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PHOTOACOUSTIC OBSERVATION OF SOLID-LIQUID INTERFACE BY MEANS OF TOTAL INTERNAL REFLECTION TECHNIQUE

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Photoacoustic signal induced in a thin region on the solution side at a glass-dye solution interface was measured by changing an angle of incidence. It was contemplated that the method could be extended to observation within the effective thickness as small as 100 nm and on the solution of as low concentration as 10^{-5} in absorbance.

In recent years, photoacoustic spectroscopy (PAS) has been applied to investigations of liquid samples with a piezoelectric transducer (PZT).[1-6] In these applications, it has been demonstrated that photoacoustic spectrometry has the lower detection limit of less than 10^{-3} in absorbance and a wide dynamic range for the response. These prominent characteristics arise from the sensitive PZT detection and the use of a laser as a high power light source, in comparison with the conventional spectrophotometry in which optical density is measured. On the other hand, total internal reflection spectroscopy (IRS), which is popularly known as an attenuated total reflection technique (ATR) in infrared spectroscopy, has been employed in many surface studies.[7-12] Advantages of the total internal reflection technique (TIR) reside in that its observation region is confined within a layer 0.1 to 10 times as thin as a probe radiation wavelength on the solution side at the glass-aqueous solution interface and that the thickness of the layer (effective thickness) can be easily controlled by adjusting properly an angle of incidence of the radiation beam. The former feature is due to an exponential decay of the radiation field in the optically rarer phase resulting from the total reflection. In order to examine a concentration distribution profile of chemical species at a solid-liquid interface, we took advantages of both methods and carried out photoacoustic observation of a glass-dye aqueous solution interface by means of the TIR by changing an angle of incidence of a light beam. Photoacoustic observation has already been done on sodium fluorescein solution at a fixed angle of incidence by Iwasaki et al..[13] The present attempt is the first experiment to observe the interface region of variable depth by changing the angle of incidence in TIR. In the present work, a simple instrument was assembled and dependence of photoacoustic signal (PA signal) on the effective thickness at the interface was studied with solutions of different dye concentrations.

Figure 1 shows a schematic diagram of the instrumental arrangement. The output beam from the helium-neon laser (NEC GLG5000) was modulated at 5.4 Hz by the optical chopper (ITHACO 218). The laser was operated at 632.8 nm and its power was

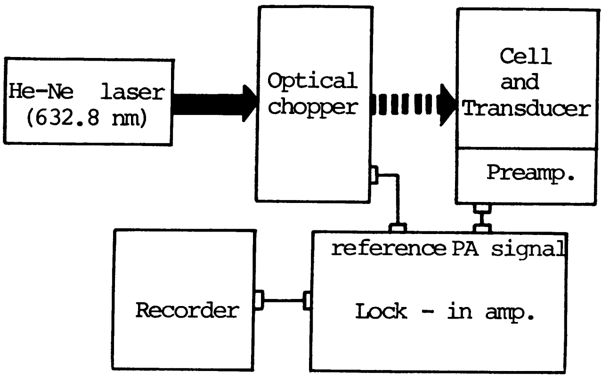

Fig. 1. Schematic diagram of instrumental arrangement

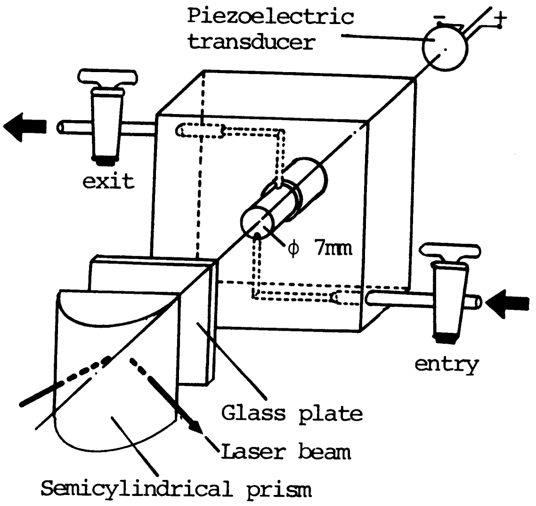

Fig. 2. Cell for PAS by TIR

nominally 0.5 mW. It was ensured in a preliminary experiment that PA signal decreased in a proportional manner to a reciprocal of modulation frequency in the range of 5 to 100 Hz and the S/N ratio was higher at 5.4 Hz than at the higher modulation frequency. A periodic pressure fluctuation induced at the glass-dye solution interface by absorbed radiation was detected by a disc form PZT supplied by MURATA MFG. CO., LTD.. The output signal was processed by a lock-in amplifier (Princeton Applied Research 5101) preceded by a homemade preamplifier and was recorded on section paper by an X-Y-t recorder (National VP-6422A, VQ-065A). The design of a cell used in the present study is shown in Fig. 2. The cell was machined from a metacrylate resin block. A hole with the diameter of 7 mm was drilled into the center of the block. A semicylindrical glass prism with a glass plate was attached onto the cylindrical hole with epoxy cement so that the angle of incidence was adjustable only by rotating the cell on the axis of the cylinder. A drop of liquid paraffin was filled between the prism and the plate to prevent the laser beam from reflecting at their boundary. The disc form PZT was also enclosed on the other side of the hole with epoxy cement. The cell was fixed on a finely adjustable elevator attached to a rotary stage so that the angle of incidence could be easily changed over the range of 0° to 90°. This apparatus was placed in a box made from iron to shield it from external electric noises. A dye solution was fed to and swept away from the cell by a mini-pump (TOYO KAGAKU SANGYO., LTD. TMP-6L). Before each measurement, the inlet and outlet cocks of the cell were closed after ensuring that there had been no air bubbles in the cell. Brilliant Blue FCF (Erioglaucine A) purchased from TOKYO KASEI KOGYO CO., LTD. was used without further purification. Dye solutions of various concentrations were prepared by

Table 1. PA signal intensity at normal incidence

Concentration of dye mol dm^{-3}	PA signal intensity μV
0.005	77.5
0.010	73.5
0.020	74.8
0.030	75.8
0.040	80.0
0.050	74.5
0.100	81.0
average	76.8 ±1.5

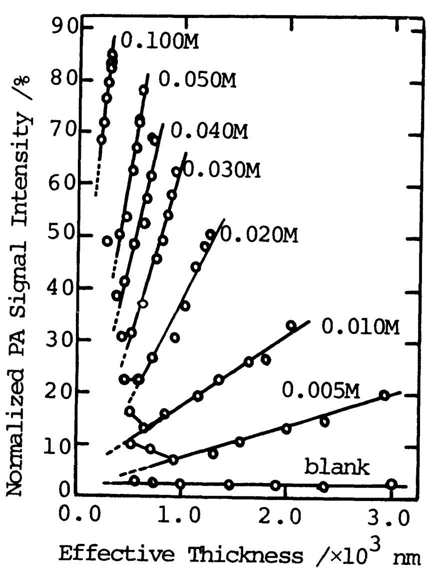

Fig. 3. Dependence of PA signal intensity on effective thickness.

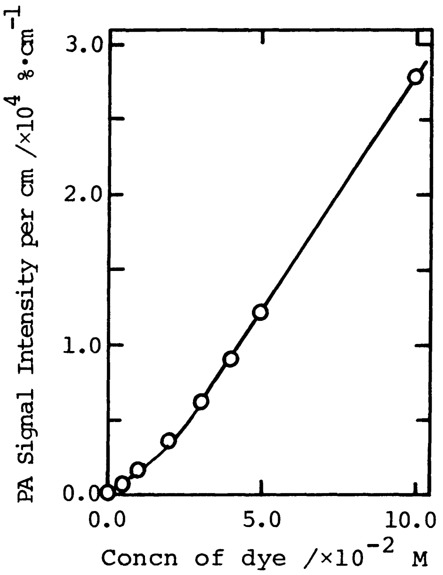

Fig. 4. Dependence of PA signal intensity on concentration of Brilliant Blue FCF (dye).

dilution of 0.100 M (1M = 1mol dm^{-3}) solution with distilled water.

PA signals were measured at several angles of incidence in the range from the critical angle (66.5°) to the grazing angle and at normal incidence (0°) for each solution. The PA signal intensities at 0° for every dye solution are shown in Table 1. All of the signal intensities are nearly identical, because radiation from the laser is completely absorbed even by the dye solution of the lowest concentration (0.005 M) owing to a high molar absorption coefficient of 1.19×10^5 $cm^{-1}mol^{-1}dm^3$ at 632.8 nm. This signal intensity corresponds to the total light energy going from the interface into the dye solution. Figure 3 shows dependence of the PA signal intensity on the effective thickness. PA signal intensities measured at oblique angles were normalized with respect to the intensity measured at 0°. The signal intensity measured at 0° for distilled water, which served as the blank solution, was extremely strong, because the laser beam directly impinged on the surface of PZT. The signal intensities for the blank solution were, therefore, normalized with respect to the average intensity (76.8 μV) of those at 0° for different solutions containing the dye. The effective thickness depends not only on the angle of incidence but also on the dye concentration. In the calculation of the effective thickness, these two factors were taken into consideration, according to the equations formulated by Hansen.[14,15] We assumed that the refractive index of glass equaled to 1.45 and the complex one of the dye solution to $1.33-1.38i\times C$, where i and C denote an imaginary unit and the dye concentration in M, respectively. Also, the effective thickness was evaluated for natural (non-polarized) radiation. As shown in Fig. 3, linear relationships are obtained between the effective thickness and the PA signal intensity for every dye solution and their intercepts on the ordinate agree with that for the blank solution within an experimental error, except that for the 0.100 M solution. The signal intensities at the smaller effective thickness, namely at the larger angle of incidence, deviate from a straight line. This is due to an additional photoacoustic signal from cell material induced by the laser beam which impinged beyond the observation area of 7 mm in diameter because of enlargement of a cross section on the interface of the laser beam with increasing the angle of incidence. The normalized PA signal intensities in Fig. 3 were divided by their own effective thickness to keep the path length constant. In spite of change in the angle of incidence, the signal intensities per centimeter for the same concentration are in agreement among them, as expected from the linearity shown in Fig. 3. As seen in Fig. 4, the plot of the signal intensity per centimeter against the dye concentration shows a linearity in the concentration range of 0.020 to 0.100 M and, however, deviates from the linearity with decreasing dye concentration. This deviation seems to come from underestimation of the effective thickness in a higher concentration range rather than overestimation in a lower range due to the uncertainty of the molar absorption coefficient. More detailed study of this phenomenon is going on now.

From the present work, it was shown that the intensity of PA signal by the TIR was proportional to the effective thickness as well as the dye concentration and also that it could be possible to observe light absorbing species in the region within approximately 200 to 3000 nm from the glass-aqueous solution interface. The detection limit of 3.2×10^{-2} in absorbance could be attainable at the S/N ratio of 1.7, in spite of the low power (0.5 mW) of the helium-neon laser. It was contemplated that the present method could be extended to observation within the effective thickness as small as 100 nm and on the solution of as low concentration as 10^{-5} in absorbance by increase of the power of the light source together with improvement of the preamplifier, the cell design, and the shielding of PZT.

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