reactions, in agreement with Geske and Maki's polarographic study of NB¹⁰.

The decrease in i_2/i_1 with increasing [NB] can be quantitatively accounted for by considering the homogeneous electron-transfer reactions that can occur between the reactant NB, NB⁻, and NB⁻².



Eqs. (6) and (7) are electron-transfer self-exchange reactions ($K_{eq} = 1$) while eq. (8) is the comproportionation reaction between NB and NB⁻² yielding the radical anion, NB⁻ ($K_{eq} = \exp((F/RT)(E^0(\text{eq. (3)}) - E^0(\text{eq. (4)})) \sim 3 \times 10^{13}$ ¹¹). In dilute NB solutions, reactions (6) and (7) have a negligible effect on the observed voltammetric behavior, since both sides of these equations are identical, leaving the concentrations of NB, NB⁻, and NB⁻² unperturbed. However, as previously described¹², the comproportionation of NB and NB⁻² (eq. (6)) (in dilute or concentrated solutions) can reduce the magnitude of the second reduction wave, i_2 , by 58% when the concentration of supporting electrolyte is significantly less than that of NB (i.e., [NB]/[TBAP] $\gg 1$). This decrease in i_2 results from electrostatic repulsion (migration) of NB⁻ away from the negatively-charged depletion layer surrounding the electrode¹².

In solutions containing a high concentration of NB, the self-exchange reactions (eqs (6) and (7)) can modify the fluxes of the various redox active species if the electron-transfer rate constants, k_{et}^6 and k_{et}^7 are sufficiently large. According to eq (2), as the concentration

of NB increases, the effect of the electron hopping reactions is to increase the apparent diffusivities of all species involved. At first glance, this suggests that electron hopping would have the effect of increasing the observed currents for both the first and second one-electron reductions of NB. This conclusion is incorrect. An increase in the flux of NB to the electrode surface as a result of the self-exchange electron-transfer reaction, eq. (6), is necessarily accompanied by an increase (of equal magnitude) in the flux of NB⁻ away from the electrode. Similar to the combined effects of the comproportionation reaction and migration¹², the increase in the flux of electrogenerated NB⁻ away from the surface will reduce the magnitude of the second reduction wave.

To quantitatively access the effects of electron-hopping on i_1 and i_2 , we numerically calculated the steady-state fluxes and concentration profiles of NB, NB⁻, NB⁻², and supporting electrolyte ions, incorporating the combined effects of the comproportionation and electron hopping reactions¹³. The flux of each species was assumed to be a combination of the physical flux, governed by the Nernst-Planck equation

$$J_i = -D_i \frac{dC_i}{dr} - \frac{z_i F}{RT} C_i D_i \frac{d\phi}{dr} \quad (9)$$

where D_i is taken to be equivalent to D_{phys} in eq. (2), and the electron flux^{3c}

$$J_{\text{et}} = -nD_{\text{et}} \left[\frac{dC_i}{dr} + \frac{nF}{RT} C_i \left(1 - \frac{C_i}{C_E} \right) \frac{d\phi}{dr} \right] \quad (10)$$

where C_E is the sum of the local concentrations of the individual redox species that participate in a given electron-transfer reaction. For example, $C_E = C_{\text{NB}} + C_{\text{NB}^-}$ for reaction (6). (It should be noted that there are two J_{et} terms for the NB⁻ species, corresponding to the two electron-transfer reactions with the neutral and dianion species, eqs. (6) and (7), respectively.) For NB and NB⁻², the appropriate D_{et} terms are

$k_{et}^6 \lambda^2 (C_{NB} + C_{NB^-})/6$ and $k_{et}^7 \lambda^2 (C_{NB^-} + C_{NB^{2-}})/6$, respectively. For NB^- , the D_{et} terms are $k_{et}^6 \lambda^2 (C_{NB} + C_{NB^-})/6$ and $k_{et}^7 \lambda^2 (C_{NB^-} + C_{NB^{2-}})/6$, since NB^- is included in both reactions (6) and (7). In principle, the comproportionation of NB and NB^{2-} may also contribute to the various D_{et} 's; however, as previously shown¹², if k_{et}^8 is moderately large ($> 10^7 \text{ M}^{-1}\text{s}^{-1}$), then NB and NB^{2-} do not coexist in solution at any location. Thus, the contribution of reaction (8) to the flux must be negligibly small and is not included in solving eq. (10). We assume that the reactants must be in direct contact for electron-transfer to occur. Approximating NB , NB^- , and NB^{2-} as spherical reactants of equal radii, λ is equal to twice the radius of NB , r_{NB} , which can be obtained from $r_{NB} = (3MW/4\pi\rho N_A)^{1/3}$, where N_A = Avogadro's number, MW is the molecular weight of NB , and ρ is the density of pure NB . Using $\rho = 1.2037 \text{ g/cm}^3$ ¹⁴ yields $\lambda = 6.8 \text{ \AA}$.

Fig. 2 shows the simulated ratio i_2/i_1 as a function of the C_{redox} and the parameter $k_{et}^6 \lambda^2 / 6D_{phys}$. Other parameters used in the calculation are: $r_0 = 12.5 \text{ }\mu\text{m}$; $[TBAP] = 0.5 \text{ M}$; $k_{et}^7 = k_{et}^6$; $k_{et}^8 = 10^8 \text{ M}^{-1}\text{s}^{-1}$; and $D_{TBA^+} = D_{ClO_4^-} = 10^{-6} \text{ cm}^2/\text{s}$. Fig. 2 shows that as the concentration of NB increases from 0.01 to 10 M, the ratio i_2/i_1 decreases markedly from the classical value of 1.0. By adjusting the parameters used in the simulations, it is readily shown that the magnitude of i_2/i_1 is essentially independent of the comproportionation rate constant when $k_{et}^8 > 10^7 \text{ M}^{-1}\text{s}^{-1}$. The simulated results, however, have a strong dependence on $[TBAP]$ and the electrode radius, r_0 , due to the effects of these parameters on the diffusional and migrational fluxes¹².

Fig 3 shows simulated steady-state concentration profiles of NB , NB^- , and NB^{2-} corresponding to the first and second reductions of NB as a function of $k_{et}^6 \lambda^2 C_{NB} / 6D_{phys}$ for $C_{NB} = 4.9 \text{ M}$. The effect of electron-hopping on the distribution of electroactive species is clearly evident in these curves; as the self-exchange rate k_{et}^6 increases, the concentration profile of NB near the electrode surface becomes steeper (resulting in an increase in i_1) while the concentration of NB^- everywhere within the depletion layer decreases (resulting in a decrease in i_2). Both effects are anticipated based on the

qualitative arguments presented above. Note the profiles of NB and NB⁻² do not significantly overlap at potentials corresponding to the second reduction wave (Fig 3B), justifying the assumption that the comproportionation reaction (eq. (8)) does not contribute to the electron-hopping transport mechanism.

Fig. 4 compares simulated and experimental values of i_2/i_1 for NB reduction. Since D_{phys} cannot be measured directly, values of D_{phys} used in the simulation of i_2/i_1 at different NB concentrations are estimated from the Stokes-Einstein equation for self-diffusion using measured values of η .

$$D_{\text{phys}} = kT/4\pi\eta r_{\text{NB}} \quad (11)$$

For example, from eq. (11), $D_{\text{phys}} = 4.1 \times 10^{-6}$ and 2.1×10^{-6} cm²/s for NB concentrations of 3.9 and 8.7 M, respectively (within a factor of 2 of D_{app} from limiting current measurements). Other parameters used in the simulation are listed in the figure caption. The rate constants k_{et}^6 and k_{et}^7 were varied to obtain the best agreement between the experimental and simulated data. The agreement between these values (Fig. 4) is very good considering the approximations made in evaluating the physical parameters of the system. We speculate that the largest source of error in the calculations results from treating D_{phys} as a true constant within the depletion layer. Previous experimental studies have provided evidence that the bulk and depletion layer values of D_{phys} in concentrated redox solutions may vary significantly (by a factor of 5)¹⁵. Using $\lambda = 6.8$ Å, the simulated curve in Fig. 4 corresponds to $k_{\text{et}}^6 = 8.4 \times 10^8$ M⁻¹s⁻¹, slightly smaller than the diffusional-controlled value predicted from the Smoluchowski equation¹⁶ ($k_{\text{diff}} = 8\pi N_A \lambda D_{\text{phys}} \sim 1 \times 10^9$ M⁻¹s⁻¹) and an order of magnitude larger than a previous value obtained in dilute acetonitrile solutions from electron-spin resonance studies, 3×10^7 M⁻¹s⁻¹¹⁷. At a NB concentration of 5.8 M, the simulated value of i_1 is 2.3 x larger than the predicted current when k_{et}^6 is set to zero. Under these solution conditions, greater than 1/2 of the total apparent flux of NB can therefore be attributed to electron-hopping between NB and NB⁻. Based on the observed limiting current (~5 µA, Fig. 1) and electrode area (4.9 x

10^{-6} cm^2), the electron flux at the electrode surface is 1 A/cm^2 , more than $1/2$ of which results from the self-exchange reaction, eq. (6).

CONCLUSION. The experimental results presented here provide strong evidence for electron conduction in a monomeric fluid solution resulting from a self-exchange electron-transfer reaction. Although the numerical results are highly specific to the Pt microelectrode/NB system, it is clear that the approach presented here for measuring electron-transfer rate constants may be extended to other electrode geometries and chemical systems using standard numerical methods.

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 13. A hemispherical electrode is assumed in the numerical calculations. Previous studies (ref. 12) show that this approximation of the microdisk electrode yields very accurate values of i_2/i_1 for reactions coupled to a homogenous reaction.
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FIGURE CAPTIONS.

Figure 1. Voltammetric response of a 12.5 μm radius Pt microdisk electrode in NB/toluene solutions containing 0.5 M TBAP and between 3.9 and 8.7 M NB.

Figure 2. Simulated values of the ratio of the limiting currents corresponding to the second (i_2) and first (i_1) one-electron reductions of an electroactive species as a function of its concentration, C_{redox} , and the electron-transfer parameter, $k_{\text{et}}^6 \lambda^2 / 6D_{\text{phys}}$. An electrolyte (1:1) concentration of 0.5 M is assumed in these calculations.

Figure 3. Simulated steady-state concentration profiles of NB, NB^- , and NB^{2-} surrounding a hemispherical microelectrode of radius r_0 at electrode potentials corresponding to the limiting current plateaus of the (A) 1st and (B) 2nd one-electron reductions of NB. The concentration of each species is normalized to the bulk solution concentration of NB used in the simulation (4.9 M). The top panels in (A) and (B) represent the profiles in the absence of electron-hopping (i.e., $k_{\text{et}}^6 = k_{\text{et}}^7 = 0$). In the top panels $k_{\text{et}}^6 = 10k_{\text{et}}^7$. The short vertical lines indicate the distance from the electrode surface where the concentration of the NB is equal to 1/2 of the bulk concentration. The bulk concentration of supporting electrolyte (1:1) assumed in the simulation is 0.5 M.

Figure 4. Experimental and simulated ratio of the limiting currents corresponding to the second (i_2) and first (i_1) one-electron reductions of NB as a function of NB concentration, C_{NB} . The parameters used in the simulation are: $k_{\text{et}}^6 = 8.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, $k_{\text{et}}^7 = 8.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, $\lambda = 6.8 \text{ \AA}$, $r_0 = 12.5 \mu\text{m}$, and $[\text{TBAP}] = 0.5 \text{ M}$. Values of D_{phys} employed in the simulations are corrected for variations in the bulk solution viscosity (see text).

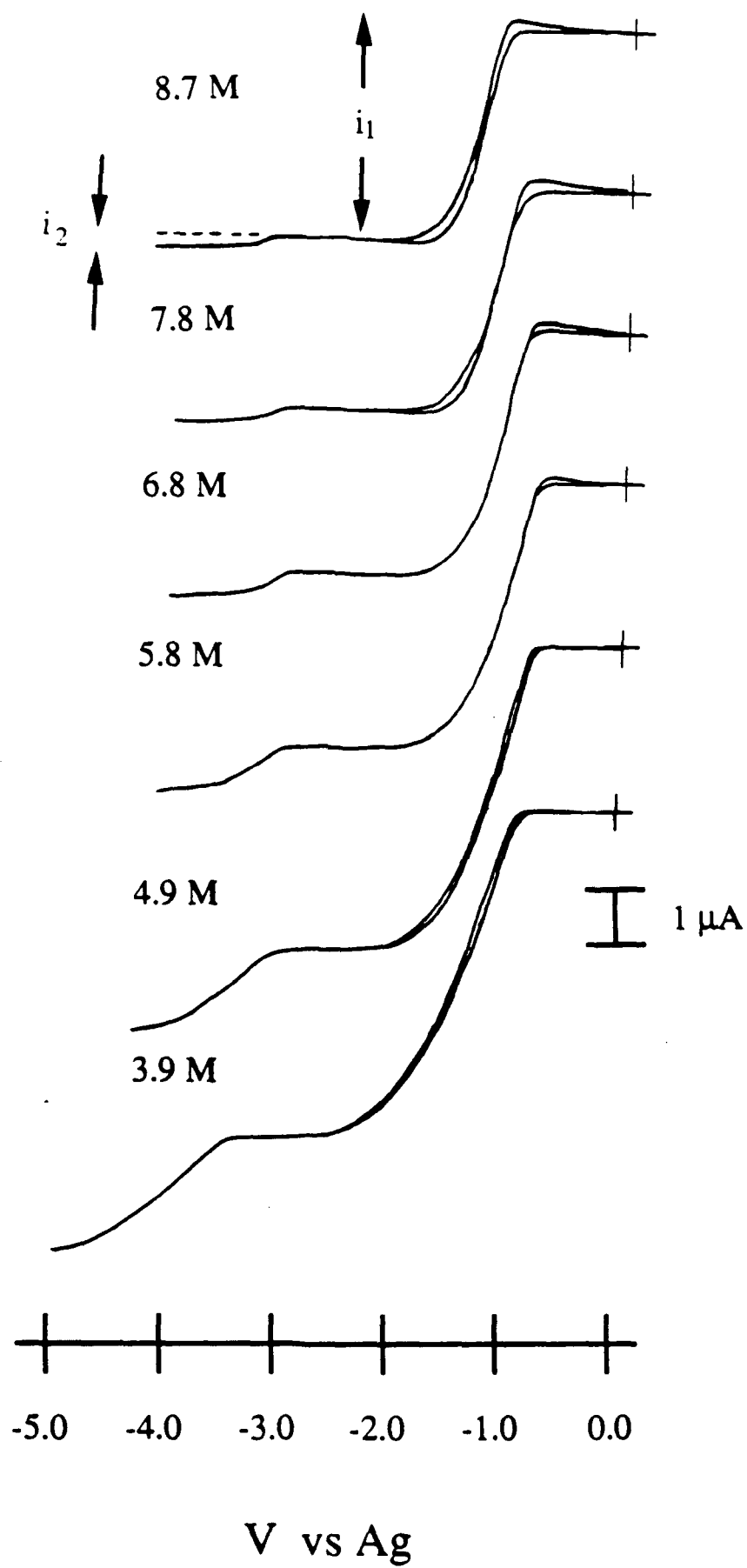


Fig 1

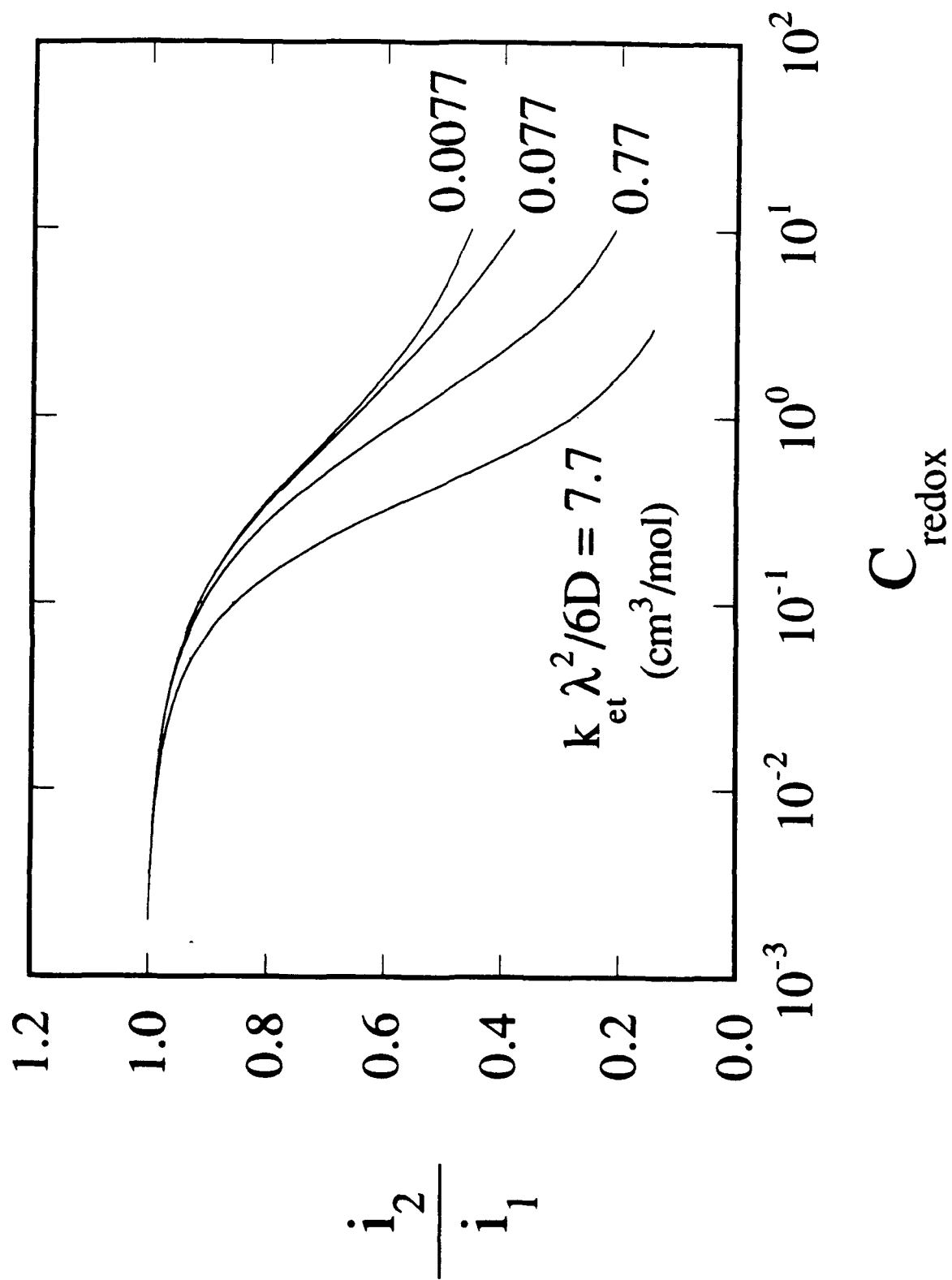
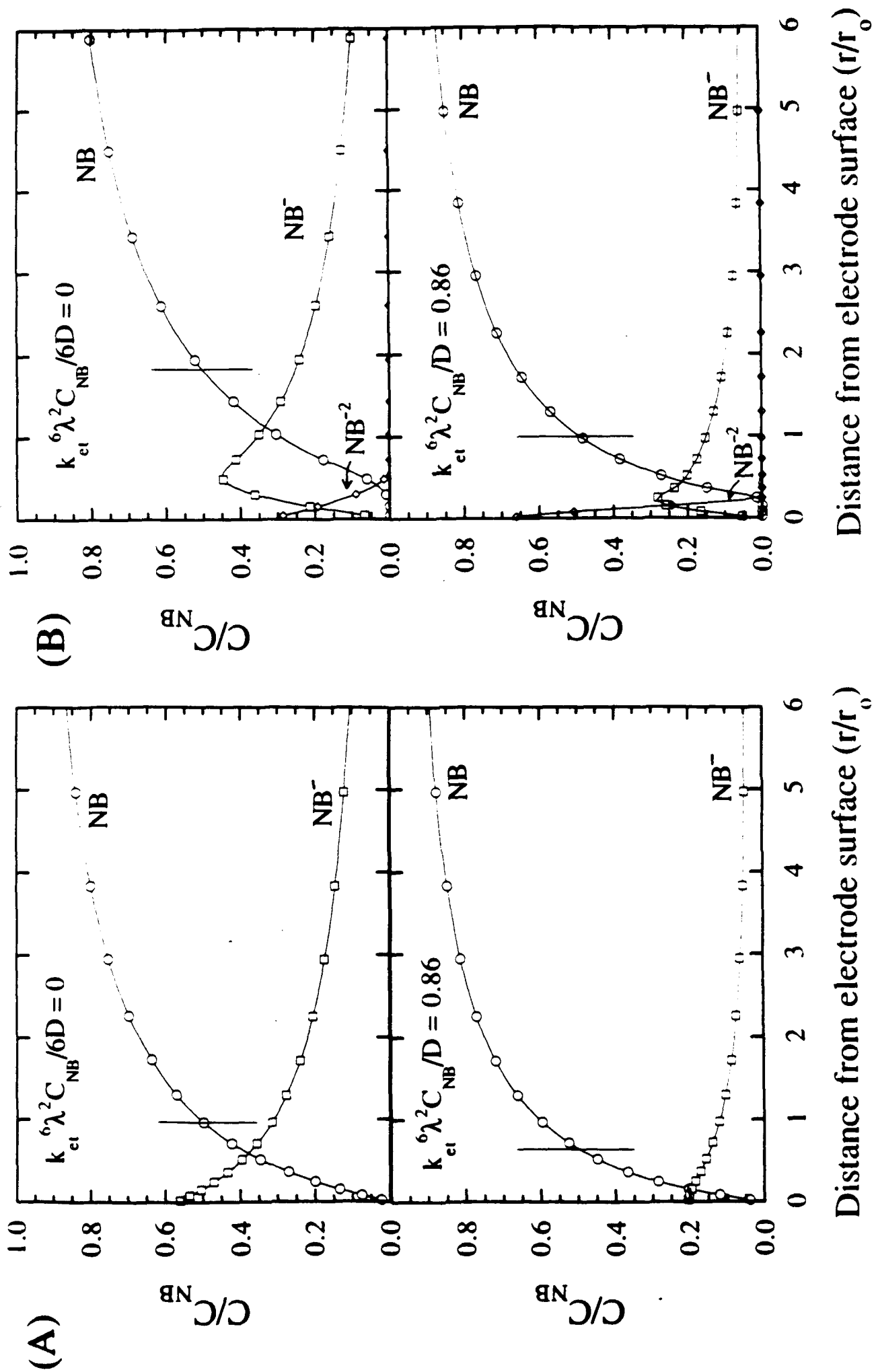


Fig 2



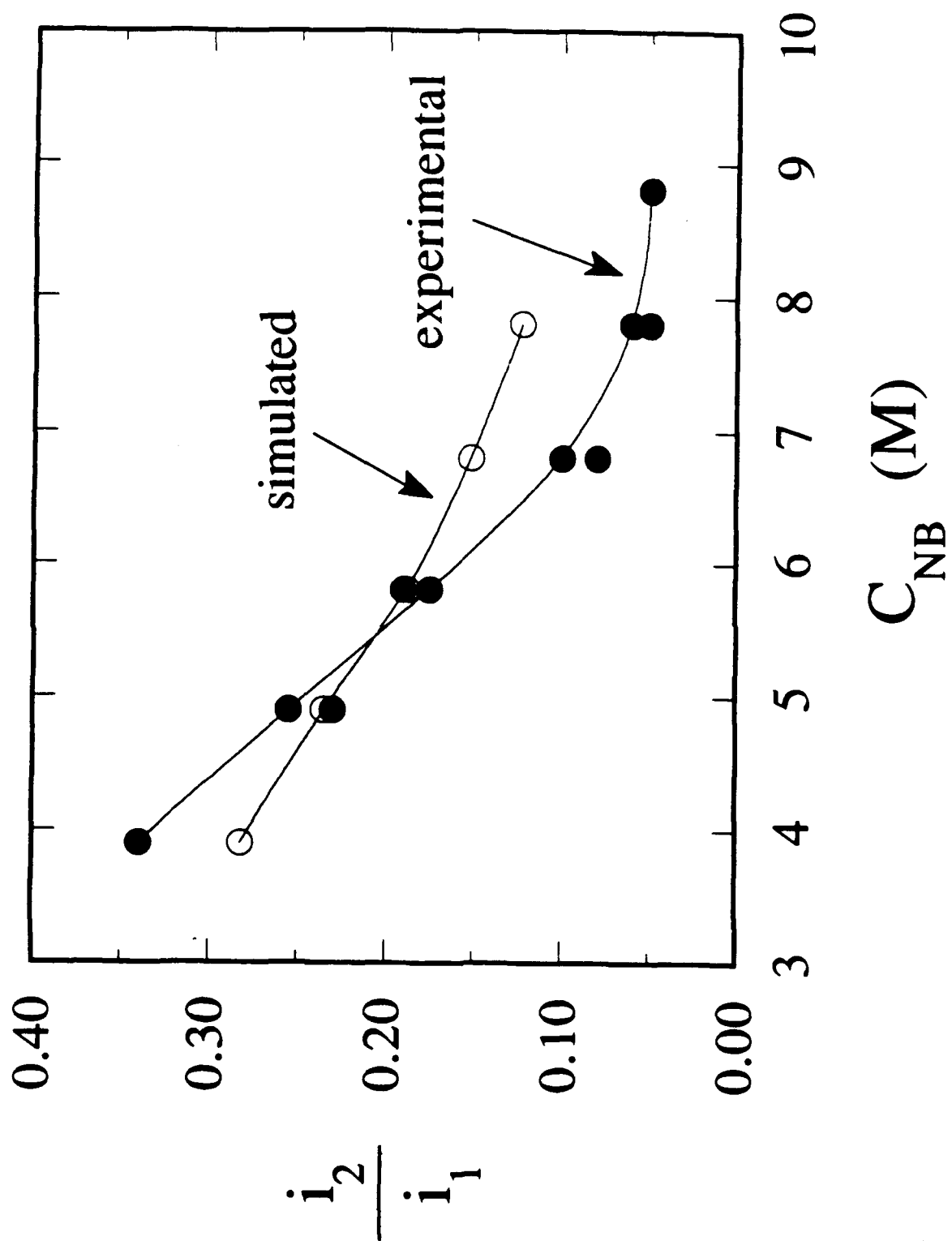


Fig 4