perature sensitive. Both electrode pairs show approximately the same thermal hysteresis.

The E–T patterns obtained with the fluoride and the glass (H^+) electrodes of the combination type, are shown in Figure 5. It can be seen that the fluoride electrode shows a heavy thermal hysteresis, whereas the glass electrode shows a thermal hysteresis dependent on the actual pH of the solution.

It should be noted that E–T patterns should always be obtained under fixed temperature cyclic change in order to obtain reproducible patterns appropriate for comparison of the thermal drift performance of each membrane electrode–reference electrode pair. Also, meaningless E–T patterns will result if there is a potential drift not attributable to temperature changes (i.e., if the potential has not been stabilized during the $t_0 - t_1$ period).

CONCLUSIONS

The thermal hysteresis of membrane electrode–reference electrode pairs expressed in terms of the potential–temperature pattern obtained during a fixed cyclic temperature change should be considered as a valuable quality characteristic for the particular potentiometric sensor system. An electrode pair with significant thermal hysteresis (broad E–T pattern), should be considered as a "slow" transducer, and a low sample throughput should be expected with direct potentiometric measurements, because more time for thermal equilibration is needed.

In the case of reference electrodes one of the primary constructional targets is always a small temperature coefficient. This fact ensures a small contribution of the reference electrode to the observed thermal hysteresis of the whole electrochemical cell. Therefore, thermal hysteresis is mostly attributed to the membrane electrode and must be considered as a constructional characteristic dependent not only on the type of the sensing membrane but also on the heat capacity and the thermal conductivity of the various compartments and internal solutions of the electrode body. Probably, miniaturization of the membrane electrodes will greatly improve their thermal hysteresis characteristics.

Registry No. SCN^-, 302-04-5; F^-, 16984-48-8.

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Observation of Concentration Gradients by the Laser Beam Deflection Sensor

Sir: Laser beam deflection and lensing methods have been used extensively to probe refractive index gradient (mirage effects) due to temperature gradients. Recently developed photothermal deflection (PTD) and thermal lensing techniques are based on this principle (*1*). In these techniques, the temperature gradient is produced in a medium when absorption of photons by molecules in the medium, or on the surface, occurs subsequently followed by thermal relaxation. A corresponding refractive index gradient is formed since the refractive index is temperature dependent.

A refractive index gradient can be created by using other conditions affecting this physical property, i.e., a concentration gradient of a solute in a medium (*2, 3*). The mirage effect produced by this phenomenon can then be observed employing the laser beam deflection sensor. The magnitude of this effect will depend on the chemical system, the medium, and the solute.

In many analytical processes, concentration gradients are formed. Having a sensitive tool to measure these gradients could, in some cases, improve sensitivity of quantitative determinations and provide additional information about the chemistry involved (*4*). For instance, in chromatographic techniques, separation occurs between the concentration gradient signals of various components of an analytical mixture (*5, 6*). In electrochemical experiments, concentration gradients of both reactants and electrogenerated products are formed at the electrode surface (*7*). Theoretical analysis has recently been performed on the shape as well as the degree of deflection of the laser beam passing through the diffusion layer due to concentration gradients present above the electrode surface (*8*) but neither comprehensive descriptions nor any experimental results have been reported.

Concentration gradients produced during electrolysis have been studied by optical methods including interferometric techniques (*9, 10*) as well as absorbance measurements (*11*).

In this communication, we report our preliminary results of the observation of the mirage effect produced by concentration gradient. The deflection of an unabsorbed He–Ne laser beam passing parallel to the surface was monitored by using a beam position sensor. Reactants used for this study were *p*-benzoquinone, which produces a stable anion radical upon electrolysis, and oxygen producing a superoxide anion radical. Both of these radicals are transparent to the probing beam, He–Ne laser.

EXPERIMENTAL SECTION

The experimental setup consisted of an electrochemical cell, laser and laser beam position sensing device. The electrochemical cell was made of Teflon and was equipped with a rectangular (5 mm × 20 mm) platinum working electrode (platinum was sputtered on a glass slide), a silver wire pseudoreference electrode, and a platinum wire counter electrode. Quartz windows were installed on opposite sides of the cell walls to allow the laser beam to probe the solution close to the platinum surface of the working electrode. The beam had a spot size of about 50 μm. The cell was positioned by use of an X-Z-tilt stage (*12*). A laser beam (Laser Model 1303D, Uniphase, Sunnyvale, CA) was focused with a lens of *f* = 5 cm. The position of the laser beam was determined with an X-Y optical position indicator (Model UDT 431 with PIN-SC/25, United Detector Technology, Culver City, CA). A lock-in amplifier was applied to determine the amplitude of laser deflection, which was a measure of the refractive index gradient. More detailed information about the experimental setup is published elsewhere (*12*).

The solutions were prepared by dissolving 1,4-benzoquinone (Eastman Organic, reagent grade; BQ) and tetra-*n*-butylammonium perchlorate (Southwestern Analytical, Austin, TX, Polarographic grade; TBAP) in dimethyl sulfoxide (Matheson, Coleman and Bell (MCB), Spectrograde; Me_2SO). All of these reagents were used as received. In oxygen reduction experiments, the 0.1 M TBAP solution in Me_2SO saturated with oxygen was used. The surface of the solution was then blanketed with a helium gas layer above the solution by flowing it over the electrochemical cell. In all of the experiments described here, the electrode potential was modulated between −0.30 and −0.52 V for benzoquinone reductions and −0.35 and −1.40 V for oxygen reduction vs. the Ag wire pseudoreference electrode. Except in frequency dependency experiments, the potential was modulated at a frequency of 0.5 Hz in a square wave or a triangular mode, in which the potential sweep rate of 500 mV/s was used. The laser beam was passing along a shorter axis of the rectangular platinum electrode.

The experimental conditions were varied to determined their effects on the signal amplitude and the phase shift of the beam deflection. The electrode potential was controlled with a Stonehart Model BC-1200 potentiostat (Stonehart Associates, Inc., Madison, CT) along with a Princeton Applied Research (PAR) Model 175 universal programmer.

RESULTS AND DISCUSSION

The objective of this work was to investigate the laser beam deflection signal due to the concentration gradient generated by nonequilibrium chemical processes. The electrochemical experiments were chosen since concentration profiles are well-defined in double potential step experiments near the electrode surface (*7, 13*). In our experiments, we used double potential step or triangular sweep methods to generate the concentration gradient near the flat electrode surface.

Laser angular deflection due to the presence of the refractive index gradient dn/dx can be written as (*16, 17*)

$$\theta = \frac{d}{n}\frac{dn}{dx} = \frac{d}{n}\frac{dn}{dc}\frac{dc}{dx}$$

where n is a refractive index and d is the distance parallel to the surface of the electrode over which the refractive index gradient exists, and where dc/dx is produced by an electrochemical reaction O + ne = R. The sensitivity of the electrochemical reaction monitored by the laser deflection method will depend on the magnitude of the difference $dn_O/dc_O - dn_R/dc_R$. High sensitivity can be obtained when the oxidant or the reductant is insoluble and is deposited on the electrode surface. In these cases the opposing gradient would not exist. Therefore, the theoretical detection limit for this case can be calculated as

$$C_{\min} = \frac{n\theta_{\min}(\pi Dt)^{1/2}}{d(dn/dc)\exp(-x^2/4Dt)}$$

where $\theta_{\min}$ can be approximated to be 10^{-9} rad (*16*) and dn/dc = 10^{-2}/mol (*14, 15*). For our conditions (d = 0.5 × 10^{-2} m; x = 25 μm; t = 1 s), this value can be approximated to about 10^{-9} M. However, when the oxidant and reductant are both soluble, then corresponding opposing gradients are formed and the detection limit will be mugh higher. The detection limit can be related to the differences in the refractive indexes of the oxidant and reductant.

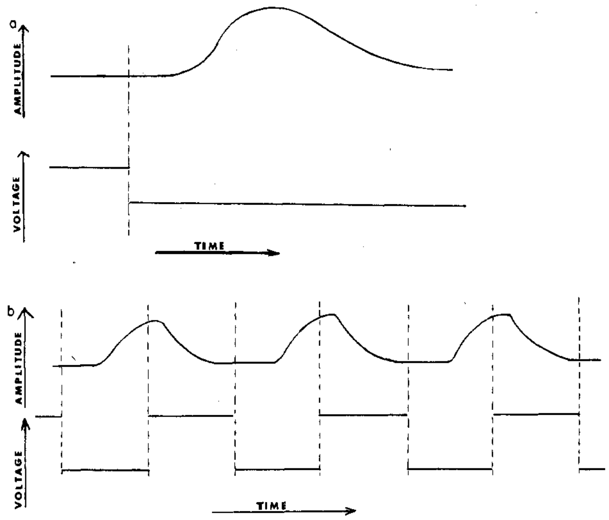

Figure 1. The laser beam deflection signal response to (a) a single potential step diffusion control experiment and (b) a repetitive potential step experiment with frequency of 0.5 Hz (pulse voltammetry experiment). A 0.10 M TBAP saturated with oxygen in Me_2SO was used for both measurements.

The beam deflection signal should decrease as a function of its distance from the electrode surface since in electrochemical experiments the concentration gradient decreases with increase in distance. The signal is also expected to decrease for an increase in electrolysis time at a given distance from the electrode since the concentration flux will be smaller for longer electrolysis times.

Two redox systems, i.e., oxygen and *p*-benzoquinone were used in this study. Both are known to undergo a reversible electrochemical reduction to produce anion radicals (*18–22*). The products of these reactions are superoxide and benzoquinone anion radicals, respectively, after a one electron reduction in Me_2SO. The superoxide radical is known to be stable for days in Me_2SO under proper conditions (*18*). The reversibility was shown in our experiments by cyclic voltammograms, in which both cathodic and anodic peaks were well-defined.

A typical response of the laser beam deflection detection system to a large magnitude single potential step is shown in Figure 1a for the superoxide formation in oxygen reduction. At the beginning, immediately after the potential step to −1.4 V, no signal was observed. This is because it takes approximately 0.5–0.6 s for the electrogenerated superoxide to reach the area through which the center of the probing beam is passing. The signal then reaches a maximum and decays. This would be expected, since at the beginning of the potential step, there would be a large flux of the product toward the bulk of the solution from the electrode surface. As the electrolysis time increases, the amount of the product increases in the probing region, but the flux would decrease due to a rather high concentration of the product accumulated in the bulk. All these are expected from the Cottrell equation (*7*).

A deflection signal obtained from the double potential step experiment for oxygen reduction is shown in Figure 1b, representing a similar behavior as in the chronocoulometric experiment. Similar signals were observed when a fast potential sweep between two potential limits is applied. Smaller signals were obtained from potential sweep experiments; the amount of products generated would be smaller in potential sweep than in double potential step experiments. However, the signal-to-noise ratio remained about the same. Similar results were obtained when *p*-benzoquinone was used as an electroactive compound.

One of the parameters that should be optimized during the experiment is the frequency of the potential modulation.

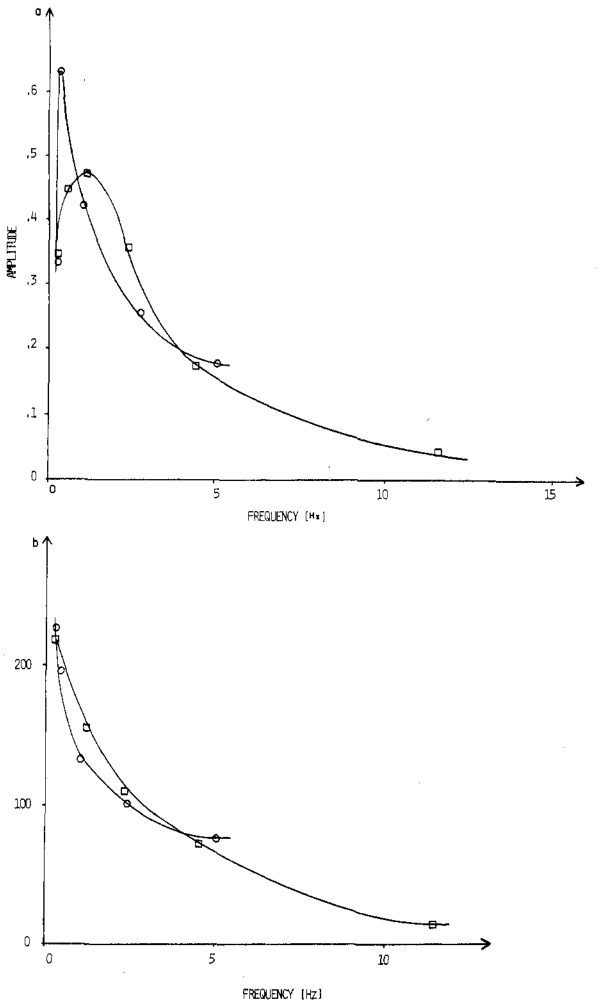

Figure 2. Amplitude (a) and phase shifts (b) of the deflection signal vs. frequency: (□) double potential step; (○) potential sweep. A 0.6 mM *p*-benzoquinone solution in Me_2SO with 0.1 M TBAP was used for these measurements.

Figure 2 presents (a) the signal amplitude and (b) the phase shift accompanying the signal detection vs. frequencies. In both cases, the signal reaches a maximum at 0.5 Hz of electrochemical modulation and then falls off for an increase in modulation frequency. The initial increase in signal is due to a decrease in the electrolysis time. Further decrease in electrolysis time leads to the reduction in the signal amplitude, because the electrogenerated product cannot even diffuse to the zone where the center of the probing beam is located. This also explains the decay of the phase shifts for the signal as a function of the modulation frequency shown in Figure 2b. The time after the beginning of the pulse until the diffusion front reaches the beam is constant and it becomes a larger fraction of the pulse duration with an increase in frequency.

Another important parameter affecting the magnitude of the signal is the distance of the center of the probing beam from the electrode surface at a given frequency. Figure 3 shows how deflection signals fall off as a function of the beam distance.

The deflection signal should be directly proportional to the concentration of an electroactive species in the solution, since in electrochemical experiments the concentration gradient dc/dx is proportional to the concentration c. In our experiments an excellent linearity is observed down to about 1×10^{-5} M, for *p*-benzoquinone reduction, which can also be regarded as a detection limit.

Finally, the loss of oxygen from its saturated Me_2SO solution was monitored for about 5 h using this technique. Dissolved oxygen would be lost through an equilibrium between the solution and the gas (helium) phase according to Henry's law. The drop of the oxygen concentration due to electrolysis may not be significant. The combined rate of the oxygen loss from solution monitored by this method is shown in Figure 4. Cyclic voltammograms were also recorded intermittently at the same electrode to check the dissolved oxygen concentration, and the detection limit using cyclic voltammetric method is indicated in the figure. Clearly, this technique has a detection limit for oxygen at least 1 order of magnitude lower than the cyclic voltammetric method.

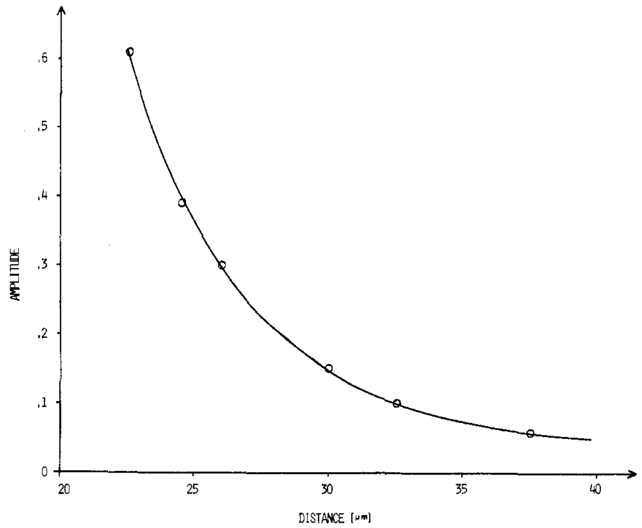

Figure 3. Amplitude of the deflection signal vs. the distance of the laser beam from the electrode surface. The solution contained 0.6 mM *p*-benzoquinone in Me_2SO.

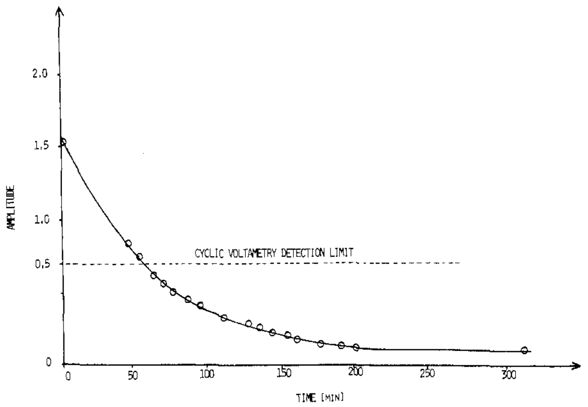

Figure 4. Observation of the O_2 concentration drop with time using a platinum electrode for oxygen reduction with the laser beam deflection detection.

In conclusion, the limit of concentration gradient detection of organic species using laser beam deflection technique can be approximated to $(dc/dx)_{min} = \theta_{min} n/[d\ dn/dc] \sim 10^{-5}$ M/m. In many physical, chemical, and biological processes the formation of the gradient occurs. Using this method, one can investigate these events.

Concentration gradients generated by electrochemical double potential step experiments were studied by use of a laser beam deflection technique. The deflection effect might be due to a consequence of the total molecular and/or ionic concentrations changes in diffusion layer during the electrode reaction. This includes the changes due to electroactive compounds and also the removal/addition of anions/cations to maintain electroneutrality in the diffusion layer. Although an accurate picture of the diffusion layer and spectroscopic information was not obtained with this experimental arrangement, the technique complements other methods. We believe that the technique discussed here should be suitable 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*)

$$\theta = (d/n)\, dn/dx \qquad (1)$$

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