

ELECTROCHEMISTRY IN CONCENTRATED ORGANIC REDOX SOLUTIONS.
UNUSUAL REACTION MECHANISMS AND TRANSPORT PHENOMENA.

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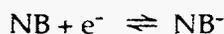
Fundamental studies of organic redox mechanisms are generally performed in solutions containing millimolar levels of a redox species and an excess quantity of a supporting electrolyte. Recently, we began exploring new methods using ultramicroelectrodes (i.e., electrodes having one or more dimension(s) less than ca. 10 μm) to study electron-transfer reactions in solutions in which the redox species is present in molar quantities [1-12]. The key advantage of using an ultramicroelectrode (UME) in concentrated solutions is that the ohmic potential drop can often be reduced to negligible values. In many instances, it is possible to study organic redox reactions in the *absence of a solvent*. Electrochemical measurements using macroscopic electrodes under such extreme solutions conditions are generally prohibited due to the ohmic potential loss in solution.

There are several reasons for studying electron-transfer reactions in highly concentrated solutions. First, the vast difference in the redox concentrations employed in fundamental studies (0.1 to 10 mM) and technological applications (0.1 to 1 M) presents difficulties for electrochemists and electrochemical engineers in the scale-up of redox processes. For example, in situations where the primary electron-transfer step is coupled to one or more homogeneous chemical reactions, the predominant reaction pathway may be extremely sensitive to the concentration of the reactant. This is frequently the case if the electrochemical mechanism involves multi-step homogenous reactions of varying reaction order. Transport rates may also vary significantly as a function of redox concentration, a consequence of the dependence of diffusional and migration processes on solution composition. Thus, it is plausible, and even likely, that the proposed scale-up of an electrochemical synthesis, based on fundamental investigations performed using dilute redox solutions, will not proceed without complication. Second, there are fundamental issues uniquely associated with concentrated redox solutions that are yet to be explored. For example, very little is known about the structure of the electrical double layer and interfacial chemical equilibria in the absence of an inert solvent. "Solvation" clearly has a different meaning under these conditions. In addition, homogeneous self-exchange electron-transfer reactions can result in a significant enhancement of the molecular fluxes of reactants and products in highly concentrated redox solutions [3].

In this report, we discuss and give several examples of voltammetric studies in concentrated organic solutions and demonstrate that quantitative measurements can be performed under these unusual solution conditions. A brief description of experimental methods and theory of UME techniques is presented in Section I. The remainder of the article presents examples of transport phenomena (Section II), coupled homogeneous reactions (Section III), and magnetic field effects (Section IV) in highly concentrated organic redox solutions.

I. Principles and Methods.

Fig. 1 shows the voltammetric response of a 12.5 μm -radius Pt disk UME in a solution comprising nitrobenzene (NB) and 10 mM tetrabutylammonium hexafluorophosphate ($\text{TBA}^+\text{PF}_6^-$) as the supporting electrolyte. NB is the redox-active species and is present in solution at a concentration of 9.7 M. No "inert" solvent is present in this solution. The sigmoidal-shaped voltammogram corresponds to the 1-e^- reduction of NB, eq. (1).



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The voltammogram is characterized by a well-defined half-wave potential, $E_{1/2}$ and a transport-limited current, i_{lim} . The steady-state limiting current, i_{lim} , at the microdisk UME is given by

$$i_{lim} = 4nFD C_{redox} a \quad (2)$$

where D and C_{redox} are the diffusion coefficient and bulk concentration of the redox species, respectively, and a is the electrode radius. Eq. (2) describes the current resulting from diffusional transport of the redox species, such as in the case for NB reduction (Fig. 1); a more complex set of equations derived by Amatore et al. [13] is used to predict the current for charged reactants when an excess quantity of supporting electrolyte is not present. However, eq. (2) applies to the reduction or oxidation of neutral reactants, regardless of the concentration of supporting electrolyte.

If the same voltammetric experiment is attempted using a macroscopic electrode, e.g., a 1 mm-radius disk, the i - V response is essentially perfectly linear, reflecting the fact that nearly all of the applied potential is lost as ohmic potential drop in the cell (iR_s) that results from the passage of current through an effective solution resistance R_s . The purely ohmic response of the macroscopic electrode masks all useful information concerning the electrode reaction.

What property of the UME allows a well-defined voltammogram to be obtained in the absence of a solvent and under conditions where the redox species is present in large excess of the supporting electrolyte? A natural tendency is to assume that since the current at a UME is much smaller than at the macroscopic electrode, the iR_s drop must also be correspondingly smaller. However, the effective solution resistance R_s is governed by the electrode geometry; for a disk-shaped electrode R_s is given by eq. (3),

$$R_s = (4\kappa a)^{-1} \quad (3)$$

where κ is the conductivity of the solution. Thus, R_s is inversely proportional to the electrode radius. Since the current at a disk is proportional to a (eq. (2)), the quantity iR_s is independent of the electrode size. Thus, by itself, the reduction in current (due to the small size of the electrode) does not result in a decrease in the ohmic potential drop.

An explanation of the behavior of the UME was first described by Oldham [14]. The key aspect of the analysis is that the charge generated by the redox reaction is balanced by a redistribution of the supporting electrolyte ions. Thus, for the reduction of NB shown in Fig. 1, the electrolyte cations (TBA⁺) migrate toward the electrode surface, while the anions (PF₆⁻) migrate toward the bulk solution. The reduction of 9.7 M NB generates molar quantities of NB in the solution adjacent to the electrode; this charge is balanced by an approximately equal amount of TBA⁺. A consequence of this effect is that the resistance of the depletion layer is lowered by several orders of magnitude relative to the value computed based on the bulk solution conductivity, eq. (2). Thus the iR_s loss may be quite small at the UME.

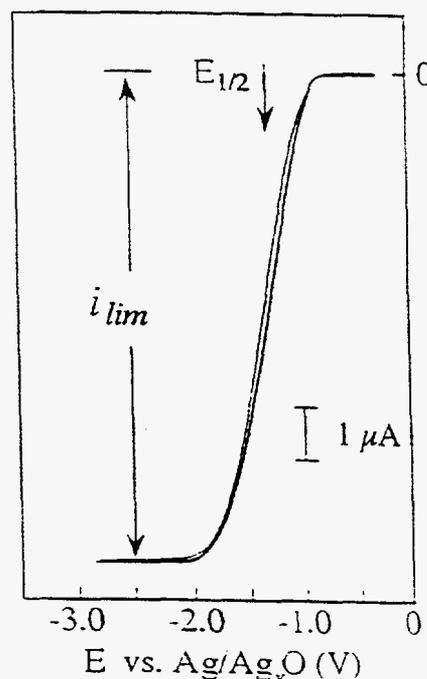


Fig. 1. Voltammetric response of a 12.5 μ m-radius Pt microdisk in a NB/10 mM TBAPF₆ solution (i.e., in the absence of a solvent). The voltammetric curve corresponds to the diffusion-limited, 1-e⁻ reduction of NB. Scan rate = 2 mV/s.

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From Oldham's analysis of the iR_s drop at a hemispherical electrode, a simple approximate expression, eq. (4), is obtained for $E_{1/2}$. Assuming for the sake of simplicity that the diffusivities of the solution species are approximately equal, Oldham's result for $E_{1/2}$ can be expressed in terms of the standard redox potential, E° , and the concentrations of the redox-active species (C_{redox}) and the supporting electrolyte (C_{SE}).

$$E_{1/2} = E^{\circ} - (RT/nF)\ln\{1 + (C_{redox}/8C_{SE})\} \quad (4)$$

Eq. (4) indicates that $E_{1/2}$ should shift by ca. 59 mV per decade increase in C_{redox}/C_{SE} , independent of the absolute concentration of the redox species. This prediction has been experimentally verified [15]. For the reduction of NB shown in Fig. 1, the ratio C_{redox}/C_{SE} is equal to ~970. Thus, from eq. (4), the measured $E_{1/2}$ value is ca. 125 mV more negative than E° . Such small shifts are easily corrected for allowing E° values to be obtained for redox reactions when no solvent is present in the solution.

The UME's employed in the following studies were constructed by sealing either a 12.5 μm -radius Pt wire or a 6.4 μm -radius Au wire in a soft glass tube and sanding one end flat to expose the metal microdisk. The electrodes were polished with successively finer Al_2O_3 grit (to ~0.01 μm), sonicated for ~2 min. in H_2O to remove polishing debris, and rinsed in methanol. A relatively high yield (~80%) of useful disk-shaped UME's are obtained by this procedure.

II. Binary Diffusivity In Concentrated Redox Systems. [11]

The relationship between the diffusion-limited current (i_{lim}) and redox concentration (C_{redox}) may be more complex than suggested by eq. (2) due to the dependence of the redox species diffusivity on the solution composition. For instance, Fig. 2 shows a plot of i_{lim} for the reduction of NB, as a function of the mole fraction of NB, x_{NB} , in mixed acetonitrile/NB solutions. NB is completely miscible with acetonitrile, allowing voltammetric measurements to be made over the entire range of possible solution compositions ($0 < x_{NB} \leq 1$). The data show that i_{lim} obtains a maximum value at $x_{NB} \sim 0.2$ (corresponding to $[\text{NB}] \sim 3\text{M}$), and decreases as the concentration of the redox species is increased. This nonlinear relationship reflects a strong dependency of D on x_{NB} . Similar behavior is observed for the reduction of other organic redox species, e.g., 4-cyanopyridine[2] and acetophenone[6].

For an electrochemical system comprising a single redox species (species i) and the solvent (species j), diffusional transport is governed by the binary mutual diffusion coefficient, D_{ij} , that is a function of the solution composition. An expression for D_{ij} that appears suitable for the analysis of transport data obtained in concentrated organic redox solutions was derived by Cullinan [16]

$$D_{ij} = (D_{ij}^{\circ})^{x_j} (D_{ji}^{\circ})^{x_i} \left(1 + \frac{d \ln \gamma_i}{d \ln x_i} \right) \quad (5)$$

where D_{ij}° is the binary diffusivity for a dilute solution of i in j , D_{ji}° is the binary diffusivity for a dilute solution of j in i , γ_i is the activity coefficient of species i , and x_i and x_j are the mole fractions of i and j , respectively. The quantity $(1 + d \ln \gamma_i / d \ln x_i)$ is a thermodynamic factor that corrects for activity effects in non-ideal solutions. For ideal solutions, $(1 + d \ln \gamma_i / d \ln x_i) = 1$ and the binary diffusion coefficient can be predicted for any solution composition from measurement of the diffusivities D_{ij}° and D_{ji}° at the solution extremes. In general, the solution activity term can not be ignored in binary organic solutions if the solution components have significantly different chemical structures.

The thermodynamic factor $(1 + d \ln \gamma_i / d \ln x_i)$ has been evaluated for the NB/acetonitrile system over the entire composition range ($0 < x_{NB} \leq 1$) using isothermal liquid/vapor equilibrium data obtained in our laboratory. The dilute solution diffusivities, D_{ij}° and D_{ji}° , are computed using eq. (2) from voltammetric measurement of i_{lim} at the solution extremes ($x_{NB} \rightarrow 0$ and $x_{NB} = 1$, respectively). Combined, these data allow computation of the binary mutual diffusivity, D_{ij} (eq. (5)), as a function of

x_{NB} for the NB/acetonitrile system. Values of D_{ij} determined by this procedure are then substituted into eq. (2) to compute i_{lim} for any arbitrary solution composition.

The results of the above analysis are shown in Fig. 2. For comparison, values of i_{lim} computed assuming ideal solution behavior, i.e., $(1 + d \ln \gamma_i / d \ln x_i) = 1$, are also shown in order to demonstrate the importance of the solution activity effect. It is apparent from these results that the Cullinan equation qualitatively captures the dependence of D_{ij} , and, thus, i_{lim} , on solution composition. Agreement is particularly good in highly concentrated NB solutions ($x_{\text{NB}} \geq 0.4$). At intermediate compositions ($0.05 < x_{\text{NB}} \leq 0.4$), the Cullinan equation tends to predict values of i_{lim} that are slightly smaller than the experimental values. A survey of similar studies reported in the literature suggests that this latter behavior reflects self-association of one or both of the solution constituents. When association does occur, the factor $(1 + d \ln \gamma_i / d \ln x_i)$ has a more complex form which takes into account the diffusion of molecular clusters [17]. However, the experimental and theoretical values of i_{lim} are within a factor of two for all values of x_{NB} .

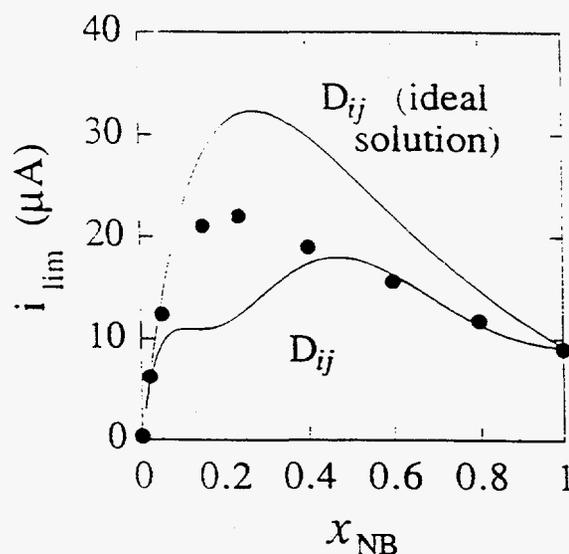
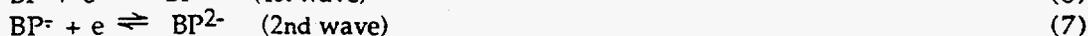
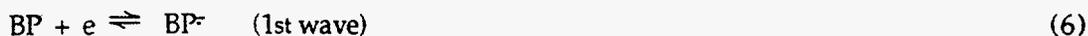


Fig. 2. Plot of i_{lim} versus mole fraction NB. Experimental data are indicated by dark circles. Theoretical curves are computed from eqs. (2) and (5) with and without the use of the activity correction term in eq. (5).

III. Coupled Homogeneous Reactions. [12]

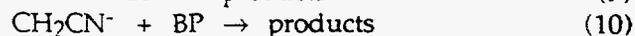
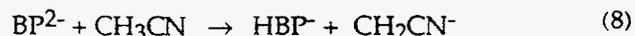
Investigations of complex electrochemical mechanisms that involve homogeneous chemical reactions coupled to the primary electron-transfer step are also possible in highly concentrated solutions. For instance, the hydrodimerization of adiponitrile has been quantitatively studied by Montenegro and Pletcher¹⁸ using 10 μm -radius Hg-coated Au microdisks in aqueous solutions containing up to 1.5 M adiponitrile. As noted in the previous sections, quantitative measurements in such highly concentrated redox solutions using macroscopic electrodes are not feasible due to the large ohmic potential loss. UME's thus appear to provide a unique opportunity to study organic electrochemical reactions under conditions that closely mimic those employed in industry.

We have recently investigated the electrochemical reduction of benzophenone (BP) as a function of the redox-species concentration ($0.001 < [\text{BP}] < 4 \text{ M}$) using Au (6.4 μm -radius) and Pt (12.5 μm) microdisk electrodes. Steady-state voltammetry in acetonitrile (CH_3CN) or tetrahydrofuran (THF) solutions containing BP results in the 2-wave response shown in Fig. 3. The waves correspond to the sequential one-electron reductions of BP yielding the stable ketyl anion (BP^\cdot) and the less stable ketyl dianion (BP^{2-}).



An interesting feature of the voltammetric response is that the limiting current for the 2nd reduction wave decreases relative to that of the 1st wave as the concentration of BP is increased. In $\text{CH}_3\text{CN}/\text{TBAPF}_6$ solutions containing greater than 0.2 M BP, the height of the 2nd wave is smaller than that of the 1st wave, resulting in an *inverted* voltammetric wave (Fig. 3). A more conventional voltammetric behavior (i.e., the 2nd wave does not invert) is observed in the THF/ TBAPF_6 solutions.

However, wave inversion is also observed in THF solutions when CH_3CN is added to the solution. A mechanism for the observed behavior has been proposed which involves proton abstraction from CH_3CN by BP^{2-} to form HBP^- and CH_2CN^- , followed by nucleophilic attack of these anions on the parent species, BP, eqs. (8)-(10).



Combining eqs. (6)-(10) yields a net reaction for the 2nd reduction of BP that involves three molecules of BP and two electrons. Thus, 0.67 electrons are transferred per molecule of BP for the 2nd reduction, i.e., $n = 0.67$. This value is smaller than the expected value of $n = 2$ in the absence of coupled chemical reactions. Furthermore, because $n = 1$ for the 1st wave, the conclusion that $n = 0.67$ for the 2nd wave immediately provides an explanation for the apparent *inversion* of voltammetric wave. Numerical simulations of the voltammetric curves based on the above reaction sequence are in reasonable agreement with experimental observations and will be presented in detail elsewhere.

IV. Magnetic Field Effects. [5,6,9,10]

We have observed that diffusion-limited currents at UME's may be significantly enhanced or diminished in concentrated redox solutions by applying an external magnetic field across the cell, Fig. 4. The diffusion of electrogenerated ions through the magnetic field results in a magnetic force, F_{mag} , that alters the net direction of ion drift near the electrode surface. For a large collection of diffusing ions in solution, the magnetic force generated per unit volume of solution (Newtons/m^3) is given by

$$F_{\text{mag}} = J \times B \quad (11)$$

where J is the flux of ions through a microscopic volume element ($\text{coul/m}^2\text{s}$), and B (Tesla, T) is the externally applied magnetic field. If F_{mag} is sufficiently large, the acceleration of ions by the magnetic field may result in convective solution flow, a consequence of momentum transfer between the ions directly accelerated by the field and the solvent molecules and other (non-diffusing) ions comprising the solution.

In order to study the dependence of F_{mag} on the orientation of the magnetic field, microdisk

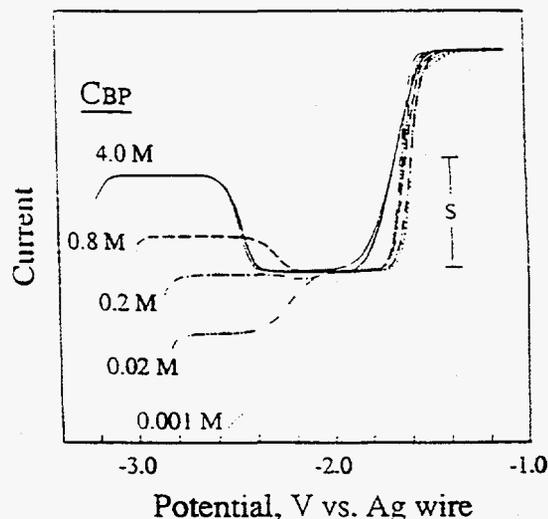


Fig. 3. Voltammetric response of a $6.4 \mu\text{m}$ -radius Au microdisk in CH_3CN solutions containing BP and 0.2 M TBAPF_6 . The concentrations of BP are indicated on the figure. The current scale S for the voltammetric curves are: 0.001 M ($S = 1.175 \text{ nA}$); 0.02 M ($S = 56 \text{ nA}$); 0.2 M ($S = 45 \text{ mA}$); 0.8 M ($S = 1.2 \text{ mA}$); 4.0 M ($S = 0.59 \text{ mA}$).

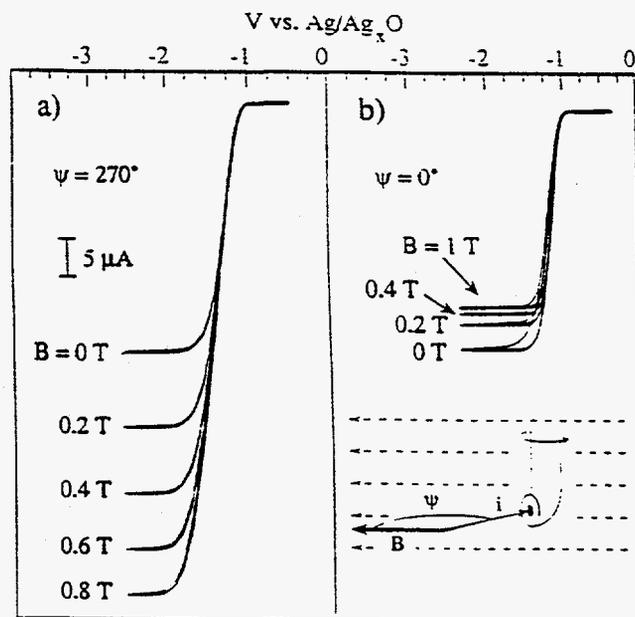


Fig. 4. Voltammetric response of a $12.5 \mu\text{m}$ -radius Pt microdisk electrode for NB reduction as a function of applied magnetic field strength and orientation. The CH_3CN solution contained 2 M NB and 0.2 M TBAPF_6 . a) $\psi = 270^\circ$ (electrode surface parallel to the magnetic field). b) $\psi = 0^\circ$ (electrode surface perpendicular to the magnetic field).

electrodes were constructed with a 90° bend in the glass tubing, such that rotation of the electrode results in a change in the angle Ψ between the field, \mathbf{B} , and the net current, i . Fig. 4 shows the dependence of i_{lim} for NB reduction on the angle Ψ for varying magnetic field strengths (0 to 1 T). The application of a uniform magnetic field parallel to the electrode surface ($\Psi = 90$ or 270°) results in an enhancement of the mass-transport limited voltammetric current, i_{lim} . Conversely, a small decrease in the current is observed when the field is oriented perpendicular to the electrode surface ($\Psi = 0$ or 180°). Other orientations of the field result in values of i_{lim} that are intermediate between these two limiting cases.

The magnetic field effect presented in Fig. 4 is qualitatively similar to that observed using other redox systems, e.g., reduction of acetophenone. For the steady-state reduction of NB, the enhancement and diminishment of the voltammetric current apparently results from the magnetic force, F_{mag} , that is exerted directly on the electrogenerated product, NB^- , as it diffuses/migrates away from the electrode. Because the reactant (NB) and the solvent (CH_3CN) are neutral, and since, the fluxes of the two electrolyte ions (PF_6^- and TBA^+) must be zero at steady-state, NB^- is the only charged species with a finite flux which can interact directly with the magnetic field (eq. (11)).

We believe that new electroanalytical techniques for investigating organic reactions can be developed by the coupling of UME's with magnetic fields. For instance, an electrogenerated species has a radially divergent flux away from a disk-shaped UME; thus if a magnetic field is applied orthogonal to the surface, the resulting magnetic force will result in the ions moving along a spiral-shaped pathway as they diffuse away from the surface. This cyclotron-like motion has the effect of increasing the residence time of the electrochemically-generated product at the electrode surface. By altering the electrode geometry, or by using several closely spaced UME's, it may be possible to "trap" electrogenerated species for short periods of time, during which they can be probed by spectroscopic methods. Such capabilities might allow new ways of studying reaction kinetics of organic redox systems.

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