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Journal of Photoacoustics

A Companion Volume to Spectroscopy Letters

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A Companion Volume to *Spectroscopy Letters*

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LASER-PIEZOELECTRIC-PHOTOACOUSTIC OBSERVATION
OF THE ELECTRODE SURFACE

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(ABSTRACT)

Preliminary spectrometric investigations of the electrode-solution interface by pulsed dye laser-piezoelectric transduced (PZT) photoacoustic spectroscopy (PAS) are described. The deposition of the radical cation bromide ($HV^{\dot{+}}Br^-$) formed on reduction of heptylviologen in aqueous solutions on a Pt electrode attached to a PZT was monitored and less than monolayer coverages of $HV^{\dot{+}}Br^-$ could be detected ($S/N = 1$). The apparatus for PZT-PAS and the nature of the PAS response upon pulsed laser excitation are described.

INTRODUCTION

Photoacoustic detection with a microphone is suitable for measurements of solid samples which have large surface-to-volume ratios, such as powders,

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in the gas phase. However, for bulk solid samples and liquids where the surface-to-volume ratio is not large, this method often does not yield good signal-to-noise (S/N) ratios. For such samples, a piezoelectric transducer (PZT) in direct contact with the samples can be used (1). As in microphone detection photoacoustic spectroscopy (PAS), the samples are irradiated with high intensity modulated light and the photoacoustic signal is detected with a phase-sensitive amplifier. Piezoelectric transducer-photoacoustic spectroscopy (PZT-PAS) offers several advantages over gas-microphone detection: a) The detection system is very simple. b) The PZT has a wide frequency response so that a modulation frequency in the megahertz range can be used, if necessary. One can also use a fast intense pulsed laser as a light source. In this case, the phase-sensitive detector is replaced by a boxcar integrator or a transient signal averager. c) The PZT can be operated over a wide range of temperatures. d) The PZT is less sensitive to air pressure fluctuations. Thus, photoacoustic measurements can be carried out in the open air without an enclosed airtight chamber; this arrangement may be useful for many practical applications, e.g. in situ measurements.

There have been many studies concerned with spectrometric investigation of the in situ electrode-solution interface, for example by specular or attenuated total reflectance methods (2-4) in attempts to obtain information about the electrode reaction mechanism or electrogenerated intermediates. Conventional absorption techniques have not been widely applicable because of difficulties in measuring the small differences in absorption between the incident and transmitted light at low surface coverages on the electrode. However, in the PZT-PAS technique, the photoacoustic signal is proportional to the intensity of the incident light. Therefore, if a laser is used as a light source, the signal can be enhanced, and PZT-PAS may become useful in the characterization of the electrode - solution interface.

A recent report from this laboratory described the application of a PZT-PAS technique to the electrode-solution interface (5). In that work

a xenon lamp-monochromator was used as a light source. This limited the sensitivity of the technique and while measurements of optical changes at the electrode surface could be made, monolayer coverages could not be detected. In this paper we demonstrate the application of a pulsed dye laser to in situ detection of monolayer coverages on electrode surfaces.

EXPERIMENTAL

Figure 1 is a block diagram of the apparatus. The laser, used as a light source, was a flash lamp-pumped pulsed dye laser (Chromatix, CMX-4). The body of the electrochemical cell was constructed from glass tubing (21 mm diameter) with a quartz window fixed to one end with silicone rubber sealant (Dow Corning). The working electrode was made of a thin platinum foil (0.1 mm thickness). The working area of the electrode was 0.4 cm^2 .

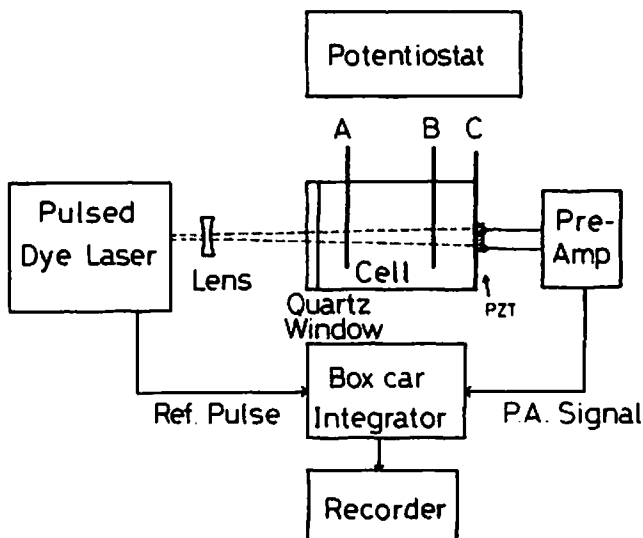


Figure 1 Block diagram of the apparatus. A: counter electrode (Pt wire), B: reference (Ag), and C: working electrode (Pt foil).

A small PZT slip (4 mm X 6 mm, Tohoku Metal Co. Ltd., N-21) was attached to the back of the working electrode with epoxy cement. In some experiments a reference platinum foil of the same size as a working electrode was placed very close to the working electrode to allow subtraction of the background photoacoustic signal caused by light absorption of a platinum foil. An identical PZT slip was also attached to the reference platinum foil. Laser light, whose beam diameter was somewhat expanded with a concave lens, irradiated both platinum foils simultaneously. The laser pulse width with Rhodamine 6G dye was ~ 1 μ sec and the pulse repetition rate was 30 Hz.

Electrochemical measurements were made with a PAR Model 173 potentiostat (Princeton Applied Research, Corp.) and a digital coulometer (PAR Model 179). A Pt counter electrode and a Ag wire quasi-reference electrode located outside of the light path, were employed in the electrochemical measurements. The photoacoustic signal produced at the PZT was measured with a boxcar integrator (Princeton Applied Research, Corp., Model CW-1) and a home-made wide band preamplifier with a gain of 30.

Chemicals

KBr (Fischer Scientific Co.) and 1,1'-diheptyl-4,4'-bipyridium dibronide (heptylviologen or HV^{2+} dibromide) (Aldrich Chemical Co.) were used as received. All solutions for electrochemical studies were prepared with twice distilled water and degassed prior to use with prepurified nitrogen.

RESULTS AND DISCUSSION

To check the behavior of the Pt/PZT electrode, the transient photoacoustic signal response in air or in water at open circuit was measured under irradiation with the pulsed dye laser. The results are shown in Fig. 2. There are two contributions to the photoacoustic signal (6): thermoacoustic and thermoelastic. The thermoacoustic signal shows a long time decay, which strongly depends upon the thermal properties of the surrounding environment

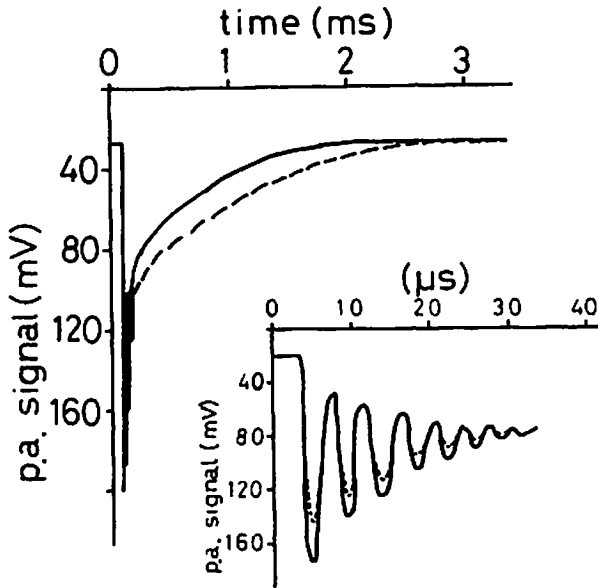


Figure 2 Transient photoacoustic response in air or in water at open circuit under irradiation with the pulsed dye laser (1 μ s). solid line: in water, broken line: in air.

and of the platinum foil and PZT. The thermoelastic signal occurred in the μ sec region and exhibited damped oscillations. When the Pt/PZT electrode was in the air, the decay component of the thermoacoustic signal was longer than that with the electrode immersed in water. This reflects clearly the differences in the thermal properties of water and air. On the other hand, the thermoelastic signal was about 20% bigger when the platinum electrode was immersed in water than that found in air. The thermoelastic signal intensity is considered to be approximately proportional to the thermal properties of the sample and the other parameters (7), as follows,

$$P_{PAS} \propto (1-R) \cdot P \cdot \tau \cdot \frac{c \cdot a}{C_p} \cdot \beta \quad (1)$$

where R is the reflectivity; P, the incident laser power; τ , laser pulse

duration; c , the velocity of the sound; α , the thermal expansion coefficient; C_p , the specific heat; β , absorption coefficient.

The increase of thermoelastic signal intensity is probably caused by the difference in reflectivity of the platinum foil in water and air, although other contributions may also exist. Thus, the two contributions to the photoacoustic signal showed different dependencies upon the surrounding environment. If the PZT is attached a few thermal diffusion lengths away from the local heated area of sample, only the thermoelastic signal should be detected. Thus, when the PZT was spaced about 1.5 mm away from the platinum foil electrode using a thicker layer of epoxy cement, and was irradiated with pulsed laser light (pulse duration 1 μ s) the thermoacoustic signal could not be detected, but a thermoelastic response was still obtained.

Measurement of an electrogenerated diheptyl viologen bromide film

A cyclic voltammogram of 2 mM HV^{2+} dibromide in 0.3 M KBr at the platinum electrode is shown in Fig. 3. The cathodic wave at -0.42 V corresponds to the one-electron reduction of HV^{2+} (5, 8-10):



and is accompanied by the characteristic deep purple color of the radical cation precipitate on the electrode surface. Reoxidation of this layer at -0.32 V vs. Ag on the return scan again produced a clean electrode surface. A single potential pulse between 0.0 and -0.45 V vs. Ag was applied to the electrode for 10 sec, and a simultaneous measurement of the electrolytic charge and the PAS signal under laser irradiation was made (Fig. 4). The PAS signal was monitored at 585 nm with a laser width of 1 μ s and a pulse repetition rate of 30 Hz. In this experiment, the time-constant of the PAS measurement was about 0.8 sec because of the response time of a boxcar integrator. The PAS signal response agreed quite well with the integrated charge and followed a $t^{1/2}$ -relation above 2 sec. The initial rise showed a somewhat different dependency because of the different time constants of the measuring systems.

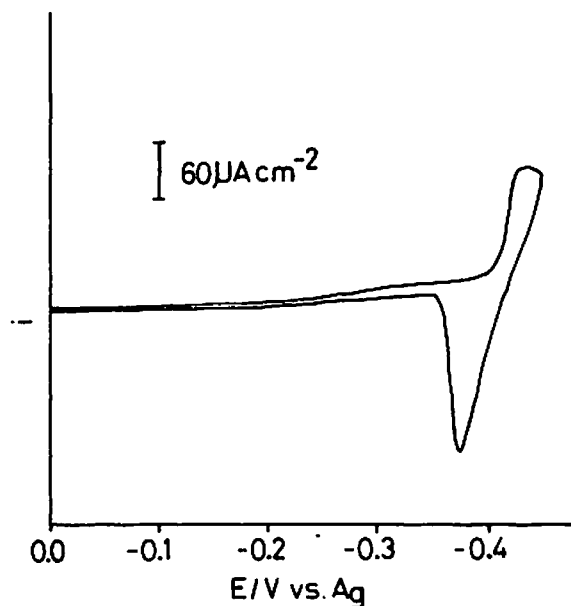


Figure 3 Cyclic voltammogram of 2 mM diheptyl viologen dibromide in 0.3 M KBr at the platinum electrode.

Another factor in the initial PAS signal is the delayed precipitation of the HV^+Br^- on generation of the radical cation, apparently because of some supersaturation (5,8). At the applied potential the electrochemical reduction of HV^{2+} is very fast and may be regarded as diffusion controlled.

The effect of film thickness on the laser photoacoustic signal was studied by changing the duration of the potential pulse applied to the electrode and determining the film thickness by measurement of the amount of charge passed with the assumption that the film thickness was uniform. The results are shown in Fig. 5. The amount of electrolytic charge was obtained by subtracting the number of coulombs needed to charge the double layer for a blank solution (0.3 M KBr solution). The PAS signal was quite linear with coverage of the film. The nonzero intercept can be attributed to either finite solubility of the HV^+Br^- or to a small amount of reaction of the film with proton or dissolved oxygen.

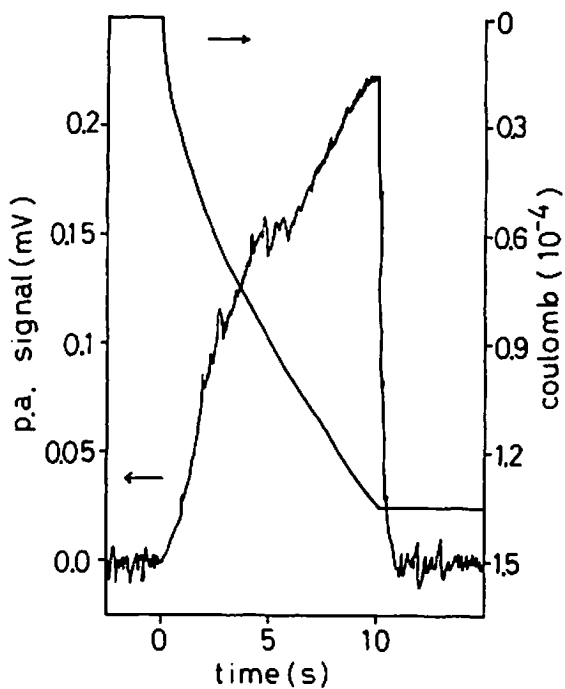


Figure 4 Simultaneous measurement of the electrolytic charge and the PAS signal under laser irradiation.

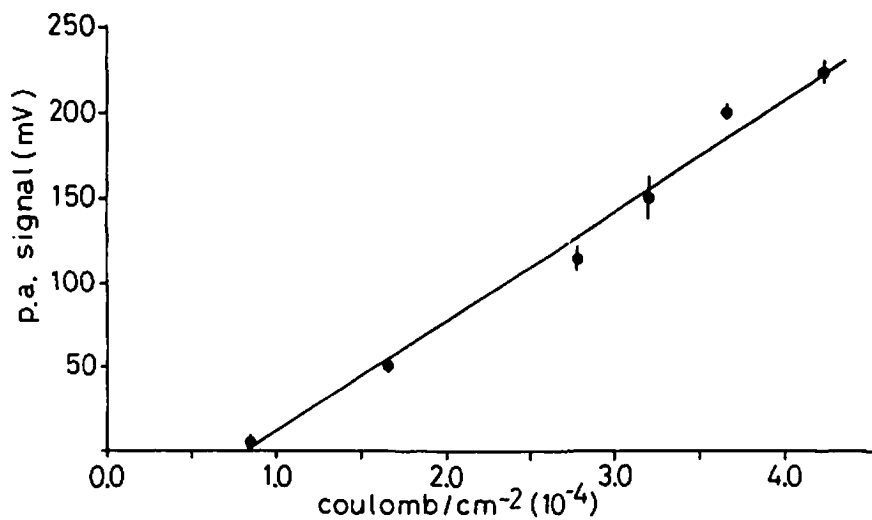


Figure 5 Effect of film thickness on the laser photoacoustic signal.

HV^{\ddagger} would react rapidly with O_2 and probably, to a small extent, with protons at the Pt electrode surface. Although dissolved oxygen was removed from the solution by bubbling prepurified nitrogen before measurement, a small amount of oxygen could still remain in the solution. The film thickness was thus taken by subtracting the number of coulombs of the nonzero intercept from those measured. The lower limit of detection (for $S/N = 1$) corresponds to about 2.5×10^{-6} coul/cm² (2×10^{13} molecules/cm²). By assuming that the diameter of heptyl viologen radical cation bromide molecule was about 18 \AA , the number of molecules adsorbed in a monolayer on the electrode is about 4×10^{13} molecules/cm². Thus, our detection limit for this highly absorbing species corresponds to less than one monolayer.

The spectrum of the electrogenerated viologen film (Fig. 6) was obtained by continuously pulsing the electrode between 0.0 and -0.41 V vs. Ag at 1 Hz to produce and remove the film while the irradiation wavelength was changed.

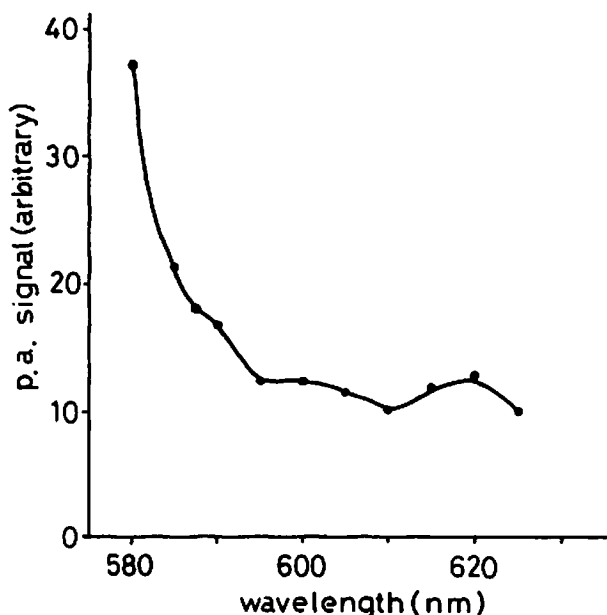


Figure 6 Photoacoustic spectrum of the electrogenerated viologen film.

This procedure insured that the viologen coverage remained low and constant during the measurement. The film thickness was estimated to be in the range of a few monolayers. Because the lasing dye was rhodamine 6G, the wavelength range available was limited to 570 to 630 nm and the complete spectrum of the viologen film deposited on the electrode could not be obtained. This photoacoustic spectrum apparently exhibited some fine structure, although the absorption spectrum of the layers on SnO₂ glass measured spectrophotometrically does not show this (11). The piezoelectric signal spectrum, obtained from the clean platinum electrode was almost the same as the power spectrum of the dye laser, and the photoacoustic spectrum was corrected by dividing the signal intensity at a given wavelength by that of the clean electrode at the same wavelength.

CONCLUSIONS

The results presented here suggest that the PZT-PAS technique is a useful one for spectral studies of the electrode-solution interface and that observation of monolayer or submonolayer amounts of products is possible. The species examined here has a high molar absorptivity so that detection of small amounts was favored. However, much more powerful pulsed and CW lasers are available and signal averaging techniques could be employed to improve the S/N ratio. Moreover, because the PZT-PAS technique is characterized by a fast time response, time-resolved photoacoustic spectroscopy might be possible by modulating the electrode potential as well as the incident light beam. By such a technique the dynamic behavior of the electrode and investigations of the kinetics of electrode reactions by monitoring intermediates and products should be possible.

ACKNOWLEDGEMENT

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