Observation of Positive/Negative Bands in a Polarized External Reflection Vis-Spectrum and the Orientation of Protonated Tetraphenylporphyrin Adsorbed at Liquid-Liquid Interface

Yoshio Moriya,* Ryoko Amano, Takuya Sato, Shin-ichi Nakata, and Nobuaki Ogawa
Department of Materials-process Engineering and Applied Chemistry for Environments, Faculty of Engineering and Resource Science, Akita University, Tegata Gakuencho, Akita 010-8502

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A *p*-polarized visible external reflection spectrum comprised of positive and negative absorption bands was certainly observed as to the protonated tetraphenylporphyrin adsorbed at toluene-aqueous sulfuric acid interface. The results were qualitatively explained that the protonated molecules in *J*-aggregate could orientate obliquely to the interface.

The various spectroscopic methods for the measurements of adsorbed species at liquid-liquid interface have been remarkably facilitated in recent years. Within the visible wavelength region, typical methods except for fluorescence spectroscopy[1] are found in the attenuated total internal reflection (ATR) spectroscopy[2] and the double phases transmission spectroscopy.[3,4] The organic phase encountered in the solvent extraction systems, however, usually contains strongly light-absorbing ligand, hence the spectrum of interfacial species may be considerably interfered by that of organic bulk species. Our previous work,[5] therefore, proposed the external reflection (ER) method. Thus, we could observe an ER spectrum with some negative absorption bands which referred only to the interfacially adsorbed species as to that of tetraphenylporphyrin (TPP) at toluene-aqueous sulfuric acid interface. In the present study, we report another spectral information for the same system by ER method using a polarizer about the molecular orientation at liquid-liquid interface within the visible region.

A double beam spectrometer (Perkin Elmer, Lambda 40) was used for this work. The simple device made up by a quartz cell (light path =2 cm) and a pair of right angle prisms was shown in Figure 1, where the height of cell was adjusted by several holders so that the four kinds of spectra could be measured independently. That is, the transmission absorption spectrum of organic phase (TA_o) and that of aqueous phase (TA_a), the ATR spectrum with the angle of incidence θ_A =74° (which is greater enough than the critical angle 66° for the system) and ER spectrum with the angle of incidence θ_E =73°. After the addition of the same volume (3 mL) of aqueous sulfuric acid and toluene, a portion of TPP solution (4.0×10^{-5} M (M=mol dm^{-3})) was added and then homogenized in the upper toluene phase. For the polarized reflection spectroscopy, a dichroic sheet polarizer (Kenko G58) was inserted across the incident beam in front of the device. The measurements were carried out at the temperature 298 K.

The ER spectrum without polarizer was observed in the same manner as described previously.[5] That is, the negative absorption bands at 412, 473 and 720 nm were observed with no interference of the organic bulk phase. We could obtain also the ATR spectrum of only for the adsorbed species (ATR^{ad}) by subtracting $TA_o \times \mathrm{cosec}\theta_A$ from ATR spectrum, where we found a band at 412 nm corresponding to that of ER spectrum.

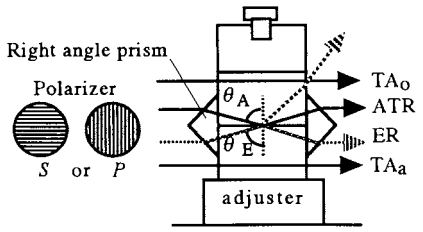

Figure 1. Simple cell components for measuring various spectra.

The polarized spectra were measured under the total concentration 1.6×10^{-6} M of TPP in the organic phase. The ER spectra of *s*- and *p*-polarized (denoted by s and p, respectively) were shown in Figure 2 together with the spectrum obtained by no setting of polarizer (denoted by n). A small band at 435 nm belongs to that of aqueous bulk phase. In the spectrum s, the absolute intensities of bands at 473 and 720 nm were strengthened (as well as the s-ATR spectrum) while that of a band at 412 nm was reduced as compared with the spectrum n. In the spectrum p, however, the two bands at 473 and 720 nm appeared with slightly positive absorbances (which resembled those of the p-ATR spectrum) while the band at 412 nm was negatively strengthened. The mean spectrum estimated by (s+p)/2 was almost the same as spectrum n, regardless of the partially polarized light of origin and of the rough setting of polarizer. It was certain that the *p*-polarized ER spectrum contained two positive peaks, which were confirmed by the obser-

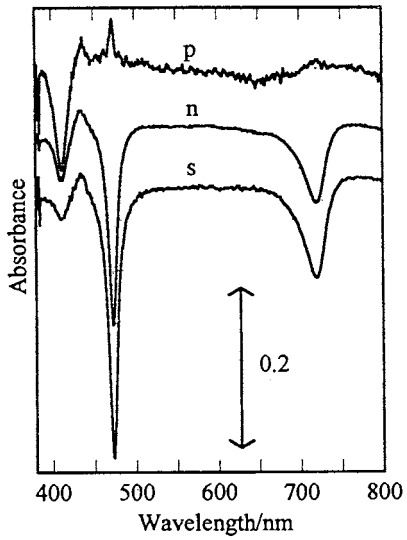

Figure 2. The *s*- and *p*-polarized ER spectra together with no polarized one(n) for the protonated TPP adsorbed at toluene-4M sulfuric acid interface.

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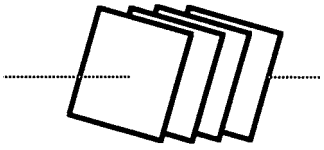
vation of the similar positive bands with slightly weakened intensities when the angle of incidence θ_E was heightened to 79° by using a pair of 30°-60°-90° prisms.

The observation of positive/negative absorption bands for a surface-boundary substances can be an intrinsic phenomenon which appears only within the *p*-polarized ER method. The feasibility of the appearance of some positive/negative peaks in the ER spectra was shown by Hansen's approximate formulae for the three phase system in the literature.[6] Using the LB film of cadmium stearate on GaAs substrate in the IR-ER method, Hasegawa et al.[7-9] showed that the characteristic IR bands of functional groups appeared with positive/negative absorbance according to the surface selection rule,[9] and that the orientation angle against the surface normal could be determined by the use of anisotropic principle.[8] The polarized spectra observed in the visible region have to be affected by the electronic transition moment for each of chromophores in the surface boundary substances. However, the positive/negative bands have never been observed at the liquid-liquid interface as long as we know. Taking into account the difficulties of IR-ER measurements for the oil-water system, it will be much useful to get spectral information on the interfacial molecular orientation from a polarized visible ER spectroscopy. From this point of view, our new observation of *p*-polarized ER spectrum with positive/ negative peaks could be significant for the qualitative analysis of interfacial species. As the angle of incidence θ_E is much higher than the Brewster's angle θ_B =48° in our system, it can then be inferred from the surface selection rule that the two positive bands at 473 and 720 nm observed in the *p*-polarized spectrum may be assigned to the chromophores having a parallel moment to the interface while another band at 412 nm to that having a perpendicular moment.

Our spectrum could belong to an aggregated species, $(H_2TPP^{2+})_n$, since the band around 473 nm was red-shifted as compared with that around 440 nm of the ion-association monomer, $H_2TPP(ClO_4)_2$ extracted in toluene.[10] For understanding the origin of spectral bands, on the other hand, we can refer to the discussion on the *J*-aggregate of water-soluble tetra-(4-sulfophenyl) porphyrin ($TPPS^{4-}$) in acidic aqueous media.[11] According to the work, two absorption bands at 492 and 707 nm were assigned to the characteristic transition of linear oscillator polarized in the long axis of rodlike aggregate ($(H_2TPPS^{2-})_n$, n=11) in slipped face-to-face stacking structure where the participation of inter-porphyrin charge resonance excited states should be taken into account while another diffuse absorption band around at 420 nm was assigned to the transition in the short axis, where the counterpart of the 491 nm band of porphyrin Soret origin appeared. In our spectra, the former two should correspond to the bands at 473 and 720 nm, and the later to the band at 412 nm. Then, it is convenient to imagine that the diprotonated TPP in a *J*-aggregate $(H_2TPP^{2+})_n$ orientate obliquely against the interface as Scheme 1.



Scheme 1.

Supposing the protonation-adsorption equilibration with the constant K:

$$n\mathrm{TPP_e} + 2n\ \mathrm{H^+} \rightleftarrows (\mathrm{H_2TPP^{2+}})_{n,\mathrm{i}}$$
$$K=[(\mathrm{H_2TPP^{2+}})_n]_\mathrm{i}[\mathrm{TPP}]_\mathrm{e}^{-1}\,[\mathrm{H^+}]^{-2} \qquad (1)$$

and the ER absorption difference ΔR_E (as shown previously[5]):

$$\Delta R_\mathrm{E} = \rho n[(\mathrm{H_2TPP^{2+}})_n]_\mathrm{i}\,(S_\mathrm{i}/V_\mathrm{o}) = [\mathrm{TPP}]_\mathrm{t} - [\mathrm{TPP}]_\mathrm{e}, \quad (2)$$

we can induce the following equation:

$$\log(\Delta R_\mathrm{E}) - \log(S_\mathrm{i}/V_\mathrm{o}) = n\log[\mathrm{TPP}]_\mathrm{e} + \log(\rho nK) + 2n\log[\mathrm{H^+}], \qquad (3)$$

where ρ, S_i and V_o refer to a coefficient (M^{-1}) at 473 nm, an interfacial area (cm^2) and an organic bulk volume (dm^3), respectively, and where the subscripts of concentrations t and e denote a total and an equilibrated, respectively. The linear plots of $\log(\Delta R_E)$-$\log(S_i/V_o)$ *vs.* $\log[TPP]_o$ gave a slope 3.9 within the lower concentration range of TPP under the constant of last two terms in eq (3), hence our *J*-aggregate could be represented as $(H_2TPP^{2+})_4$. On the other hand, the interfacial molecular density of TPP at the interfacial adsorption saturation was calculated to be 1.6×10^{18} m^{-2} from the decrement of TA_o absorbance for homogenized organic phase, which meant that the area per molecule in monolayer at the interface was 0.63 nm^2. When we use a value 3 nm^2 as a cross sectional area of diprotonated TPP which is estimated roughly from the value 3.2 nm^2 as that for tetrakis(*N*-methyl-4-pyridyl)porphine,[12] we obtain the 1.7 to 2.4 nm range of thickness for the monolayer and the orientation angle 12° of TPP against the surface normal. Then, the angle supports our spectral inference described above, though a quantitative analysis on the ER spectroscopy would have to be performed by a method as shown in the literature.[13]

Consequently, the application of ER method to the *in situ* measurements of the liquid-liquid interface enables not only to obtain a spectrum for an interfacial species of itself without any interference of organic bulk phase but also to yield much information about the interfacial molecular orientation.

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