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Measurement of Concentration Profile of Dye at Glass-Solution Interface by Photoacoustic Spectrometry Coupled with Total Internal Reflection Technique

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Synopsis. Photoacoustic signals were measured as a function of a penetration depth by changing an angle of incidence of an excitation beam. Concentration profiles were obtained from a relationship between the signal magnitude and the penetration depth by an inverse Laplace transformation. The smallest value of the penetration depth used was 34 nm.

In the previous works,[1-4] we developed photoacoustic spectrometry coupled with a total internal reflection technique (PAS-TIR) and could measure dye concentrations in a solution layer of submicrometer from a glass–solution interface. In the present paper, we demonstrate measurement of the photoacoustic signal (PAS) as a function of an angle of incidence of the excitation beam in PAS-TIR and discuss relationships between the PAS magnitude and concentration profile in the solution layer at the interface.

Experimental

Apparatus. A spectrometer and cell design used in the present study is similar to that used previously[3] except an argon ion laser (Spectra-Physics, 162D) and an active band path filter (NF Co., Ltd., UF-1BP). The laser of 15 mW at 488.0 nm was modulated at 40 Hz by an optical chopper and the plane of polarization of the laser was perpendicular to that of incidence. The laser beam passed through a convex lens (*f*=300 mm), entered a hemicylindrical internal reflection element made of dense flint glass from the cylindrical surface, and was focused on the axis of the hemicylinder on the opposite plane in contact with the solution. The PAS caused by absorption of the intermittent laser beam was detected by a piezoelectric transducer (MURATA MFG. Co., Ltd., 7D-15-4000 BKA) and was amplified by a lock-in amplifier (NF Co., Ltd., LI 574A) through a preamplifier (NF Co., Ltd., LI 75A) and the band path filter. The angle of incidence was changed by a rotary optical stage driven by a stepping motor (Oriental Motor Co., Ltd., UPD 569) and a programmable controller (Oriental Motor Co., Ltd., PC 100). The angle of incidence was changed stepwise and the corresponding PAS magnitudes were recorded on a Y-t recorder.

Reagents and Optical Parameters. New Coccine (NC) supplied from Tokyo Kasei Co., Ltd. was used without further purification. A 0.1 M (M=mol dm^{-3}) NC aqueous solution was prepared from distilled water for the measurement. The penetration depth of the beam was calculated according to expressions derived by Hansen.[5] Optical parameters used in the calculation are listed in Table 1. In general the refractive index of a solution containing light absorbing species is affected by the extinction coefficient of the solution due to anomalous dispersion.[5-7] However, the extinction coefficient of the 0.1 M NC solution is so small that the refractive index is not virtually susceptible to the anomalous dispersion.[6,7] Thus the refractive index of the NC solution was estimated to be equal to that of pure water at 488.0 nm.

Results and Discussion

Figure 1 schematically illustrates a total internal reflection. When the light beam progresses from the glass internal reflection element with a higher refractive index, n_1, toward the solution with a lower refractive index, n_2, at the angle of incidence, θ_1, beyond the critical angle, θ_c, the light beam is totally reflected and the evanescent wave emerges from the interface toward the solution. A mean square electric field strength of the evanescent wave exponentially attenuates with distance, x, from the interface. The distance at which the strength is reduced to 1/e of that at the interface is called the penetration depth, d, and is expressed by[5]

$$d=(-\lambda/4\pi)/\mathrm{Im}\{[(n_2-ik_2)^2-n_1^2\sin^2\theta_1]^{1/2}\}. \qquad (1)$$

Here the extinction coefficient of the solution, k_2, is equal to $2.303\cdot\varepsilon c\lambda/4\pi$, where ε, c, and λ denote the molar absorption coefficient, the concentration of the light absorbing species, and the wavelength of the light in vacuum, respectively. That is, the penetration depth at a constant wavelength is a function of the angle of incidence, the refractive indices of the internal reflection element and the solution, and the extinction coefficient. Therefore, the penetration depth depends only on the angle of incidence for a particular internal reflection system. Figure 2(a) shows the PAS magni-

Table 1. Optical Parameters Used in the Calculation of the Penetration Depth

	Refractive index	Extinction coefficient
0.1 M NC solution	1.337	0.0172
Dense flint glass	1.819	0[a]

a) Assumed value.

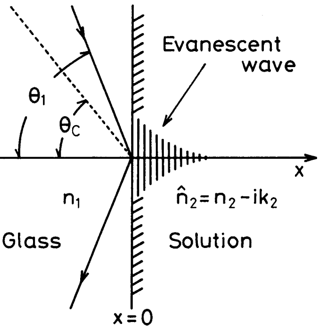

Fig. 1. Illustration of total internal reflection. n_1: refractive index of internal reflection element, n_2: refractive index of solution, k_2: extinction coefficient of solution, $\hat{n}_2$: complex refractive index of solution, θ_1: angle of incidence, θ_c: critical angle.

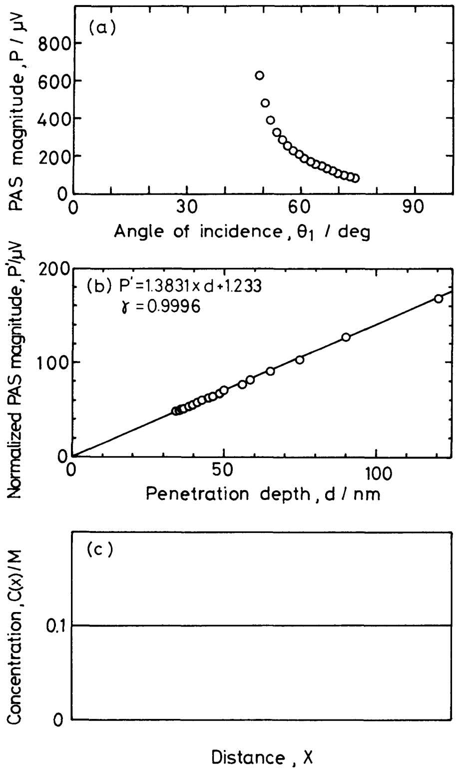

Fig. 2. (a) Relationship between PAS magnitude and angle of incidence, (b) relationship between normalized PAS magnitude and penetration depth, (c) concentration profile.

tudes for a 0.1 M NC aqueous solution against the angle of incidence from 49 to 74.5 degree.

On the other hand, the mean square electric field strength at a given position of x (see Fig. 1) is expressed by $S\cdot\exp(-x/d)$, where S is a sensitivity factor, depending on an optical coupling at the interface,[5,6,8] and was calculated from the optical parameters of the system in a similar manner to the calculation for the penetration depth.[5] The absorbed light power at x is, therefore, proportional to $\varepsilon cS\cdot\exp(-x/d)$. The overall absorption is expressed by the integration from $x=0$ to $x=\infty$. Thus the PAS magnitude, P, is given as follows:

$$P=S\int_0^\infty K\varepsilon c\cdot\exp(-x/d)\mathrm{d}x, \qquad (2)$$

where K is a coefficient depending on instrumental parameters and photoacoustic characteristics of the internal reflection system.[3] When the molar absorption coefficient and the photoacoustic characteristics of the solution are constant over the full range, Eq. 2 is rearranged to

$$P'=P/SK\varepsilon=\int_0^\infty c(x)\cdot\exp(-x/d)\mathrm{d}x. \qquad (3)$$

Hereafter P' is called the normalized PAS magnitude. The right hand side of Eq. 3 expresses a Laplace transformation of the concentration profile, $c(x)$, when $1/d$ is considered as a parameter. Consequently, the concentration profile can be obtained by the inverse Laplace transformation of the normalized PAS magnitude as a function of the penetration depth. In practice, three concentration profiles were assumed and compared with a regression function for a plot of the normalized PAS magnitude against the penetration depth at each angle of incidence. Figure 3 shows the assumed concentration profiles and the corresponding Laplace transformations. The first (a) represents the enrichment of the species at the interface accompanying an interfacial phenomenon such as adsorption, the second (b) corresponds to the concentration profile of uniform distribution over the range considered, and the last (c) is the reverse case to the first. The plot derived from the results in Fig. 2(a) and the corresponding regression function are shown in Fig. 2(b). As can be seen in Fig. 2(b), the regression function can be regarded as a straight line through the origin, that is, the normalized PAS magnitude is directly proportional to the penetration depth. Accordingly, the present case corresponds to (b) in Fig. 3 and it is concluded that the concentration of the dye is constant over the solution range from the interface to the bulk. Here it should be noted that the distance from the interface, x, is a different variable from the penetration depth, d, and that graduations on the abscissa in Fig. 2(c) can not be determined, because of the nature of the Laplace transformation. However, it is significant that the above conclusion can be derived from the measurement of the PAS magnitude against the penetration depth of submicrometer.

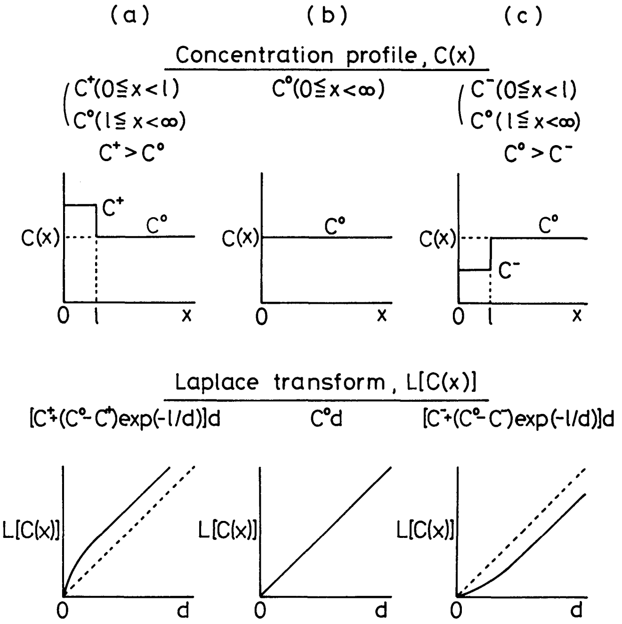

Fig. 3. Assumed concentration profiles, $c(x)$, and the corresponding Laplace transformations, $\mathrm{L}[c(x)]$.

As described previously, the available range of the penetration depth is limited by the optical parameters of the internal reflection system examined and the angle of incidence. In this study, the smallest penetration depth was 34 nm. This limit is still inadequate for exact observation of a thinner layer adjacent to the interface, such as an adsorption layer. Figure 4 shows a dependence of the relative penetration depth, d/λ, on the angle of incidence for two internal reflection elements with the different refractive indices, that is, (a) 1.819 and (b) 2.417. As expected from Fig. 4, the shorter penetration depth will be approached by using the

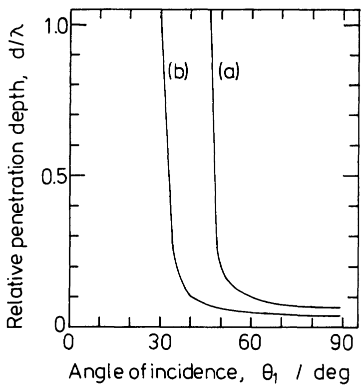

Fig. 4. Dependence of relative penetration depth on angle of incidence. (a) Refractive index of internal reflection element, $n_1=1.819$ and refractive index of solution, $n_2=1.337$, (b) $n_1=2.417$ and $n_2=1.337$.

larger angle of incidence, the higher refractive index of the internal reflection element, and the shorter wavelength of the laser. The complex concentration profiles, which are due to adsorption, electrochemical operation, and mass transfer of species in membrane, will be examined by the proposed spectrometric technique.

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References

1) T. Hinoue, Y. Shimahara, and Y. Yokoyama, *Chem. Lett.*, **1983**, 225.

2) T. Hinoue, Y. Shimahara, H. Murata, and Y. Yokoyama, *Bunseki Kagaku*, **33**, E459 (1984).

3) T. Hinoue, H. Murata, and Y. Yokoyama, *Anal. Sci.*, **2**, 401 (1986).

4) T. Hinoue, H. Murata, M. Kawabe, and Y. Yokoyama, *Anal. Sci.*, **2**, 407 (1986).

5) W. N. Hansen, "Advances in Electrochemistry and Electrochemical Engineering," ed by P. Delahay and C. W. Tobias, John Wiley & Sons, New York (1977), Vol. 9, pp. 1—60.

6) N. J. Harrick, "Internal Reflection Spectroscopy," Wiley-Interscience, New York (1967).

7) W. N. Hansen, *ISA Trans.*, **4**, 263 (1965).

8) T. Kuwana, "Electroanalytical Chemistry," ed by A. J. Bard, Marcell Dekker, New York (1974), Vol. 7, pp. 2—78.