Measurement of External Reflection Spectra of Protonated Tetraphenylporphyrin Adsorbed at Liquid-Liquid Interface

Yoshio Moriya,* Nobuaki Ogawa,† Tomokazu Kumabe, and Hitoshi Watarai††
Department of Materials Engineering and Applied Chemistry, Mining College, Akita University, Tegata Gakuencho, Akita 010
†*Department of Chemistry, Faculty of Education, Akita University, Tegata Gakuencho, Akita 010*
††*Department of Chemistry, Graduate School of Science, Osaka University, Machikaneyama, Toyonaka, Osaka 560*

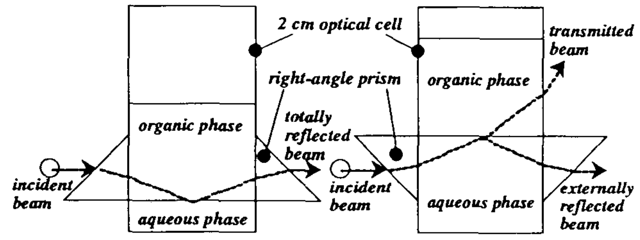
(Received November 10, 1997; CL-970855)

External reflection UV-vis spectra of the interfacially adsorbed species of protonated tetraphenylporphyrin at toluene/aqueous sulfuric acid interface were successfully observed with clear negative absorption bands and without overlapping by the spectrum of the organic phase.

Chemical reactions at liquid-liquid interfaces are an attractive subject in some fields, especially in the studies of solvent extraction. The interfacial adsorption behavior of the organic extractants have kinetically been studied by a high-speed stirring method.[1] In recent years, several direct spectroscopic approaches were employed to identify the interfacial adsorbed species. Among the approaches, an optical stir cell method and a Teflon capillary plate method have been proposed in order to characterize the interfacial species in a high specific interfacial area.[2] While, the total internal reflection (TIR) spectroscopy is one of the most informative method as well.[3,4] This could be useful especially for the ion-association adsorption of water-soluble extractants as that has been investigated in the TIR fluorescence spectroscopy.[5,6] Unfortunately, an organic phase encountered in solvent extraction usually contains strongly light-absorbing ligand and complex, hence the application of TIR spectroscopy to the interfacial species is limited. Therefore, a more effective method which enables to catch only the interfacial species is strongly desired.

In the present study, we report a successful application of an external reflection (ER) spectroscopy for the *in situ* measurements of the interfacial species of hydrophobic porphyrin at toluene/water interface. As far as we know, no experimental examples has been found on the application of ER spectroscopy to identify the adsorbed species at the liquid-liquid interface, though the reflection spectroscopy of the monolayer species at the air/liquid interface has been reported.[7]

The porphyrin tested in this work is 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP) purchased from Dojindo Laboratories. The several concentrations of TPP in toluene (Wako, GR) as the organic phase and a constant concentration 4 M($=$mol dm^{-3}) of the aqueous solution of sulfuric acid as the aqueous phase were adopted in our experiment for comparison with other report.[2] Hitachi 280 double beam spectrophotometer was used for the spectral measurements. The optical arrangement for TIR spectroscopy and ER spectroscopy are schematically illustrated as (a) and (b) in Figure 1. On both light-path sides of the 20 mm quarz cell, a pair of right-angle prism was set with appropriate position so that the incident beam struck the center of the interface with the incident angle 74.4° for (a) or 72.5° for (b) in Figure 1. The former angle in the arrangement (a) was greater enough than the critical angle 63.3° for toluene/4 M sulfuric acid interface. In the ER spectroscopy, however, the incident beam is separated into an externally reflected beam and a transmitted-refracted beam (with a refraction angle 58.4° in this system). The upper inside of the cell was treated with dichloro-dimethylsilane in toluene for hydrophobic coating, so as to make a flat toluene/water interface.[5,6] At first for the spectral measurements, reference scan for the toluene/(4 M sulfuric acid) interface was taken and stored as a blank, then 15 to 40 μL portions of TPP solution (4.0×10^{-5}M) were added stepwise to the organic phase. The temperature of inner sample solutions was kept at 298±0.5 K by a thermostatic circulator. The interfacial adsorption equilibration was achieved within 1 h.



(a) Total internal-reflection method (b) External-reflection method

Figure 1. Schematic drawing of the optical arrangements for the measurement of reflection spectroscopy of the interfacial adsorbed species.

The results of the spectral measurements under the total TPP concentration $[\mathrm{TPP}]_{\mathrm{T,org}}$ of 1.6×10^{-6} M are shown in Figure 2. In the Figure, the absorption spectrum A for the organic bulk phase after adsorption equilibration has at least five absorption maximums at the wavelength (λ_{max}): 419, 515, 548, 592 and 648 nm within the region 370-800 nm. In the TIR spectrum B in Figure 2, however, two new peaks were observed at 475 and 722 nm in addition to the peaks observed for the spectrum A. Therefore, the two new peaks could be belonged to the interfacial species. The peak at 475 nm agreed in general to the corresponding peak at 472 nm of the transmission absorption spectrum measured by the Teflon capillary plate method.[2] The peak can be ascribed, most probably, to a coagulated species, $(H_2TPP^{2+})_n$.[8] In contrast to the TIR spectrum B, the ER spectrum which was focused in this study was clearly observed as a negative absorption spectrum with three absorption minimums at $\lambda_{\mathrm{min}} = 412$, 475 and 722 nm, as the spectrum C in Figure 2. The λ_{min} for the latter two agreed to the corresponding λ_{max} observed in the TIR spectrum B. Moreover, the band around 412 nm, which may be hidden by the strong Soret band in the case of TIR spectrum, could be also belonged to the interfacial species as mentioned later. The absorption spectrum D for the aqueous bulk phase under the equilibration had only an weak band around 436 nm assigned to a monomeric H_2TPP^{2+}, which scarcely affected the ER spectrum (we may correct the ER spectrum C by using a certain factor of the

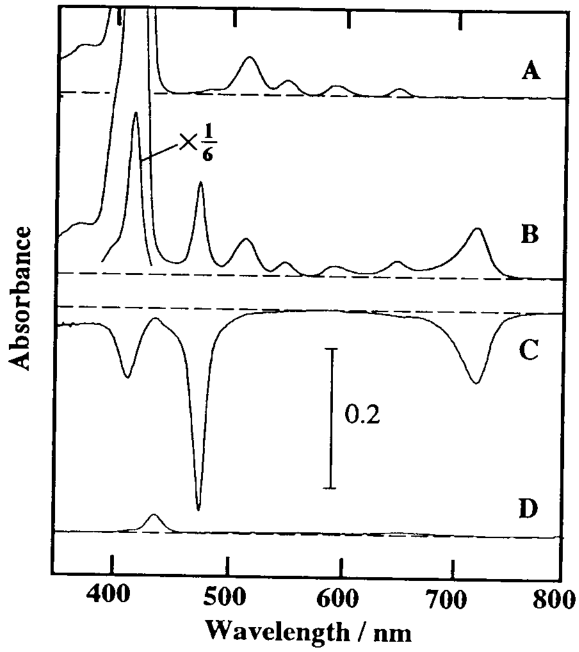


Figure 2. Several spectra measured under the adsorption equilibration of TPP at the toluene/4M-H_2SO_4 interface. The total TPP concentration is 1.6×10^{-6} M. A: absorption spectrum of organic bulk phase, B: TIR spectrum, C: ER spectrum, D: absorption spectrum of aqueous bulk phase.

absorbance of D, if necessary). Thus, we found that a UV-vis spectrum according only to the interfacial species without any interference of bulk species is obtained by the ER method.

It is convenient, hereinafter, to use the term of reflection difference, ΔR_T for TIR or ΔR_E for ER spectrum defined by the absorbance difference from the blank spectrum, in stead of the term 'absorbance'. The ΔR_E at 412, 475 and 722 nm were measured under the concentration region $1\times10^{-7}<[\mathrm{TPP}]_{T,org}/\mathrm{M} <2.0\times10^{-6}$ and plotted for the equilibrated TPP concentration in the organic bulk phase, $[\mathrm{TPP}]_{eq,org}$ as shown in Figure 3. The value of ΔR_E at each of the three wavelengths increased steeply with the increase of $[\mathrm{TPP}]_{eq,org}$ and then reached to a plateau above *ca.* 1.3×10^{-6} M in a similar pattern. The similarity means that the band around 412 nm is not influenced by the organic bulk species within experimental errors. It was supported by the ER spectra for the TPP/(1 M Na_2SO_4 neutral aqueous solution) interface, where we could not observe any band under the same conditions as in Figure 2. It is clear that all of the three ER bands belong to only one species, because a constant ratio of $\Delta R_E{}^{412}/\Delta R_E{}^{475}/\Delta R_E{}^{722} \fallingdotseq 1.0 / 2.7 / 1.0$ was obtained for the variation of $[\mathrm{TPP}]_{eq,org}$. It is one of the attractive results obtained in this work that the intensity of ER spectral band around 412 nm (which may be a Soret band) is relatively smaller than that of the strongest band (419 nm) of TPP in bulk as compared with that of the other bands. Consequently, Figure 3 shows that the saturated curve shape of the three solid lines are due to an interfacial adsorption phenomenon.

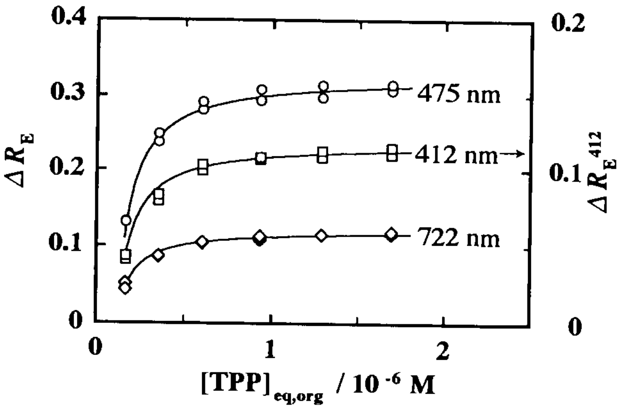


Figure 3. Relation between the external-reflection difference (ΔR_E) and the equilibrated TPP concentration in the organic phase ($[\mathrm{TPP}]_{eq,org}$).

In the case of partial adsorption at an interface as shown in Figure 3, the ΔR_E should be in proportion to the interfacial concentration of TPP. When the interfacial concentration (mol cm^{-2}) of the aggregated species $(H_2TPP^{2+})_n$ is shown as $[(H_2TPP^{2+})_n]_i$, an equation:

$$\Delta R_E = \rho(\lambda)\, n[(H_2TPP^{2+})_n]_i\, (S_i/V_o) \qquad (1)$$

should be valid, where $\rho(\lambda)$ is a coefficient (M^{-1}) at a λ, S_i is an interface surface area (cm^2) and V_o is an organic bulk volume (dm^3). The ρ is a function of reflection coefficient at normal incidence which varies with the incident angle. Therefore, the ρ is only a function of λ, since the incident angle is constant in our optical cell arrangements. The concentration $n[(H_2TPP^{2+})_n]_i(S_i/V_o)$ in equation (1) is written as follows:

$$n[(H_2TPP^{2+})_n]_i\,(S_i/V_o) = [\mathrm{TPP}]_{T,org} - [\mathrm{TPP}]_{eq,org}\,. \qquad (2)$$

When we use the value $\Delta R_E{}^{475} = 0.237$ for $[\mathrm{TPP}]_{eq,org} = 3.5\times10^{-7}$ M with a 23.6% reduction of $[\mathrm{TPP}]_{T,org} = 4.6\times10^{-7}$ M by the interfacial adsorption, the value of $n[(H_2TPP^{2+})_n]_i\,(S_i/V_o)$ is 1.1×10^{-7} M from the equations (1) and (2). Then, we obtain the value of ρ^{475} to be 2.2×10^{6} M^{-1}. The numerical value is much higher than that of the molar extinction coefficient times 1 cm (light-path length), $\varepsilon^{472}\times1 = 3.4\times10^{5}$ M^{-1} in the transmission absorption spectroscopy.[2] The value of ρ^{412} ($\fallingdotseq \rho^{722}$) can also be calculated out from the spectrum to be 8.1×10^{5} M^{-1}. Thus, we suggest that the ER spectroscopy using a pair of right-angle prism is easily applicable to analyze the adsorbed species at liquid-liquid interface with high sensitivity.

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