for probing diffusion layers in electrochemical processes for systems containing no chromophores. It would be advantageous to use the absorbance measurement methods for studying systems containing electrogenerated chromophores, as McCreery and co-workers (*10*) pointed out. In fact the deflection of the very same laser beam can provide absorbance information if an additional modulated excitation beam irradiates the interphase. The species forming the gradient absorb the excitation beam and, after the relaxation process, form a temperature gradient proportional to molar absorptivity and the concentration gradient magnitude. This method is capable of providing selective and localized information about gradients. Only the cross-section area between probe and excitation beam will contribute to the modulated signal and only the gradients formed by the species absorbing the excitation beam will be probed (*23, 4*).

Another important conclusion can be associated with the high sensitivity of the technique with respect to concentration gradients. Any concentration gradient formed above the surface studied with photothermal deflection spectroscopy (PDS) will produce a deflection signal and therefore will contribute to the total signal or noise depending on its correlation with the excitation beam modulation. For example, one can envision a situation where the photochemical reaction or photodesorption occurs at the surface. This will produce a concentration gradient of the products above the surface. This gradient will deflect the laser beam in a similar fashion to temperature gradients produced during PDS experiments. This effect will enhance or decrease the PDS signal depending on the orientation of appropriate refractive index gradients.

This conclusion is not limited entirely to the surface PDS experiments but also applies to other photothermal techniques such as thermal lensing or PDS in homogeneous gas or liquid solutions. In fact any concentration gradient present in the investigated system will deflect any light beam. On the other hand, careful investigation can supply additional chemical information about the system when accounting for this effect.

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Selective Observation of Concentration Gradients by the Laser Beam Deflection Sensor Applied to in Situ Electrochemical Studies. A Novel Approach

Sir: A laser beam passing through a transparent medium which is characterized by the refractive index gradient dn/dx, undergoes deflection θ (mirage effect) (*1, 2*)

$$\theta = (d/n)\, \mathrm{d}n/\mathrm{d}x \qquad (1)$$

where n is a refractive index of the medium and d is a path length of the laser beam through the gradient.

Boccara and collaborators used this phenomenon to propose a photothermal deflection technique (PDS) (*1, 2*). PDS is based on the photothermal effect following an optical excitation of a compound. If the fluorescence quantum yield of the excited compound is low, the excitation energy will be released in the form of heat through the radiationless transition to the ground state. Generated heat will produce a temperature gradient in the medium and therefore a refractive index gradient: $dn/dx = (dn/dT)(dT/dx)$. The PDS method has been shown to be useful in obtaining spectroscopic information of a material present at the surface (*2–7*). It has been used for opaque materials, solid–gas interfaces, and solid–liquid interfaces. Recently, the technique has been used to study the corrosion products produced at the semiconductor–electrolyte interface (*8, 9*). The technique was shown to be more sensitive than most other techniques based on photothermal effects (*1*).

Electrochemists have constantly been looking for in situ techniques to study the electrode surface as well as the species present in the diffusion layer as a result of an electrochemical reaction (*10*). Optical methods (*10*) as well as techniques related to the photothermal effects (*11–16*) have been used for this purpose. Most optical techniques require well-defined electrode surfaces and elaborate optics. For high surface area electrodes, techniques such as photoacoustic spectroscopy or those involving piezoelectric detection have been used (*11–16*).

A refractive index gradient will be generated in the presence of not only temperature but also concentration gradients: $dn/dx = (dn/dc)(dc/dx)$. Concentration gradients are formed during many chemical processes. Investigations of these concentration gradients can provide qualitative and quantitative information about the chemical system and the process. We recently described the experiment in which we monitored concentration gradients formed during the electrochemical process in the diffusion layer above the electrode surface (*17*). During these investigations, a laser probe beam was propagating in parallel, close to the electrode surface. Deflection of the laser beam provided information about the magnitude of refractive index gradient present in the solution above the electrode. This gradient resulted from the contribution of the components due to products and substrates present in the diffusion layer. Therefore, observation of one component was impossible unless all other species were insoluble in an electrolyte. In the present paper we introduce a method which allows selective monitoring of electrochemical species based on their spectroscopic properties.

In our investigations we chose *p*-benzoquinone (BQ) in a dimethyl sulfoxide (Me_2SO) solution for this preliminary study, since its electrochemistry is reasonably well understood (*18–23*) and also its first electron transfer product, anion radical, is known to absorb in the visible region (*24–28*). The spectra of its anion radical and its protonated free radical (see below) have been recorded in protic media employing pulse radiolysis (*25–29*) or other methods (*24*).

EXPERIMENTAL SECTION

An appropriate amount of BQ (Eastman Organic's Reagent Grade) was dissolved along with tetra-*n*-butylammonium perchlorate (TBAP; Southwestern Analytical, Austin, TX, polarographic grade) in Me_2SO (Mallinkrodt's reagent grade). TBAP (0.10 M) was used as a supporting electrolyte. Solutions were deaerated by bubbling with Ar gas and then blanketed during experiments. The electrochemical cell body was made of Teflon with two quartz windows on both sides to allow the probe laser beam to monitor the refractive index gradient above the electrode and a third quartz window on the top of the cell for the excitation beam. The cell had a flat platinum working electrode, a silver wire pseudoreference electrode, and a platinum wire counter electrode. The working electrode (5 mm × 20 mm) was prepared by sputtering platinum onto the quartz slide substrate under reduced pressure. Cyclic voltammograms were recorded with a Stonehart Associates, Inc. (Madison, CT), Model BC-1200 potentiostat along with a Princeton Applied Research Model 175 universal programmer.

Figure 1 represents the experimental arrangement used for the cyclic voltametric as well as the laser beam deflection experiments.

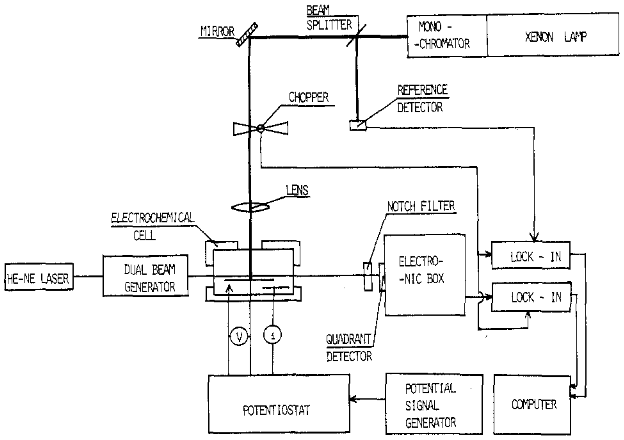

Figure 1. Block diagram of the experimental setup.

In this arrangement, we used a dual beam deflection sensor described in detail elsewhere (*30*). When the He–Ne laser was turned on, the two focused parallel beams separated from each other by 2.5 mm were produced in the dual beam generator. These probe and reference beams entered the electrochemical cell mounted on an X-Z-tilt positioner. The reference beam was used to compensate for mechanical vibrations, laser pointing instability, and intensity fluctuations. As mentioned above, the electrochemical cell was equipped with windows, allowing the laser beams to probe the solution close to the platinum surface. Both laser beams were focused at about 25 μm above the electrode to a spot size of about 50 μm in diameter. Special care was taken to place both beams in the same distance in respect to the electrode surface. The excitation beam modulated at a frequency of 10 Hz was focused to a spot of about 2 × 1 mm on the surface of the electrode just below the probe laser beam but away from the reference laser beam. Meanwhile the electrode potential was modulated between −0.30 V and −0.50 V in a triangular mode with the sweep rate of 5 mV/s. The laser beam deflection was sampled at the potential of −0.50 V during each cycle. The position of the probe and the reference beams was monitored with a one quadrant detector working as a dual bi-cell. The signal was analyzed and collected with a lock-in analyzer (Model 5204 Princeton Applied Research, Princeton, NJ) and a microcomputer. The instability in the xenon lamp intensity was measured with a reference photocell and is accounted for in the calculations. On the basis of these data, the amplitude and phase of the signal were calculated. The wavelength of the excitation beam was varied in order to obtain the visible spectra of the electrochemical species forming the concentration gradients above the electrode surface. The spectral bandwidth of monochromator was 5 nm. The dual beam apparatus was mounted on a vibration isolated laboratory table.

THEORETICAL SECTION

As was mentioned above, a probe laser beam passing through the concentration gradient that is present in the transparent medium will undergo deflection

$$\theta = (d/n)(dn/dc)dc/dx$$

Morever an additional deflection signal can be expected if the excitation beam absorbed by the species forming the concentration gradient irradiates uniformly the medium. This effect will arise due to the uneven distribution of the absorbing species in the medium. The amounts of energy absorbed and then released as heat, during the dark relaxation process, will differ with the concentration. Therefore a temperature gradient profile corresponding to the concentration gradient will be produced. For example, when a pulsed excitation beam of intensity I_0 (J/cm^2 per pulse) is used then

$$\frac{dT}{dx} = Z\frac{I_0}{C_h\rho}\epsilon_\lambda\frac{dc}{dx} \tag{2}$$

where Z is coefficient describing the fraction of absorbed energy converted to heat, C_h is the specific heat of the medium

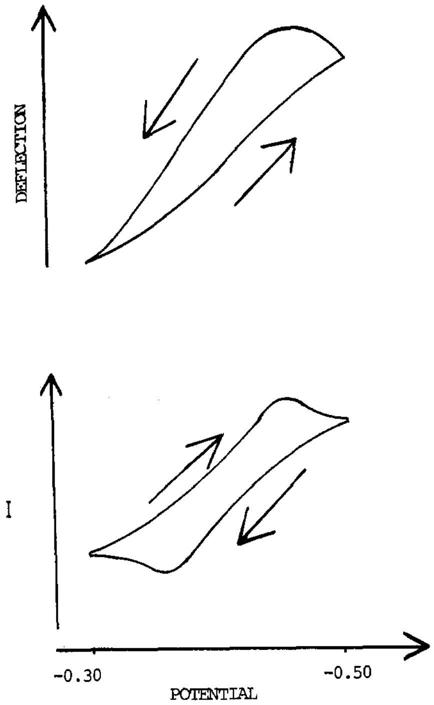

Figure 2. Cyclic voltammogram and deflection signal recorded on an oscilloscope. The lower trace is the cyclic voltammogram of 6.3 mM BQ in Me_2SO recorded at a scan rate of 5 mV/s. The upper trace is the corresponding laser beam deflection signal at an excitation beam wavelength of 470 nm.

in J/(g·deg), ρ is the density of the medium in g/cm^3, and ϵ_λ is the molar absorptivity in L/(cm·mol). This temperature gradient will form the periodic refractive index gradient dn/dx which will deflect the laser beam by θ' (*28*)

$$\theta' = \frac{d}{n}\frac{dn}{dT}Z\frac{I_0}{C_h\rho}\epsilon_\lambda\frac{dc}{dx} \qquad (3)$$

The modulated deflection signal θ', corresponding to pulsing frequency, is expected to increase proportionally with molar absorptivity and the concentration gradient magnitude. In formula 3 we assumed uniform irradiation of the concentration gradient by the pulsed light source. Therefore no significant light intensity gradient in the deflection direction can exist in the medium. This condition will hold for low concentrations of the absorbing species and/or appropriate geometry of the experimental arrangement.

In our experiments we generate the concentration gradients above the electrode during cyclic voltametric experiments. In some cases we hold dc/dx constant by monitoring deflection at the same potential during the cycle. While varying the wavelength of the excitation beam, in order to collect the absorption spectrum of the product. In others we monitor changes of the signal at the same wavelength (ϵ_λ constant) which provides information about the variation in the concentration gradient magnitude of electrogenerated species which absorb at this wavelength. The modulated deflection signal arises at the cross section of the excitation and probe beam and therefore describes the system at this particular place.

The condition requiring low concentration of the product holds in our experiments since the average concentration of the $BQ^-\cdot$ is about 10^{-3} M. Additionally, the electrode surface works as a mirror and therefore helps the uniform irradiation of the concentration gradients.

RESULTS AND DISCUSSION

Figure 2 shows a typical response of the system recorded on an oscilloscope for an excitation wavelength of 470 nm. The lower curve shows a cyclic voltammogram, whereas the upper curve represents the laser beam deflection signal. While the cyclic voltammogram has some ohmic component due perhaps to the unfavorable cell geometry used for this study, it shows a reversibility of the BQ reduction. The deflection signal, on the other hand, reflects the concentration profile of the electrogenerated species ($BQ^-\cdot$) very closely with some time delay.

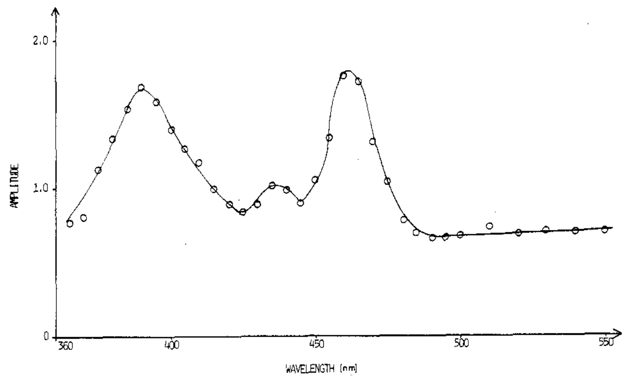

Figure 3. Laser beam deflection absorption spectrum recorded during the scan at an applied potential of -0.50 V vs. a Ag wire pseudoreference electrode.

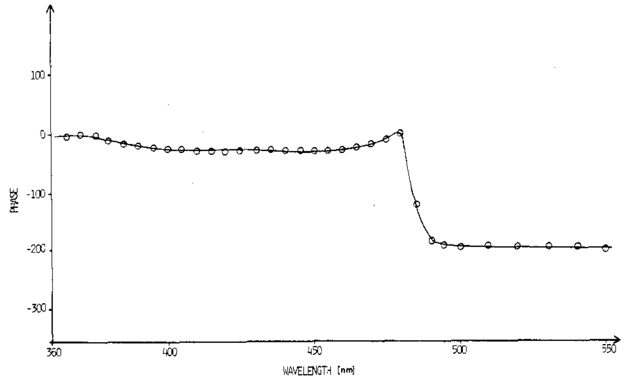

Figure 4. Phase component of the laser beam deflection signal vs. wavelength. See Figure 3 for experimental conditions.

The spectral region covering 360–550 nm is scanned with the modulated excitation beam, which results in a spectrum shown in Figure 3. These data are collected during the cyclic voltammetric experiment at a potential of −0.5 V. The spectral feature shown here indicates that there are two products electrogenerated giving a transition at about 400 nm and one at about 460 nm, respectively. Also, a large background signal is noted beyond 490 nm which is attributed to the absorption of the electrode. Further, it is realized in Figure 4 that the background signal is accompanied by a large phase shift.

p-Benzoquinone is generally recognized to undergo an ece (electrochemical–chemical–electrochemical) reaction when reduced in nonaqueous media (*18–23*), i.e.

$$BQ + e^- \rightleftharpoons BQ^-\cdot \qquad (1)$$

$$BQ^-\cdot + H^+ \rightarrow BQH\cdot \qquad (2)$$

$$BQH\cdot + e^- \rightleftharpoons BQH^- \qquad (3)$$

and

$$BQH^- + H^+ \rightarrow BQH_2 \qquad (4)$$

We believe that spectra of two consecutive products, i.e., $BQ^-\cdot$ and $BQH\cdot$, are shown in Figure 3. For the time spent recording the spectrum, it is not unreasonable to produce a protonated species from $BQ^-\cdot$. The peak at around 460 nm and its vibrational feature at about 435 nm are in excellent agreement with those reported in the literature for $BQ^-\cdot$ with the exception of a large red shift in our spectrum (*24–29*). Further, the peak at about 400 nm is in agreement with those reported for the free radical, which was generated by pulse radiolysis of BQ in water of pH 2.0 (*25*). The assumption there was that the anion radical produced would protonate quickly to give $BQH\cdot$. A large red shift seen in our $BQ^{-}\cdot$ peak can be explained by the lack of the hydrogen bonding in Me_2SO. It has been shown that a large blue-shift is observed for the anion radical of 9,10-anthraquinone due to the hydrogen bonding (*32*). The spectral shift may not be as important for the free radical, however, as for $BQ^{-}\cdot$, since the former does not carry a charge on it. The absorption maxima are believed to arise from the $\pi \rightarrow \pi^*$ transition, and spectral features are due to the C–O stretching vibration in the excited state (*33*).

It is interesting to note the large phase shift around 480 nm. The signal attributed to concentration gradients corresponding to electrogenerated species is characterized by a phase close to zero, while the signal due to platinum absorption has a phase close to −200. After the excitation occurs, some time passes before the heat will diffuse from the platinum surface into the area where the laser probe beam is located. However, the temperature gradient due to the products and substraces, which are present on the probe laser path, is generated almost immediately after the excitation (limited only by the relaxation time of the species). The magnitude of the phase difference corresponds to the distance of the surface from the center of the laser probe beam. The sign of it will indicate its location above or below the probe beam.

In conclusion, in this paper we described a selective method which allows us to monitor the electrode process in situ. We are able to distinguish between a signal originating at the surface from that due to a dissolved product on the basis of signal phase. The electrogenerated species are detected in the form of the concentration gradients. This technique provides spacially resolved information since only the concentration gradients in the intersection volume between probe and excitation beams will contribute to the modulated signal characterized by the phase 0. It should be pointed out that in formula 3 the deflection signal is not proportional to magnitude of the concentration but rather to the concentration gradient. Therefore, the higher the gradient, the lower the molar absorptivity which can be measured.

Since this paper describes a new effect which relates to the presence of concentration gradients in the analyzed systems, the authors would like to direct the attention of the investigators using other photothermal techniques such as photothermal deflection spectrophotometry (PDS), thermal lens spectrophotometry (TL), and photoacoustic spectroscopy (PA) to their findings. Any concentration gradient formed by absorbing species which is present in the system or is generated during the experiment, will produce a temperature gradient after excitation and therefore contribute to appropriate signal. This effect can be regarded as a noise, but in fact it can provide additional information about the system.

Registry No. BQ, 106-51-4; $BQ^{-}\cdot$, 3225-29-4; $BQH\cdot$, 68825-65-0.

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