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Phase-Sensitive Detection in Potential-Modulated in Situ Absorption and Probe Beam Deflection Techniques: Theoretical Considerations

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A mathematical framework is presented for the quantitative analysis of in situ potential modulation spectroelectrochemical techniques based on phase-sensitive detection for the study of solution-phase redox systems under strict diffusion control. In the case of arrangements in which the probing beam is parallel to the electrode surface, the phase of the optical signal with respect to the applied potential, assuming negligible double-layer charging currents, was found to be proportional to $y(\omega/2D)^{1/2}$, where y is the distance normal to the electrode, ω is the frequency of the perturbing signal, and D is the diffusion coefficient of the species responsible for absorption or refraction. Good agreement was found between theoretical predictions and the few available experimental results for both absorption and probe beam deflection-type experiments. In particular, in the case of solutions containing the chromophore trianisylamine and nonabsorbing *p*-benzoquinone, the phase angle difference between absorption and diffraction calculated from theory and measured experimentally yielded a common value of $\sim 30^\circ$.

Methods based on the response of a system to judiciously selected external perturbations afford increased detection sensitivity^{1,2} and information content³ over their dc counterparts. Non-steady-state voltammetric techniques have been shown to be valuable tools in both fundamental and applied research.⁴ In particular, impedance spectroscopy, perhaps the most popular among these methodologies, relies on the analysis of phases and amplitudes of the electrical response induced, most commonly, by the application of periodic signals, either potential or current, to electronic circuitry including electrochemical devices, as a function of the excitation frequency. The major limitation of these methods stems from complications in the analysis of the data due to double-layer charging and the need for multiparameter fits and their overall lack of specificity common to all purely electrochemical measurements.

Strategies involving the coupling of electrochemical modulation and optical detection can be used in certain cases to isolate the response of a single species to the perturbation signal without interference from non-faradaic contributions.^{5–7} This approach was proven key to the development of in situ UV–visible² and infrared spectroscopy⁸ for the study of species adsorbed on electrode surfaces using dispersive instrumentation. It may be expected that full exploitation of the unparalleled advantages this approach offers will lead to rapid progress in areas of fundamental and technological importance, such as electron-transfer theory, sensors, electrosynthesis, and electrochemical energy conversion.

This work presents a simple general theoretical approach for the analysis of changes in the absorption and refraction of light induced by application of a periodic electrical perturbation of small amplitude to a planar electrode immersed in a quiescent electrolyte solution containing solution-phase species involved in heterogeneous electron transfer. Such modifications in the optical properties of the media are generated by corresponding temporal and spatial variations in the concentration profiles of species involved in reactions at the interface, and their analysis requires for the equations that govern mass transport to be solved subject to the appropriate boundary conditions. Attention will be focused on determining phase rather than amplitude relationships among the various electrical and optical observables and their use to enhance detection and characterization of reactants and/or products of redox-active species in solution.

THEORETICAL CONSIDERATIONS

Of specific interest here is to determine the time-dependent concentration profiles of solution-phase species R and P involved in a redox process $R \rightarrow P$, induced by changes in the applied potential at the interface of the general form

$$E(t) = E_{dc} + \Delta E \sin \omega t \quad (1)$$

It will be assumed in what follows that mass transport of these species is accurately described by Fick's second law (see Appendix

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(2) Kolb, D. M. In *Spectroelectrochemistry Theory and Practice*; Gale, R. J., Ed.; Plenum Press: New York, 1988; p 87.

(3) Sluyters, D. In *Comprehensive Treatise of Electrochemistry*; Yeager, E., O'MBockris, J., Conway, B. E., Sarangapani, S., Eds.; Plenum Press: New York, 1984; Vol. 9, Chapter 8, pp 177–292.

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(5) Heineman, W. R.; Hawkridge, F. M.; Blount, H. N. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13, pp 1–113.

(6) McCreery, R. L. In *Physical Methods of Chemistry*; Rossiter, B. W., Hamilton, S. F., Eds.; John Wiley & Sons: New York, 1986; Vol. II, pp 591–661.

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(8) Bewick, A.; Pons, S. In *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Wiley-Heyden: London, 1985; Vol. 12.

I) in a single dimension. Implicit in this approach is the neglect of effects due to migration in an electric field, natural convection, and nonplanar diffusion as well as charging currents associated with double-layer effects. Under conditions in which the rate of the redox reaction is fast enough, the ratio of the concentrations of R and P, c_R and c_P , respectively, assuming the activity coefficients are unity, will be prescribed by the instantaneous value of $E(t)$ via the Nernst equation, i.e., ideal kinetic reversibility. This and other related problems have been discussed in detail by Smith within the context of ac polarography,⁹ a technique in which a sinusoidal potential perturbation of small amplitude is superimposed on a linear potential scan. As shown therein, if the term E_{dc} in eq 1 can be regarded as constant, or equivalently, if the scan rate is slow compared to the rate of change of the alternating potential, explicit expressions for the measured current at the fundamental and harmonic frequencies can be obtained using a series expansion for the appropriate exponential function and comparing terms of equal power in the resulting system of integral equations.

Equations that describe temporal and spatial variations of the concentration profiles at the fundamental frequency can be more readily obtained by seeking solutions for c_R and c_P in terms of the sum of a transient, $\bar{c}(y,t)$ and an oscillatory contribution $\tilde{c}(y,t)$, i.e.

$$c(y,t) = \bar{c}(y,t) + \tilde{c}(y,t) \quad (2)$$

and thus analogous to that given eq 1. Assuming that the changes in $\bar{c}(y,t)$ are slow compared to the rate of change of the oscillatory component, $\tilde{c}(y,t)$ may be expressed as

$$\tilde{c}(y,t) = A^* \cos \omega t = \operatorname{Re}\{A^* \Psi(y) \exp(j\omega t)\} \quad (3)$$

where A^* is the maximum amplitude of the sinusoidally varying concentration of frequency ω and $\Psi(y)$ is a function of distance. Since all the equations to be solved here are linear, the real term in eq 3 will lead to real terms in the solutions; hence, all derivations can be performed in complex notation. It must be stressed that, although the concentration is real and, thus, from a strict viewpoint, the imaginary part should not appear in eq 3, some of the mathematical steps involved in the derivations can be greatly simplified by retaining this notation.

An analytic expression for $\Psi(y)$ can be obtained by replacing $\tilde{c}(y,t)$ in eq 3 into Fick's second law to yield a second-order differential equation in total derivatives (see Appendix I for a more complete mathematical derivation), for which the solution can be written as follows:

$$\Psi(y) = \exp[-(j\omega/D)^{1/2}y] \quad (4)$$

Hence, from eq 3

$$\tilde{c}(y,t) = A^* \exp[-(j\omega/D)^{1/2}y] \exp(j\omega t) \quad (5)$$

This equation specifies, as required, that the concentration oscillates at the correct frequency along the y -axis and is in phase

with the electrical excitation signal at the boundary; i.e., $y = 0$. This formalism affords a rather expedient means for deriving well-known expressions in electroanalytical chemistry as illustrated for ac voltammetry in Appendix II.

1. Absorption. It will be assumed for simplicity that the absorbance is proportional to the number of chromophores in the path of the beam, that the beam is perfectly collimated, and that the light intensity is homogeneous along its entire cross section. Less restrictive situations may be found in ref 10 and references therein. Of special interest here are experimental arrangements in which the probing beam is oriented normal and parallel to the electrode surface.

a. Normal Incidence. Consider a beam of light propagating through the solution along the axis y normal to the surface of a perfectly reflecting planar electrode placed at a distance d from a flat transparent window parallel to the plane of the electrode. Upon reflection, the beam will travel along the same path but in opposite direction and upon crossing the cell window directed to a suitable detector. This configuration can be realized in the laboratory using a beam splitter. If only one of the species involved in the redox process absorbs light at the wavelength λ at which the measurements are performed, the intensity of the light emerging from the cell, I , may be shown to be given by

$$I = I_0 \exp[-2\epsilon(\lambda)k \int_0^d c(y,t) dy] \quad (6)$$

where I_0 is the light intensity entering the cell, the factor of 2 accounts for the doubling of the path length, $\epsilon(\lambda)$ is the wavelength-dependent molar absorptivity of the species in question, and $k = 2.303$. Introduction of eq 5 into eq 6 makes it possible to define a normalized modulated absorbance as follows:

$$\frac{I}{\bar{I}} = \exp[-2\epsilon k \int_0^d \tilde{c}(y,t) dy] \quad (7)$$

where the quantity $\bar{I} = I_0 \exp[-2\epsilon k \int_0^d \bar{c}(y,t) dy]$ represents the attenuation of the light intensity due to the nonoscillatory component of the time-varying concentration. Provided the changes in concentration induced by the periodic perturbation are small, the argument in the exponential can be approximated by the first two terms in the Taylor series expansion, yielding after rearrangement

$$1 - \frac{I}{\bar{I}} = \frac{I_{ac}}{I_{dc}} = 2\epsilon k \int_0^d \tilde{c}(y,t) dy \quad (8)$$

The ratio I_{ac}/I_{dc} in this equation is readily amenable to experimental determination using, for example, a lock in amplifier, by regarding I_{ac} as the photomultiplier output at the modulation frequency and I_{dc} as its dc output. If it is further assumed that the changes in concentration are confined to a volume of solution very close to the electrode surface, d may be regarded as arbitrarily large. Under these conditions, the upper limit of integration may be set as infinity, an approach that simplifies

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Table 1. Phase Angle Associated with Potential Modulation Techniques Involving Electrical and Optical Detection of Solution-Phase Species

physical measurement	phase angle
faradaic current ^a	$\pi/4$
normal incidence absorption	$-\pi/4$
parallel absorption	$y(\omega/2D)^{1/2}$
beam deflection	$y(\omega/2D)^{1/2} + \pi/4$

^a Complications derived from double-layer effects are neglected.

considerably the mathematical formalism. In particular, replacing $\tilde{c}(y, t)$ in eq 5 into eq 8 yields

$$\frac{I_{ac}}{I_{dc}} = 2\epsilon k \int_0^\infty A^* \exp[-(j\omega/D)^{1/2}y] \exp(j\omega t) dy =$$

$$2\epsilon k A^* \left(\frac{D}{j\omega}\right)^{1/2} \exp(j\omega t) = 2\epsilon k A^* \left(\frac{D}{\omega}\right)^{1/2} \exp[j(\omega t - \pi/4)] \quad (9)$$

that is, the optical response lags the modulated surface concentration or, equivalently, the applied potential by an angle of $\pi/4$ (see Table 1). In contrast, the current associated with the faradaic process is proportional to the flux of material at the interface. Furthermore, as shown in detail in Appendix II,

$$D \frac{\partial \tilde{c}}{\partial y} \Big|_{y=0} = A^* (j\omega D)^{1/2} \exp(j\omega t) =$$

$$A^* (\omega D)^{1/2} \exp[j(\omega t + \pi/4)] \quad (10)$$

that is, the phase in this case is $\pi/2$ with respect to the optical signal as derived by Sagara et al.¹¹ and Hinman et al.¹² based on a different formalism.

b. Parallel Configuration. A different experimental arrangement involves the use of a narrow beam of light propagating along an axis parallel to the electrode surface to monitor modulations in the solution absorbance induced by perturbations at the electrode surface. For an electrode of length w along this specific observation axis, and assuming, as before, one-dimensional diffusion, the normalized optically modulated signal can be obtained by integrating the profile along that axis yielding

$$\frac{I_{ac}}{I_{dc}} = \epsilon k w \tilde{c}(y, t) = \epsilon k w A^* \exp[-(j\omega/D)^{1/2}y] \exp(j\omega t) =$$

$$\epsilon k w A^* \exp[-(\omega/2D)^{1/2}y] \exp\{j[\omega t + (\omega/2D)^{1/2}y]\} \quad (11)$$

This expression indicates that the phase in this case is a function not only of the frequency of the perturbation but also of the specific distance from the electrode surface at which the beam is placed.

2. Refraction. A beam traveling in a medium in which the index of refraction n varies along a component normal to the direction of propagation will deflect toward regions of increasing

n . The extent of bending will be proportional to $\partial c/\partial y$ and also to $\partial n/\partial c$, the variation of n with concentration. Beam deflection is thus insensitive to the nature of the species that cause the change in n . Nevertheless, it seems useful from a didactic viewpoint to regard these effects as arising from a single species and to assume that the n is a linear function of concentration, i.e., $\partial n/\partial c = N$, as is the case with reactions in which a single species is consumed or generated at the electrode surface. On this basis, the oscillatory deflection $\tilde{\Phi}$ will be given by

$$\tilde{\Phi} = \frac{w}{n} N \frac{\partial \tilde{c}}{\partial y} \quad (12)$$

where as before w is the length of the electrode along the direction of observation. An explicit expression for the derivative can be obtained from eq 5 above, namely

$$\frac{\partial \tilde{c}}{\partial y} = A^* \{-(j\omega/D)^{1/2}\} \exp[-(j\omega/D)^{1/2}y] \exp(j\omega t) =$$

$$-A^* (\omega/D)^{1/2} \exp[-(\omega/2D)^{1/2}y] \exp[j\{\omega t + y(\omega/2D)^{1/2} + \pi/4\}] \quad (13)$$

It becomes evident from this analysis that, for a single species, the modulated absorption and beam deflection for this parallel geometry are $\pi/4$ out of phase with respect to one another, as specified in eqs 11 and 13, respectively. Most importantly, it suggests that judicious adjustment of the phase would lead to enhanced detection of solution-phase species involved in redox processes, according to their respective absorptive, refractive, and mass transport characteristics.

In the case of a redox system consisting of a reduced and oxidized soluble species, an additional term should be added to eq 12 to account for refractive effects due to the second species, as discussed by Barbero et al.¹³ for dc beam probe deflection measurements. On this basis, the modulated signal will be proportional to the difference between two terms of the form given in eq 13, namely

$$\tilde{\Phi} \cong \frac{w}{n} N_R \frac{\partial \tilde{c}_R}{\partial y} - \frac{w}{n} N_P \frac{\partial \tilde{c}_P}{\partial y} = \frac{w}{n} N_R A_R^* (\omega/D_R)^{1/2} \times$$

$$\exp[-(\omega/2D_R)^{1/2}y] \exp[j\{\omega t + y(\omega/2D_R)^{1/2} + \pi/4\}] -$$

$$\frac{w}{n} N_P A_P^* (\omega/D_P)^{1/2} \exp[-(\omega/2D_P)^{1/2}y] \exp[j\{\omega t + y(\omega/2D_P)^{1/2} + \pi/4\}] \quad (14)$$

where $N_R = \partial n/\partial c_R$ and $N_P = \partial n/\partial c_P$.

For the case in which $D_R = D_P$, eq 14 reduces to

$$\tilde{\Phi} \cong \frac{w}{n} (N_R - N_P) A^* (\omega/D)^{1/2} \exp[-(\omega/2D)^{1/2}y] \times$$

$$\exp[j\{\omega t + y(\omega/2D)^{1/2} + \pi/4\}] \quad (15)$$

for which the phase is the same as that for a single species. Under

(11) Sagara, T.; Wang, H. X.; Niki, K. *J. Electroanal. Chem.* **1994**, 364, 285–288.

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these specific conditions, a signal will be detected provided N_R and N_P are different.

COMPARISON WITH EXPERIMENTAL DATA

The simple model presented in the previous section provides a theoretical foundation for a series of experimental observations reported by various authors as will be discussed in detail below.

1. Potential Modulation for Normal Incidence. Sagara et al.¹⁴ and much earlier Pons and co-workers¹² introduced a spectroelectrochemical ac voltammetry method to measure rates of heterogeneous electron-transfer reactions involving solution-phase species. The equations derived by these authors reduce to those in section a above, assuming, as the theory developed in this paper requires, that the reaction be controlled purely by diffusion. Under such conditions, capacitive effects are ignored and the magnitudes of the rate constants for electron transfer are regarded as effectively infinite. As shown in eq 9, the modulated optical signal is $-\pi/4$ out of phase with respect to the applied potential.

In another series of experiments, Sagara and co-workers¹¹ reported changes in the amplitude of the optical response induced by modulation of the applied potential as a function of the phase angle for a system consisting of adsorbed cytochrome c_3 on Ag and methyl viologen in aqueous solution. In the case of adsorbed species, and assuming once again that the rate constants for electron transfer are infinitely large, the optical response in the absence of solution-phase species would be precisely in phase with the applied potential in the voltage range in which the actual reaction occurs. On this basis, it becomes possible to discriminate between signals derived from adsorbed and solution-phase species even if the standard redox potential is the same. In fact, Sagara, using the so-called phase shift technique, obtained enhancements in the electroreflectance response to either cyt c_3 or MV by simply adjusting the phase.

2. Potential Modulation Absorption: Parallel Geometry. McCreery and co-workers^{15,16} performed square wave potential modulation experiments involving the reduction of 1.36 mM TAA in acetonitrile (AN) solutions using a lock-in amplifier (LIA) and a HeNe laser beam oriented parallel to the electrode surface. As described by these authors, the LIA phase referenced to the potential modulation wave had to be adjusted to achieve maximum amplitude as y was varied. Comparison of these values with those calculated using the phase angle expression shown in Table 1 yielded for a frequency of 5 Hz were found to be in excellent agreement. In fact, regression analysis of theoretical versus experimental values yielded a linear correlation with a slope of 0.997 and $R = 0.986$. (see Figure 1, panel A). Also, the amplitude as a function of distance, calculated from eq 11, reproduced quite well the experimental data, as shown in Figure 1, panel B.

In a different set of measurements involving the same experimental arrangement, McCreery and co-workers¹⁶ detected a modulated photomultiplier response while applying a square wave potential to a Pt electrode in AN solutions containing *p*-benzoquinone (pBQ) in a range in which pBQ reduces to generate the corresponding hydroquinone (HQ). Since pBQ and HQ do not

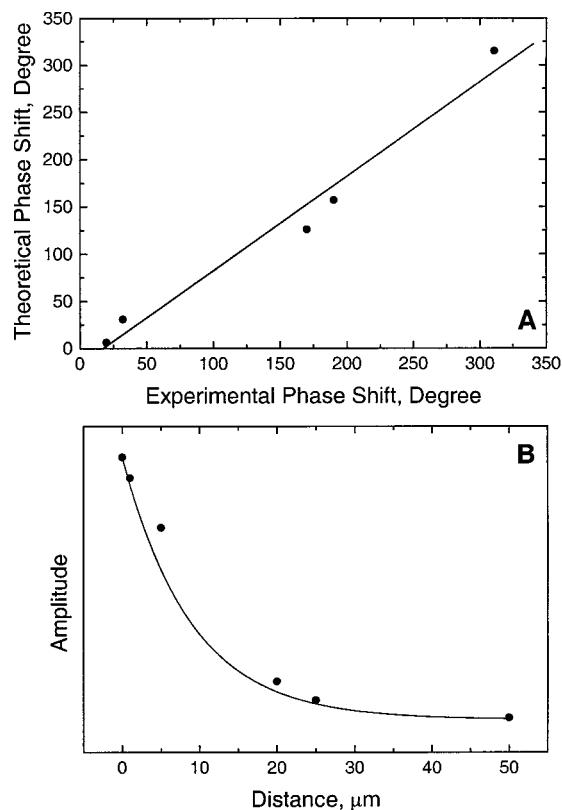


Figure 1. Correlation plot of the calculated and observed phase angles¹⁶ (panel A) and amplitude of the modulated response as a function of distance from the electrode (panel B), where solid circles represent the experimental data¹⁶ and the solid line the calculated curve.

absorb at 633 nm this effect was attributed to changes in the index of refraction of the solution induced by concentration gradients generated by the redox reaction at the interface. On the basis of these observations, these workers monitored the LIA response in solutions containing both Trianisylamine (TAA) and pBQ, for $[pBQ]/[TAA] = 10$ over the potential region embracing the E° of the two redox couples. The results obtained allowed the response of each of the redox couples to be detected based on their different LIA phases. In the case of 0.66 mM TAA and 10 mM pBQ AN solutions, the difference in the phase was found to be $\sim 30^\circ$ for $\nu = 5$ Hz and $y = 3 \mu\text{m}$. According to the data reported in the literature,¹⁷ the values of the diffusion coefficients for pBQ and the reduction product HQ are virtually identical and therefore eq 15 is applicable. Since a signal was experimentally observed, it can be assumed that N_R is different from N_P . A simple calculation using the above equations using values of 1.25×10^{-5} and $2.7 \times 10^{-5} \text{ cm}^2/\text{s}$ for the diffusion coefficients^{15,18} of TAA and pBQ, respectively, the distance between the probe beam and the electrode surface, $3 \mu\text{m}$ and a frequency of 5 Hz, leads to a phase difference of 30.5° between the two signals, which assuming that the charging current were small in these experiments, is in remarkable agreement with the experimental result.

3. Potential Modulation Beam Deflection. Pawliszyn and co-workers¹⁹ measured the amplitude of the beam deflection, A_{bd} ,

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(17) Yasukawa, T.; Uchida, I.; Matsue, T. *Biophys. J.* **1999**, 76, 1129.

(18) Rees, N. V.; Alden, J. A.; Dryfe, R. A. W.; Coles, B. A.; Compton, R. G. *J. Phys. Chem.* **1995**, 99, 14813.

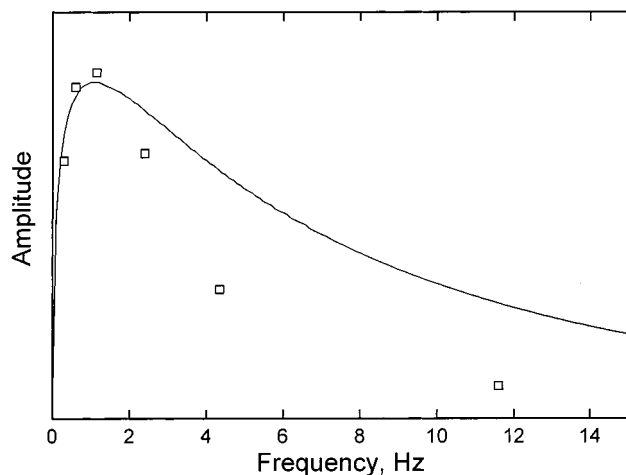


Figure 2. Experimental points¹⁹ (squares) and theoretical curve (solid line) for amplitude of the deflection modulated response vs frequency.

as a function of frequency ν ($= \omega/2\pi$) upon application of a repetitive double potential step perturbation to an electrode immersed in a DMSO solution containing 0.6 mM pBQ in 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). For the laser beam placed 25 μm away and parallel to the electrode surface, a plot of the amplitude versus ν yielded a clearly defined maximum at $\nu \sim 1.5$ Hz (see scattered points, Figure 2). This behavior is also reproduced semiquantitatively, by the theory (see solid line, where the amplitude of the maximum was adjusted to fit the experimental data) using $y = 25$ μm and a value of $D = 2.7 \times 10^{-5}$ cm^2/s , reported in aqueous solutions, common to both species (see above). Also in accordance with theory is the dependence of A_{bd} on y (see Figure 3, panel A), calculated for $\nu = 2.5$ Hz, which appears to be the same as that used experimentally, as well as that of the phase φ with ν (Figure 3, panel B), assuming that the data in the bottom panel of Figure 2, ref 19, was measured as a lagging shift.

CONCLUDING REMARKS

The mathematical formalism presented in this work affords a basis for the rigorous analysis of a variety of in situ ac-modulated spectroelectrochemical measurements based on phase-sensitive detection. In particular, it enables, in certain cases, the response of individual species in mixtures containing two or more solution-phase constituents involved directly or indirectly in an electrochemical process to be isolated. Such unique virtues are derived from the explicit dependence of the phase on the diffusion coefficient, as shown in Table 1, provided the diffusion coefficients for the species in question are sufficiently different and afford, in addition to the applied potential and the energy of the probing beam, a new dimension to enhance specificity. Although the number of experimental illustrations reported in the literature is rather limited, the availability of a solid theoretical foundation will make it possible to expand the applicability of these methods to a wider range of problems.

ACKNOWLEDGMENT

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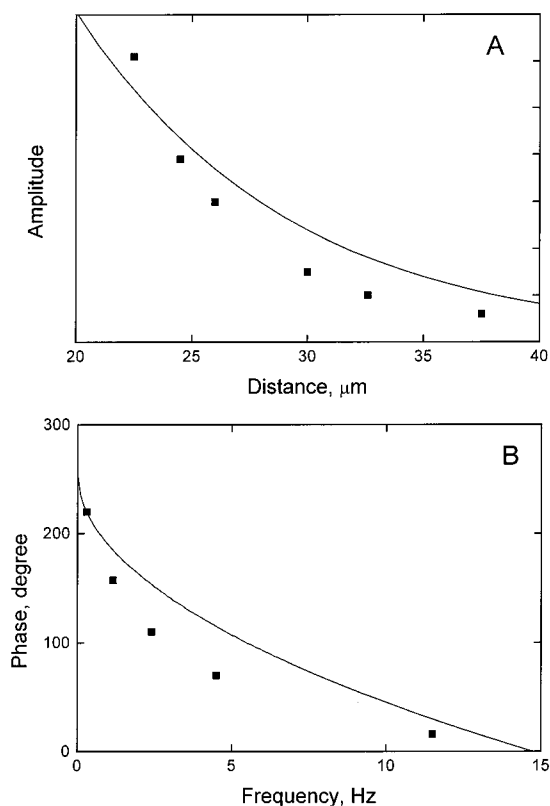


Figure 3. Experimental points¹⁹ (squares) and theoretical curves (solid lines) for (A) amplitude vs distance of the probe beam from the electrode surface and (B) phase shift of the deflection-modulated response vs frequency.

wish to express their appreciation to Prof. H. Finklea for his insightful comments.

APPENDIX I

According to Fick's second law, diffusion to an infinite plane electrode in a stagnant medium can be expressed as

$$\frac{\partial c(y,t)}{\partial t} = D \frac{\partial^2 c(y,t)}{\partial y^2} \quad (16)$$

Consider, as before, solutions of $c(y,t)$ of the form

$$c(y,t) = \bar{c}(y,t) + \tilde{c}(y,t) = \bar{c}(y,t) + A^* \Psi(y) \exp(j\omega t) \quad (17)$$

Hence, upon replacing this expression into eq 16, one obtains a new differential equation

$$\frac{\partial^2 \Psi}{\partial y^2} - \frac{j\omega}{D} \Psi = 0 \quad (18)$$

with the boundary conditions $\psi = 1$ at $y = 0$ and $\psi = 0$ as $y \rightarrow \infty$. This equation can be solved analytically to yield

$$\Psi(y) = \exp[-(j\omega/D)^{1/2} y] \quad (19)$$

after using the boundary conditions specified.

APPENDIX II

In the case of very fast heterogeneous electron-transfer reactions, the applied potential prescribes the ratio of concentra-

tions of reactants and products through the Nernst equation. For perturbations of very small amplitude, this equation can be linearized, to yield an expression that relates the amplitudes of the applied potential E^* and those of the concentrations of R and P, A_R^* and A_P^* , respectively, i.e.

$$E = \bar{E} + \tilde{E} = E_{dc} + E^* \exp(j\omega t) \quad (20)$$

where

$$E_{dc} = E^{o'} + \frac{RT}{nF} \ln \frac{\bar{c}_R(0,t)}{\bar{c}_P(0,t)} \quad \text{and} \quad E^* = \frac{RT}{nF} \left(\frac{A_R^*}{\bar{c}_R(0,t)} - \frac{A_P^*}{\bar{c}_P(0,t)} \right) \quad (21)$$

Because of conservation of mass at the electrode surface

$$D_R \frac{\partial c_R(y,t)}{\partial y} \Big|_{y=0} = -D_P \frac{\partial c_P(y,t)}{\partial y} \Big|_{y=0} \quad (22)$$

and, thus, by replacing concentrations by the expressions in eqs 2 and 5,

$$A_P^* = -A_R^* \xi \quad (23)$$

where $\xi = (D_R/D_P)^{1/2}$; hence, it becomes possible to express either one of the A_i^* coefficients in terms of E^* , to yield

$$E^* = \frac{4RTA_R^*}{nFc_R^0} \cosh^2 \left(\frac{a}{2} \right) \quad (24)$$

where c_R^0 is the bulk concentration of the reactant, $a = (nF/RT) \cdot (E_{dc} - E_{1/2})$, and $E_{1/2} = E^{o'} + (RT/nF) \ln(D_P/D_R)^{1/2}$.

The current density associated with the faradaic process is related to the flux of material at the electrode surface via the expression

$$i(\omega t) = -nFD_R \frac{\partial c_R}{\partial y} \Big|_{y=0} = nFA_R^* (j\omega D_R)^{1/2} \exp(j\omega t) = nFA_R^* (\omega D_R)^{1/2} \exp[j(\omega t + \pi/4)] = -nFA_P^* (j\omega D_P)^{1/2} \times \exp(j\omega t) = -nFA_P^* (\omega D_P)^{1/2} \exp[j(\omega t + \pi/4)] \quad (25)$$

where A is the area of the electrode and eq 21 was used. Hence, from eqs 8 and 9, the faradaic current and the optical response are 90° out of phase with respect to one another. Furthermore, the ratio of the magnitudes of the current and reflectance signal induced by the modulated applied potential is given by

$$\frac{|i(\omega t)|}{|I(\omega t)|} = \frac{nF\omega}{2\epsilon k} \quad (26)$$

i.e., for a fixed perturbation frequency, the faradaic current and optical responses are proportional to each other as found before by Hinman et al., using a different approach.¹² In the case of solution-phase redox couples involving at least one UV-visible chromophore, these considerations afford a basis for implementing a spectroscopic analogue of a highly sensitive electrochemical technique known as ac voltammetry.⁹ This method relies on the superposition of an ac signal of small amplitude onto a slow linear potential scan, while the amplitude of the current response is monitored. Although restricted to optically absorbing species, this spectroscopic approach offers a definite advantage over current measurements in that the response is not affected by contributions to the electrical signal derived from other sources, particularly, double-layer capacity effects.

By replacing A_R^* from eq 20, the current, as derived by Schmidt following a different route,⁹ becomes

$$i = \frac{n^2 F^2 (\omega D_R)^{1/2} c_R^0 E^*}{4RT \cosh^2(a/2)} \exp[j(\omega t + \pi/4)] \quad (27)$$

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