Measurement of Local Reactivity at Liquid/Solid, Liquid/Liquid, and Liquid/Gas Interfaces with the Scanning Electrochemical Microscope: Principles, Theory, and Applications of the Double Potential Step Chronoamperometric Mode

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A numerical model for scanning electrochemical microscopy (SECM) double potential step chronoamperometry (DPSC) has been developed and examined experimentally. The concept of this new mode of SECM is to generate a reactant in an initial potential step at a tip ultramicroelectrode (UME) positioned close to a target interface. The electrogenerated species diffuses from the tip to the interface, where it may be involved in a chemical process. The reactant is subsequently collected by electrolysis in a second potential step, and the form of the corresponding current-time curve provides information on the nature of the interaction between the initial tip-generated species and the interface. If the species is consumed in an irreversible interfacial process, the current flow during the second potential step is less than when the interface is inert with respect to the species of interest. The theoretical predictions are first examined with DPSC studies on the electrogeneration and collection of ferricyanide ions from aqueous ferrocyanide solutions, at a tip positioned close to aqueous/glass, aqueous/1,2-dichloroethane (DCE), and aqueous/air interfaces, as model examples of inert liquid/solid, liquid/liquid, and liquid/gas interfaces. The case of an active interfacial process is illustrated through studies of the electrogeneration and collection of Br₂, from aqueous sulfuric acid solutions of potassium bromide, at a tip positioned close to aqueous/DCE and aqueous/air interfaces. The transfer of Br₂ across these interfaces is found to be irreversible and effectively diffusion-controlled on the SECM time scale, putting a lower limit on the interfacial transfer rate constant of 0.5 cm s^{-1} . The experiments carried out at aqueous/ air interfaces represent the first demonstration that SECM can be used to probe liquid/gas interfaces, thereby further diversifying the range of novel environments that can be studied with this instrument.

Introduction

Scanning electrochemical microscopy (SECM) is continuing to develop as a powerful device for probing a wide range of interfacial processes with high spatial and temporal resolution,¹ including redox reactions,^{2–10} ion transfer,^{11–13} adsorption/ desorption processes,¹⁴ and dissolution phenomena.^{15,16} A major factor in the growing number of applications of SECM has been the parallel development of new modes for which quantitative mass transport models can readily be developed.

Initial work by Kwak and Bard led to the development of a finite-element model for the steady-state feedback response of the UME tip for both conductive and inert surfaces.¹⁷ the results of which have been widely used.¹ The steady-state model was subsequently developed to include the chronoamperometric positive and negative feedback responses, simulated using both a Krylov integrator¹⁸ and the alternating direction implicit finite difference method (ADIFDM).¹⁹ The latter method was used to investigate the effect of unequal diffusion coefficients of the redox mediator couple on the chronoamperometric positive feedback response.²⁰ The effects of finite heterogeneous kinetics and arbitrary substrate size on the feedback responses were also considered.³ Models for the chronoamperometric feedback and generation/collection modes for complex electrode reactions involving coupled homogeneous kinetics have also been introduced.21-23

The single potential step chronoamperometric mode has proved to be a particularly powerful method for inducing and monitoring reversible transfer processes at both liquid/solid interfaces.^{14a,15} and immiscible liquid/liquid interfaces.¹³ In this

application, the UME probe is positioned in a liquid phase, close to the interface of interest at which the transfer process is initially at equilibrium. The electrolysis of a target species at the UME probe (in the potential step chronoamperometric mode) depletes its concentration locally, which, in turn, provides the thermodynamic force for the interfacial transfer process in the direction of the phase containing the UME probe. This serves to enhance the flux of electroactive material to the UME, compared to the situation where the interface is inert, and the current flowing provides quantitative information on the interfacial transfer kinetics. Reversible reactions studied using this SECM equilibrium perturbation mode include dissolution,¹⁵ adsorption/ desorption,^{14a} and solvent extraction/stripping processes.¹³

In order to diversify the range of processes that can be studied with SECM transient methods, we now consider SECM double potential step chronoamperometry (DPSC) as a new methodology for initiating and monitoring heterogeneous reactions at the local level. When used in conjunction with UMEs in particular, DPSC has proved to be a powerful approach for characterizing the diffusion coefficients of electrogenerated species²⁴ and the lifetimes of transient species involved in solution processes.²⁵ However, DPSC has not previously been used to investigate the kinetics of processes confined to a target interface. The basic concept of SECM DPSC is to employ the UME probe to electrochemically generate a reactive species (B in Figure 1) in an initial (forward) potential step for a fixed period. The species could be generated through the electrolysis of an inert precursor in the solution (A in Figure 1) or via the anodic dissolution of a pure or amalgam metal electrode.

During the forward step the electrogenerated species B diffuses away from the probe and intercepts the interface. If B interacts with the interface through either an irreversible or

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Figure 1. Schematic of the processes in the tip/substrate gap for SECM DPSC using the irreversible transfer of a solute across a water/organic (w/o) interface as an example. During the forward step, species B is electrogenerated from A [a(i) and b(i)] in the aqueous phase. If B is inert with respect to the target interface, it simply slowly leaks from the tip/interface gap by hindered diffusion [a(i)]. Consequently, when the potential is stepped to reverse the electrode reaction, much of B is available for collection [a(ii)]. In contrast, if B is active with respect to the w/o interface, as in b(i) and (ii) where it partitions into the o-phase, there is a net depletion of B in the w-phase, resulting in a smaller collector flux [b(ii)] compared to the inert interface case [a(ii)].

reversible process [Figure 1b(i)], e.g., adsorption, absorption, or a chemical reaction, its concentration profile will be modified compared to the situation where there is no interaction and the species simply slowly leaks out of the probe/interface gap by hindered diffusion [Figure 1a(i)]. Consequently, when the potential is reversed, in a final step to collect the species by electrolysis, the flux of B at the UME—and the corresponding current-time characteristics—will be strongly dependent on the nature of the interaction of B with the target interface.

For the particular case of an irreversible process, illustrated using the case of transfer (or absorption) in parts b(i) and b(ii) of Figure 1, it may be anticipated that there will be a decrease in the concentration of B in the probe/interface gap which, in turn, will result in a diminution of the UME current during the reverse potential step. After the mass transport problem is solved for this situation, the reverse current—time characteristics should thus provide quantitative information on the kinetics of the local interfacial process.

The quantitative application of SECM requires that the distance between the tip and target interface is known.¹ An attractive feature of the DPSC mode is that when the species of interest is electrogenerated via the diffusion-controlled electrolysis of a precursor in solution, which is inert with respect to the target interface, the forward current—time behavior provides unambiguous independent information on the probe/ interface separation,^{18,19,21} enabling the quantitative interpretation of the reverse current—time characteristics.

In this paper, a numerical model for SECM DPSC is developed using the ADIFDM. Specific consideration is given to the case where the species of interest, electrogenerated at the UME probe through the diffusion-controlled electrolysis of a solution precursor, may undergo irreversible first-order loss at the interface. The model allows for arbitrary diffusion coefficients of the precursor and reactant species.

The methodology is illustrated through several model systems. For the case of an inert interface, the theoretical characteristics are verified through studies of the electrogeneration and collection of ferricyanide from a ferrocyanide solution at a Pt UME positioned close to aqueous/glass, aqueous/DCE, and aqueous/air interfaces. The investigation of reactive interfaces is illustrated through studies of the transfer of Br₂, electrogenerated from Br⁻ in aqueous sulfuric acid at a Pt UME, across aqueous/DCE and aqueous/air interfaces. The latter studies serve to demonstrate that SECM can be used to probe physicochemical processes at liquid/gas interfaces,²⁶ as well as liquid/liquid and liquid/solid interfaces studied hitherto.

Theory

We consider the situation where the solution initially contains only a precursor species A that does not interact with the interface. At time t = 0, the potential of the UME probe is stepped to a value to cause the following diffusion-controlled electrolysis:

$$A \pm ne^- \to xB \tag{1}$$

resulting in the generation of the reactive species B.

The transport of species A and B in the axisymmetric cylindrical geometry of the SECM is governed by the following general dimensionless diffusion equation (where the subscript i denotes A or B):

$$\frac{\partial C_i}{\partial \tau} = \lambda_i \left[\frac{\partial^2 C_i}{\partial R^2} + \frac{1}{R} + \frac{\partial C_i}{\partial R} + \frac{\partial^2 C_i}{\partial Z^2} \right]$$
(2)

The dimensionless terms in eq 2 are defined as follows. R is the radial coordinate in the axisymmetric cylindrical geometry (starting at the center of the UME) normalized with respect to the electrode radius, a. Z is the coordinate normal to the UME surface normalized with respect to a. Dimensionless time is defined by

$$\tau = t D_{\rm A} / a^2 \tag{3}$$

where D_A is the diffusion coefficient of A. The parameter

$$\lambda_i = D_i / D_A \quad (i = A \text{ or } B) \tag{4}$$

reflects the fact that A and B may have different diffusion coefficients. The concentrations of A and B have been normalized with respect to the bulk concentration of A, $[A]^{\infty}$, such that

$$C_{\rm A} = [{\rm A}]/[{\rm A}]^{\infty} \tag{5}$$

$$C_{\rm B} = [{\rm B}]/x[{\rm A}]^{\infty} \tag{6}$$

The following boundary conditions are true following the initial potential step at $\tau = 0$ and prior to the reverse step at $\tau = \tau_{switch}$:

$$0 \le \tau < \tau_{switch}, \quad Z = 0, \quad 0 \le R \le 1;$$

 $C_{\rm A} = 0, \quad -\lambda_{\rm B}(\partial C_{\rm B}/\partial Z) = \partial C_{\rm A}/\partial Z \quad (7)$

$$0 \le \tau < \tau_{\text{switch}}, \quad Z = 0, \quad 1 < R \le RG:$$
$$\partial C_{\text{A}} / \partial Z = 0, \quad \partial C_{\text{B}} / \partial Z = 0 \quad (8)$$

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$$0 \le \tau < \tau_{switch}, R = 0, 0 < Z < L:$$

 $\partial C_A / \partial R = 0, \partial C_B / \partial R = 0$ (9)

$$0 \le \tau < \tau_{switch}, R > RG, 0 < Z < L:$$

 $C_A = 1, C_B = 0$ (10)

$$0 \le \tau < \tau_{switch}, \quad Z = L, \quad 0 < R \le RG:$$

 $\partial C_A / \partial Z = 0, \quad \partial C_B / \partial Z = KC_B \quad (11)$

In eqs 8-11

$$L = d/a \tag{12}$$

$$RG = r_s/a \tag{13}$$

where d is the distance between the tip and the target interface and r_s is the radius of the probe (electrode plus glass insulator).

The boundary conditions have the following meanings. Equations 7 and 8 denote that the electrolysis of A to B at the UME occurs at a diffusion-controlled rate, but both species are inert on the insulating sheath surrounding the electrode. Equation 9 is a consequence of the axisymmetric cylindrical geometry, while eq 10 assumes that both species recover their bulk solution concentrations outside the thin layer zone formed by the probe and interface. This is a reasonable assumption for the probes used practically in most SECM studies.^{1,15,17,21–23}

Equation 11 reflects the activity of A and B at the interface of interest. Species A is inert on this boundary, while B is lost in a first-order irreversible interfacial process, characterized by a normalized rate constant

$$K = ka/D_{\rm B} \tag{14}$$

where k (cm s⁻¹) is a first-order heterogeneous rate constant.

For the period of the reverse step, in which B is electrolyzed to A at the UME at a diffusion-controlled rate, it is only necessary to evaluate the concentration profile for B by solving eq 2 with i = B subject to the following boundary conditions:

$$\tau_{\text{switch}} \le \tau, \quad Z = 0, \quad 0 \le R \le 1; \quad C_{\text{B}} = 0$$
 (15)

$$\tau_{\text{switch}} \le \tau, \quad Z = 0, \quad 1 \le R \le RG; \quad \partial C_{\text{B}} / \partial Z = 0 \quad (16)$$

$$\tau_{\text{switch}} \leq \tau, \quad R = 0, \quad 0 < Z < L; \quad \partial C_{\text{B}} / \partial R = 0 \quad (17)$$

$$\tau_{\text{switch}} \le \tau, \quad R > RG, \quad 0 < Z < L; \quad C_{\text{B}} = 0$$
 (18)

$$\tau_{\text{switch}} \le \tau, \quad Z = L, \quad 0 < R \le RG; \quad \partial C_{\text{B}} / \partial Z = KC_{\text{B}}$$
(19)

The limiting case of an inert interface can be simulated with K = 0 in eqs 11 and 19.

The aim of the model is to provide a solution for the current time behavior during the forward and reverse potential steps. For the forward step, the current *i*, normalized with respect to $i(\infty)$, the steady-state current for the diffusion-controlled electrolysis of A with the tip at an effectively infinite distance from the interface, is given by

$$i/i(\infty) = (\pi/2) \int_0^1 (\partial C_A / \partial Z)_{Z=0} R \, \mathrm{d}R \tag{20}$$

where27

$$i(\infty) = 4nFD_{A}a[A]^{\infty}$$
(21)

In eq 21, *F* is Faraday's constant. For the period of the reverse step the normalized current ratio is given by

$$i/i(\infty) = -\lambda_{\rm B}(\pi/2) \int_0^1 (\partial C_{\rm B}/\partial Z)_{Z=0} R \,\mathrm{d}R \tag{22}$$

The problem was solved numerically using a FORTRAN program based on the ADIFDM algorithm.²⁸ The interface boundary conditions defined by eqs 11 and 19 are readily incorporated in the general algorithm,²¹ with the consideration of double potential steps requiring only minor modifications to earlier single potential step programs.^{14a,15,20–23}

Theoretical Results and Discussion

The normalized DPSC response depends on *L*, *K*, λ_B , τ_{switch} , and, if long-time behavior is considered, *RG*. The aim here is to consider the general DPSC characteristics, and so we set *RG* = 10 and $\lambda_B = 1$ and investigate the effects of τ_{switch} and *K* on the current-time behavior for typical probe-to-interface separations.

Effect of τ_{switch} . The normalized current-time characteristics, with K = 0, for three different switching times, $\tau_{\text{switch}} = 0.01$, 0.1, and 1.0, are shown in Figure 2. For each switching time, three probe/interface separations, $\log(L) = -1.0$, -0.5, and 0.0, have been considered. The characteristics for both the forward and reverse steps are plotted together as $|i/i(\infty)|$ versus either $\tau^{-1/2}$ or $(\tau - \tau_{\text{switch}})^{-1/2}$ in order to emphasize the short-time characteristics for the forward and reverse steps, respectively.

The form of the forward transient, when the probe is close to an inert interface, has been discussed previously in connection with single potential step chronoamperometry.^{18,19} In brief, at sufficiently short times such that the diffusion field at the UME is very small compared to the probe/interface separation, the forward current—time response is identical to that for a conventional UME in a solution. However, at times sufficient for the diffusion field to intercept the interface [$\tau \approx L^2$], diffusion to and from the UME becomes hindered with the result that the current that flows is lower than that, at a corresponding normalized time, with the probe in free solution. The forward current—time behavior in Figure 2a demonstrates that, at the probe/interface distances considered for $\tau_{\text{switch}} = 0.01$, hindered diffusion is only observed at the closest distance of $\log(L) =$ -1.0.

A comparison of the reverse transients, for the three distances with $\tau_{\text{switch}} = 0.01$, clearly shows that the effect of hindered diffusion of B away from the UME (for log (L) = -1.0) is to increase the short-time current on the reverse transient. In contrast, for log(L) = -0.5 and 0.0, there is a strong concentration gradient of B driving this species away from the UME, even during the reverse step, causing a smaller current to flow at short times.

This trend is further illustrated in parts b and c of Figure 2. Together with the data in Figure 2a, it is clear that the greater the extent to which diffusion is hindered during DPSC measurements, i.e., the closer the tip/interface separation and the longer the switching time, the closer are the forms of the forward and reverse current transients. Essentially, under conditions where diffusion in and out of the probe/interface gap is strongly impeded, there is a tendency for almost all of the material generated in the forward step to be collected in the reverse step.

The effect described above is evident in parts a-c of Figure 3, which show the concentration profiles for species B for the three distances of interest at three times just after a reverse potential step at $\tau_{switch} = 0.1$. For $\log(L) = -1.0$, it can be seen that at the first time of interest [Figure 3a(i)], the gap between the probe and interface, directly under the active electrode, is filled with species B, which may be rapidly recollected. Consequently, the reverse current is initially high



Figure 2. Forward (- - -) and reverse (-) current-time characteristics plotted as $|i/i(\infty)|$ versus $\tau^{-1/2}$ (forward step) and $(\tau - \tau_{switch})^{-1/2}$ (reverse step) for $\tau_{switch} = 0.01$ (a), 0.1 (b), and 1.0 (c). For each switching time, data are shown for $\log(L) = -1.0$ (lowest current at longest times on the forward step; highest current at shortest times on the reverse step), -0.5, and 0.0 (highest current at longest times on the forward step; lowest current at shortest times on the reverse step). In (a) only two pairs of transients appear, since the characteristics for $\log(L) = -0.5$ and 0.0 are essentially identical on this switching time scale.

[Figure 2b], but then rapidly decreases as B is consumed at the UME [parts a(ii) and a(iii) of Figure 3].

For the larger probe/interface separations considered, there are concentration gradients both normal and radial to the UME that promote the diffusion of B away from the electrode during the initial collection process [parts b(i) and c(i) of Figure 3]. The diffusion process away from the electrode is greatest, and thus the initial reverse diffusion-limited current lowest, at the largest probe/interface separation. However, at these larger probe/substrate separations, a greater fraction of B is able to survive to longer times, causing a higher current than at equivalent times for close tip/substrate separations. This can readily be seen by comparing, for example, parts a(ii) and a(iii) of Figure 3 with parts b(ii) and b(iii) of Figure 3 or by examining the long-time reverse currents in parts b and c of Figure 2.

In terms of the application of DPSC to the measurement of interfacial kinetics, it follows that the technique will be most sensitive to interfacial processes at the closest probe/interface separations, as found for other SECM modes.^{1,3,7,9,10,13-15}

Effect of *K***.** Having identified that SECM DPSC will be most sensitive to interfacial kinetics at the closest probe/substrate separations, we consider the effect of interfacial kinetics on the current-time response for $\log(L) = -0.8$, typical of a close distance that is easily attainable practically in SECM. Figure 4 shows a set of transients, plotted as $|i/i(\infty)|$ versus $\tau^{-1/2}$ (forward step) or $(\tau - \tau_{switch})^{-1/2}$ (reverse step) for $\tau_{switch} = 1.0$, with K = 0, 0.1, 1, and 10. The forward transient is the same for all of the kinetic cases, since the current response is simply governed by the diffusion of the precursor species to the UME. In contrast, the form of the reverse transient is seen to be extremely sensitive to the value of *K*, with the current increasingly diminished at all times as *K* increases.

The reason for the smaller currents observed during the reverse potential step with K > 0 is clear from Figure 5, which compares the evolving concentration profiles for species B at several times during the forward step, up to and including the switching time, for K = 0 [Figure 5a] and K = 1 [Figure 5b]. When species B is inert with respect to the target interface, the forward step serves to fill the gap between the probe and the interface (particularly in the region 0 < R < 1) with B [parts a(i) and a(ii) of Figure 5], which is subsequently collected during the reverse step [Figure 5a(iii)]. In contrast, when the interface acts as a partial (irreversible) sink for B, the concentration of this species is greatly depleted during the period of the forward [parts b(i) and b(ii) of Figure 5] and reverse steps [Figure 5b(iii)], resulting in a smaller current flow when the potential is reversed.

As with previous kinetic applications of the SECM, the time scale of a measurement can be tuned to the region of interest by varying the size of the probe [eq 14] and the probe/interface separation. For the DPSC mode, the switching time may also be used with good effect to enable the most sensitive kinetic measurements. This point is illustrated in Figure 6, which shows the current-time curves plotted as normalized current versus $\tau^{-1/2}$ (forward step) or $(\tau - \tau_{switch})^{-1/2}$ (reverse step) for $\tau_{switch} = 0.1$ and 10 for various values of *K*. In conjunction with Figure 4, these data demonstrate that the DPSC technique can be made most sensitive to fast kinetics by employing a short switching time, while slower interfacial reactions can be studied most effectively by employing a longer switching time.

Experimental Section

Materials and Solutions. All aqueous solutions were prepared from Milli-Q reagent water (Millipore Corp.). Ferrocyanide solutions contained 0.050 mol dm⁻³ potassium ferrocyanide with 2.0 mol dm⁻³ potassium chloride (both Analytical Reagent, Fisher, Loughborough, U.K.) as background electrolyte. Bromide solutions contained 0.010 mol dm⁻³ potassium bromide (Analytical Reagent, Fisher) and 0.50 mol dm⁻³ sulfuric acid (Analytical Reagent, Sigma-Aldrich, Gillingham, U.K.) which served as background electrolyte. Aqueous solutions of bromine were prepared from 99.99% reagent (Aldrich), with 0.50 mol dm⁻³ sulfuric acid as an electrolyte. For immiscible liquid/liquid studies, DCE (HPLC grade, Sigma-Aldrich) was employed as the organic phase.

Apparatus and Instrumentation. Electrochemical measurements were made using a two-electrode arrangement. A silver

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Figure 3. Distribution of species B in the tip/substrate gap during the reverse potential step, for $\tau_{switch} = 0.1$ with K = 0. Data are shown for log(*L*) = -1.0 (a), -0.5 (b), and 0.0 (c) at $\tau = 0.10$ (i), 0.11 (ii), and 0.15 (iii).



Figure 4. Forward (- - -) and reverse (-) current-time characteristics plotted as $|i/i(\infty)|$ versus $\tau^{-1/2}$ (forward step) and $(\tau - \tau_{switch})^{-1/2}$ (reverse step) for $\tau_{switch} = 1.0$ and $\log(L) = -0.8$. The reverse characteristics are for K = 0 (upper solid line), 0.1, 1, and 10 (lower solid line).

wire served as a quasi-reference electrode (AgQRE), and the working electrode was a 25 μ m diameter Pt disk UME. Two designs of UME were employed: a conventional UME, which has been described previously,^{15,29} and a new design of inverted "submarine" UME,^{13,26} shown in Figure 7, to enable the study of air/liquid interfaces by a UME positioned in the liquid phase.

The submarine UME was fabricated in a way similar to the fabrication of a conventional UME, but the electrode was cut short, ca. 15 mm, so that it could be accommodated in the cell, and electrical connection was made with a flexible silicone rubber-coated, stranded copper wire. The wire-electrode connection was sealed with epoxy resin (Araldite Rapid, Ciba-Geigy) such that no connecting wire was exposed to the solution. The electrode was mounted vertically, but inverted, in the cell by inserting it into a small PTFE block through which two parallel holes had been machined. This arrangement was then



Figure 5. Evolution of the concentration distribution of species B in the tip/substrate gap during the forward potential step, up to and including the reverse step ($\tau_{switch} = 1.0$), for K = 0 (a) and 1 (b). In each case profiles are shown for $\tau = 0.01$ (i), 0.1 (ii), and 1.0 (iii) (immediately after the potential was reversed).

connected to a conventional electrode holder, itself attached to a micropositioner, via a glass capillary. The latter was inserted through the second hole in the PTFE block. The submarine electrode has been shown to function well in terms of currentdistance approach measurements, as described recently.^{13,26} Both



Figure 6. Forward (- - -) and reverse (-) current—time characteristics, plotted as $|i/i(\infty)|$ versus $\tau^{-1/2}$ (forward step) and $(\tau - \tau_{switch})^{-1/2}$ (reverse step) for log(*L*) = -0.8: (a) $\tau_{switch} = 0.1$ and K = 0 (upper solid curve), 0.1, 1, 10, and 100 (lower solid curve); (b) $\tau_{switch} = 10$ and K = 0 (upper solid curve), 0.1, and 1 (lower solid curve).



Figure 7. Schematic (not to scale) of the inverted submarine UME design for investigating the interface between a liquid phase containing the UME probe and a less dense immiscible liquid or gas phase.

types of UME were characterized by a ratio of the overall probe diameter to electrode diameter, $RG \approx 10$.

Potentials were controlled with a triangular wave/pulse generator (Colburn Electronics, Coventry, U.K.), and currents were measured using a home-built current follower (gains of $10^{-5}-10^{-9}$ A V⁻¹). A Pentium 100 MHz PC equipped with a

data acquisition card (Lab PC card, National Instruments, Austin, TX) was used to record current-potential and current-time behavior. Some current-time transients were also measured using a NIC310 digital storage oscilloscope (Nicolet, Coventry, U.K.).

UMEs were positioned initially with a 431-2 stage (Newport Corp., Fountain Valley, CA). Fine control in the z-direction normal to the plane of the interface, with a spatial resolution of around 0.1 μ m over a 40 μ m range, was achieved with a piezoelectric translator, incorporating a strain gauge sensor (translator Model P173 and controller P273, Physik Instrumente, Waldbronn, Germany).

For experiments where the liquid/liquid or liquid/air interfaces were probed, a one-piece cylindrical glass cell (40 mm diameter and 50 mm depth) was used. The cell incorporated an optical window on one side such that a zoom microscope fitted with a CCD camera (maximum resolution 2.2 μ m per screen pixel) could be used to aid positioning of the UME near the interface. For experiments concerned with confirming the theoretical model with an inert glass disk substrate, a fully detachable Plexiglas cell was used, comprising a body, lid, and base into which the substrate could be securely fixed with its surface perpendicular to the axis of the UME.

Experimental Results and Discussion

DPSC Characteristics at Inert Interfaces. In order to verify the theoretical predictions, initial experiments were carried out on the diffusion-controlled generation/collection of ferricyanide ions from 50×10^{-3} mol dm⁻³ potassium ferrocyanide solutions at a probe UME positioned close to (i) an aqueous/glass interface, (ii) an aqueous/DCE interface, and (iii) an aqueous/ air interface. All of these are examples of interfaces that are chemically inert with respect to the ferrocyanide/ferricyanide couple. For these measurements, the tip potential was stepped initially from 0.10 V, where no Faradaic processes occurred, to 0.70 V, where the oxidation of ferrocyanide was diffusioncontrolled for a period t_{switch} typically of 200 ms. The potential was then stepped back to 0.10 V to collect ferricyanide by reduction to ferrocyanide.

Figure 8 shows a series of typical generation/collection transients with the UME probe at various distances from the aqueous/glass interface. In light of previous work, which has demonstrated that the chronoamperometric oxidation of ferrocyanide under these conditions provides an excellent measure of the probe/interface separation,^{15c} the only variable involved in fitting the forward transient data was the probe/interface distance. A value of $D_{\text{Fe}(\text{CN})_6^{4-}} = 6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, deduced from the steady-state diffusion-limited current for the oxidation of ferrocyanide [eq 21], was employed to enable a comparison to be made between experiment and theory for the forward step, which was found to be in excellent agreement over the range of distances investigated.

With the tip/interface separation fixed, the only variable involved in the interpretation of the reverse transient behavior for this system is $\lambda_{Fe(CN)_6}^{3-}$. Experiment and theory were found to be in excellent agreement with $\lambda_{Fe(CN)_6}^{3-} = 1.13$, which is the value expected, given the diffusion coefficients of ferrocyanide and ferricyanide under these conditions.³⁰ The data in Figure 8 both verify the numerical model for SECM DPSC and demonstrate that measurements can readily be made on time scales less than 200 μ s with the experimental arrangement described.

Further to recent work, which has demonstrated that the feedback¹⁰ and equilibrium perturbation¹³ modes can be used to probe chemical processes at immiscible liquid/liquid inter-



Figure 8. DPSC data for the oxidation of ferrocyanide (forward step; upper curves) and reduction of ferricyanide (reverse step; lower curves) at a tip in aqueous solution positioned at distances of 1.5 (a), 3.0 (b), and 4.5 (c) μ m from a glass surface. In each case the switching time was 200 ms. The solid lines are experimental data, while the dashed lines are the theoretical characteristics. A value of $D_{\text{Fe}(\text{CN})_6^{4-}} = 6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was employed to convert normalized time to real time, while $\lambda_{\text{Fe}(\text{CN})_6^{3-}} = 1.13$ gave the best fit to the reverse current–time behavior in each case.

faces, the experimental characteristics for the generation/ collection of ferricyanide in the DPSC mode at the aqueous/ DCE interface were examined. By use of the same aqueous solution conditions outlined above (similar time scales and tip/ substrate separations between 1.5 and 9.0 μ m), excellent agreement was found between experiment and theory. A representative case is illustrated in Figure 9, which shows the DPSC characteristics for a switching time of 200 ms, with the tip positioned 3.4 μ m from the aqueous/DCE interface.

By use of the probe design shown in Figure 7, DPSC experiments were carried out close to the aqueous/air interface to determine whether SECM measurements at liquid/gas inter-



Figure 9. Typical DPSC data ($t_{switch} = 200 \text{ ms}$) for the oxidation of ferrocyanide (forward step; upper curve) and reduction of ferricyanide (reverse step; lower curve) at a tip in aqueous solution positioned at a distance of 3.4 μ m from an aqueous/DCE interface. The solid lines represent the experimental data, while the dashed lines correspond to the theoretical characteristics. A value of $D_{\text{Fe}(CN)_6^{4-}} = 6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was employed to convert normalized time to real time, and $\lambda_{\text{Fe}(CN)_6^{3-}} = 1.13$ was used for the simulation.



Figure 10. Typical DSPC data ($t_{switch} = 200 \text{ ms}$) for the oxidation of ferrocyanide (forward step; upper curve) and reduction of ferricyanide (reverse step; lower curve) at a tip in aqueous solution, positioned at a distance of 2.9 μ m from an aqueous/air interface. The solid lines represent the experimental data, while the dashed lines correspond to the theoretical characteristics. A value of $D_{\text{Fe}(\text{CN})_6^{4-}} = 6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was employed to convert normalized time to real time, and $\lambda_{\text{Fe}(\text{CN})_6^{3-}} = 1.13$ was used for the simulation.

faces were viable. DPSC characteristics were obtained on similar time scales, and the same range of tip/interface separations, as in the experiments described above. Experimental data were found to be in good agreement with theory in all cases, demonstrating that SECM can indeed be used to probe liquid/gas interfaces. Typical results are shown in Figure 10 for a tip/interface separation of 2.9 μ m. It can be seen that the experimental data are of a high quality and consistent with the theoretical predictions.

DPSC Characteristics at Active Liquid/Liquid Interfaces. Br₂ shows enhanced solubility in many organic solvents compared to aqueous solutions.³¹ The partition coefficient of Br₂ in the DCE/0.5 mol dm⁻³ sulfuric acid system was determined voltammetrically by first measuring the steady-state limiting current for the reduction of 10 mmol dm⁻³ Br₂ in 0.5 mol dm⁻³ sulfuric acid solution at a 25 μ m diameter Pt UME (*i*_{L1}) and the corresponding limiting current after shaking the solution with an equal volume of DCE (*i*_{L2}). Under these conditions, the coefficient defining the partitioning of Br₂ between DCE and aqueous solution is then given by 10858 J. Phys. Chem. B, Vol. 101, No. 50, 1997

$$K_{\rm p} = \frac{[{\rm Br}_2]_{\rm DCE}}{[{\rm Br}_2]_{\rm aq}} = \frac{i_{\rm L1} - i_{\rm L2}}{i_{\rm L2}}$$
(23)

A value of $K_p = 37(\pm 1)$ was deduced. This implies that Br₂ electrogenerated through the oxidation of Br⁻ in the aqueous phase, close to an aqueous/DCE interface, will undergo effectively irreversible transfer across the interface, providing an ideal model system for examining the DPSC technique as a probe of irreversible interfacial kinetics.

In these experiments, Br⁻ was first oxidised to Br₂ in an initial potential step, from 0.70 to 1.20 V, for a period in the range 10-200 ms, after which the potential was stepped to 0.70 V to effect the diffusion-controlled collection of Br₂ by reduction to Br⁻. All experimental data obtained at tip/interface separations from 2.5 to 9.1 μ m, for the step times defined above, were found to be in good agreement with the theoretical predictions for the irreversible diffusion-controlled loss of Br2 at the interface. For the fitting of the experimental data, a value of $D_{\rm Br^-} = 1.80 \times$ 10^{-5} cm² s⁻¹ was employed, as deduced from steady-state UME voltammetry [eq 21], together with $D_{\text{Br}_2} = 9.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, measured using UME chronoamperometry.³² Both of these values are in good agreement with those reported earlier under similar solution conditions.³³ It should be noted that the rapid transfer of Br2 across the interface (and thus out of the tip/ interface gap) results in a dramatic decrease in the concentration of Br₂ in the aqueous phase. The formation of Br₃⁻, through the equilibration of Br₂ and Br^{-,34} can thus be neglected so that the basic theoretical model described herein is valid.

A typical result for the shortest time step examined ($t_{switch} =$ 10 ms), at a tip/interface separation of 2.8 μ m, is shown in Figure 11. The data have been plotted as $|i/i(\infty)|$ vs $t^{-1/2}$ (forward step) or $(t - t_{switch})^{-1/2}$ (reverse step). The reverse current-transient is in good agreement with theory for a diffusion-controlled process, particularly for $(t - t_{switch})^{-1/2} >$ $20 \text{ s}^{-1/2}$. At longer reverse times, the experimental currents are slightly higher than those predicted theoretically. This may be attributed to a small effect of electrochemically induced backtransfer of Br₂ from DCE to the aqueous phase due to the extensive depletion of Br₂ in the aqueous phase during the collection process. Nonetheless, the transfer of Br₂ from the aqueous phase to DCE, under the conditions of these experiments, tends toward irreversibility and is effectively rate-limited by diffusion of Br₂ in the aqueous phase. Based on the data in Figure 11, a lower limit of 0.5 cm s^{-1} can be assigned to the interfacial rate constant for the transfer of Br₂ from the aqueous to the DCE phase under conditions where the latter phase is an empty sink.

DPSC Characteristics at Active Liquid/Air Interfaces. The volatility of Br₂ in aqueous solutions in contact with air under open system conditions makes the process described above—in which bromine is electrogenerated close to an interface—an ideal one to investigate the use of SECM as a probe of dynamic processes at liquid/gas interfaces. Experiments were carried out using a protocol identical to that described in the preceding section, with an inverted submarine UME positioned at distances of 2.5–9.1 μ m from an aqueous/ air interface. All experimental data for switching times of 10 ms and longer were found to agree well with the theoretical predictions for the irreversible diffusion-controlled loss of Br₂ at the aqueous/air interface using the diffusion coefficients defined above.

A typical result for the shortest time step examined ($t_{switch} = 10 \text{ ms}$), at a tip/interface separation of 2.5 μ m, is shown in Figure 12. The data have been plotted as $|i/i(\infty)|$ vs $t^{-1/2}$ (forward step) or $(t - t_{switch})^{-1/2}$ (reverse step). The reverse



Figure 11. Typical DPSC data ($t_{switch} = 10 \text{ ms}$) for the oxidation of bromide (forward step; upper solid curve) and reduction of bromine (reverse step; lower solid curve) at a tip in aqueous solution positioned at a distance of 2.8 μ m from an aqueous/DCE interface. The upper dashed line is the theoretical response for the forward step at the defined tip/interface separation, with $D_{Br^-} = 1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The remaining dashed lines are the reverse transients for various transfer rate constants k with the values marked on the plot. A value of $D_{Br_2} = 9.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was used for the simulation.



Figure 12. Typical DPSC data ($t_{switch} = 10 \text{ ms}$) for the oxidation of bromide (forward step; upper solid curve) and reduction of bromine (reverse step; lower solid curve) at a submarine UME in aqueous solution positioned at a distance of 2.5 μ m from an aqueous/air interface. The upper dashed line is the theoretical response for the forward step at the defined tip/interface separation, with $D_{Br} = 1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The remaining dashed lines are the reverse transients for various transfer rate constants k with the values marked on the plot.

transient in Figure 12 lies slightly above the theory for a diffusion-controlled process (particularly at short times), which might indicate very slight interfacial control of the transfer process. However, we were not able to go to sufficiently shorter times or closer tip/interface separations to determine whether there was a measurable interfacial resistance to the transfer process. From the data in Figure 12, it may therefore be deduced that the transfer of Br₂ from aqueous solution to air is a rapid process, which approaches a limiting rate controlled by diffusion of Br₂ in solution. The data allow a lower limit of 0.5 cm s⁻¹ to be assigned to the rate constant defining the interfacial transfer process.

Note that, in contrast to the reverse transient data for Br_2 transfer from aqueous solution to DCE (Figure 11), the reverse currents at longer times ($t^{-1/2} < 20 \text{ s}^{-1/2}$) in Figure 12 are closer to the diffusion-controlled theoretical case for an irreversible transfer process. This suggests that electrochemically induced back-transfer of Br_2 from air to aqueous solution, during the collection process, is a negligible process. In part, this may be attributed to the much higher transport rate of Br_2 in air

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compared to DCE; i.e., once Br_2 crosses the interface, it is rapidly transported away and is thus not available for backtransfer during the collection step.

Conclusions

SECM DPSC has been shown to be a powerful technique for investigating the chemical kinetics of tip-generated species at liquid/solid, liquid/liquid, and liquid/air interfaces. The technique complements earlier equilibrium perturbation transient SECM methods by allowing the study of irreversible interfacial chemical processes. The DPSC mode has been verified experimentally with the model ferrocyanide/ferricyanide system and has been used to show that the absorption of Br_2 by both air and DCE from aqueous solutions (under sink conditions) is controlled by diffusion of Br_2 in the aqueous phase, with interfacial processes providing no detectable kinetic resistance to transfer with the range of mass transfer rates attainable from SECM.

There is considerable scope for further developing the SECM DPSC mode. For example, to complement the systems in this paper, we are currently investigating reversible interfacial processes of tip-generated species using the DPSC mode. In addition to generating reactants from solution precursor species, as in the studies in this paper, it should be possible to locally inject several types of metal ions, e.g., Cu^{2+} , Ag^+ , Zn^{2+} , Pb^{2+} , Cd^{2+} , etc., into the gap between the probe and the interface through the anodic dissolution of metal or mercury amalgam UMEs. We plan to use this approach as a means of studying the adsorption and absorption of metal ions at solid/liquid and immiscible liquid/liquid interfaces.

SECM has been widely used to probe physicochemical processes at liquid/solid interfaces¹ and is proving to be a valuable tool for investigating charge and molecular transfer processes at immiscible liquid/liquid interfaces.^{10,13} The studies herein build further on recent work²⁶ by demonstrating that SECM can be used to study liquid/gas interfaces through the application of a simple submarine UME design. We anticipate that this is an area with considerable promise for further development. In particular, the use of SECM to noninvasively probe chemical and diffusion processes in Langmuir monolayers at the air/water interface is readily envisaged.

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