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Simple Devices Comprised of an Optical Cell and Prisms for Direct Spectrophotometric Measurement of Liquid-Liquid Interfacial Adsorbate

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Convenient methods with simple devices comprised of an optical cell and prisms were proposed for the direct spectrophotometric measurement of adsorbed species at liquid-liquid interface, using a protonated *meso*-tetraphenylporphyrin in an aggregate form as an interfacial adsorbate. The spectrum of the aggregate within the visible wavelength region was effectively observed by three kinds of prism-cell assembly for (1) the double-phase transmission method, (2) the multiple attenuated total-internal reflection method and (3) the external reflection method. Characteristics of spectral appearance in each of the methods were described and discussed.

Key Words : Liquid-liquid interface, Simple devices, Interfacial adsorbate, Tetraphenylporphyrin

1. Introduction

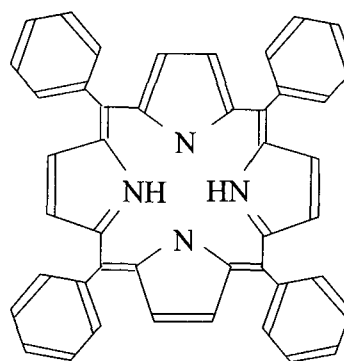
The investigation of the liquid-liquid interface as a special reaction field has received a great deal of attention in relation solvent extraction, organic synthesis, and physiological action systems. This is because the interface can adsorb many chemical species and form a specific aggregation and orientation state, which may not occur in homogeneous systems. For an understanding of the interfacial adsorption states, several methods for direct spectrophotometric measurements of interfacial adsorbates have been considerably facilitated in recent years. Within the visible wavelength region, two typical methods are found in attenuated total-internal reflection (ATR) spectroscopy^{1,2} and double-phase transmission spectroscopy as represented by the centrifugal liquid membrane method.³

The present study is concerned with simple devices comprised of an optical cell and prisms for convenient spectroscopic measurements of the adsorbed species at the horizontal liquid-liquid interface, using a common type of UV-Vis spectrometer and a high-sensitively coloration reagent. A similar kind of device comprised of an optical cell and prisms has already been proposed by Watarai et al. for total internal reflection fluorometry (TIRF).² We propose here three kinds of prism-cell assembly: for the double-phase transmission method, the multiple ATR method and the external reflection (ER) method.^{4,5}

2. Experimental

2.1 Reagents for interfacial adsorbates

For the detection of trace amount of adsorbates within the visible wavelength region, 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (H_2TPP , scheme 1) (Dojindo Laboratories) was used as a high-sensitively coloration reagent. This lipophilic porphyrin was dissolved in toluene or in dodecane, and the solution was contacted with aqueous sulfuric acid solution to yield the interfacial adsorbate of diprotonated porphyrin (H_4TPP^{2+}) as (H_4TPP^{2+}), in an aggregate form.⁶



H₂TPP

Scheme 1

2.2 Optical parts and the refractive indices

Three types of quartz cell (light path length, L : 1cm, 2cm and 5cm) and two types of quartz isosceles-triangle prism (90° - 45° - 45° with 1cm-1cm- $2^{1/2}$ cm, and 120° - 30° - 30° with 1cm-1cm- $3^{1/2}$ cm) were used for the prism-cell assembly. The upper inside of the cell, destined to contact organic phase, was pre-treated with the toluene solution of dichloro-dimethylsilane for hydrophobic coating so as to make a flat liquid-liquid interface. The value of refractive index at 298K for toluene, dodecane and 4M H_2SO_4 ($1M=1\text{mol dm}^{-3}$) were experimentally determined by an Abbe refractometer (Erma Optical Works, Ltd.) to be 1.49, 1.42 and 1.37, respectively, whereas the value 1.457 was used for that of fused quartz.⁷

2.3 Spectrophotometric measurements

For the measurements of absorption and reflection spectra, a double beam spectrometer (Perkin-Elmer, $\lambda 40$) was used. The device of the prism-cell assembly was mounted in the space in the spectrometer. A monochromatic narrow beam (*ca.* 2.5mm in diameter) was projected into the prism-cell attachment.

3. Results and discussion

3.1 The double-phase transmission method

An absorption spectrum of interfacial adsorbate could be observed by the double-phase transmission method with the prism-cell assembly illustrated in Figure 1, which used three right angle prisms and an optical cell of 4.5cm³ volume (1cm \times 1cm \times 4.5cm). Two fine capillary-tubes were attached to the Teflon stopper for the inlet-outlet of the testing solutions. After the injection of 4M H_2SO_4 solution (3.4cm³) to the cell, a portion of toluene solution of H_2TPP in the total concentration $[H_2TPP]_t = 1.6\ \mu\text{M}$ was injected through the lower inlet tube. Based on the total internal reflections at the 45° -inclined quartz/air interface of prism (P), the incident light was passed twice across the liquid-

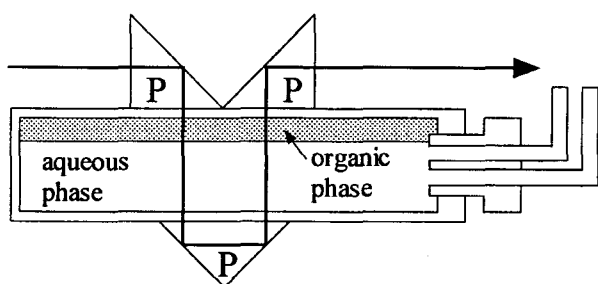


Figure 1 Schematic illustration of the double-phase transmission method. P: prism.

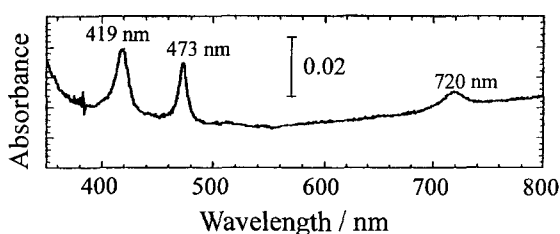
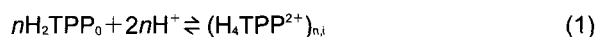


Figure 2 Double-phase transmission spectrum of the aggregate, $(H_2TPP^{2+})_n$ in the toluene-4M H_2SO_4 system. $[H_2TPP]_t = 1.6\ \mu\text{M}$.

liquid interface and led to the detector of spectrometer.

The spectrum of the aggregate $(H_2TPP^{2+})_n$ adsorbed at the toluene/4M H_2SO_4 interface is shown in Figure 2. It was measured at a thickness of 2.4mm of organic phase. The absorption band at 419nm corresponded to the Soret band of H_2TPP in toluene phase, while the two bands at 473 and 720nm corresponded to the interfacial adsorbate. The assignment for the two bands will be discussed later in 3.3. The interfacial adsorption equilibrium in the toluene-4M H_2SO_4 system could be represented by



A similar spectrum has already been observed using the optical stir cell method,⁶ Teflon capillary plate method⁶ and centrifugal liquid membrane method³ under the condition of high specific interfacial area (=interfacial area/organic bulk volume). At any rate, a double-phase transmission spectrum could easily be observed by a prism-cell assembly to be an overlapped one having an interfacial adsorbate and the solutes in two bulk phases. This method has the defect that each spectrum can not be distinguished when the band overlaps, while it has the advantage that the simultaneous spectroscopic changes can be grasped.

3.2 The multiple ATR method

ATR spectroscopy is one of the most informative methods for interfacial measurements, where an incident light is projected obliquely toward the liquid-liquid interface from the higher-refractive index medium to the lower one with the angle of incidence (θ) set higher than the critical angle (θ_c). A very intense ATR spectrum could be observed by the application of the multiple ATR method as reported in the literature¹ when a mirror and a pair of optical fibers were used. Based on a similar optical principle, a simple device can be made up by a prism-cell assembly as shown in Figure 3, though the angle of incidence may be fixed, depending on both the refractive index of organic solvent and the prism corner angle. When a pair of right angle prisms was used in the case of the toluene-4M H_2SO_4 system, the value of θ was estimated to be 74.4° ($> \theta_c = 66.9^\circ$). The ATR spectrum of interfacial species could then be amplified in proportion to the number of reflections at the liquid-liquid interface during zigzag progress of light between liquid-liquid and liquid-air interfaces (without using a mirror). Therefore, the number of reflections will be related to the L/d ratio, where L and d refer to the light path length of the cell and the thickness of the organic phase, respectively. The value of d could be controlled through adjustment of the added volume of organic phase (V_{org}). When we used a cylindrical cell (1.9cm in diameter with $L=5\text{cm}$) half filled with water, we obtained the relations shown in Figure 4, among d ,

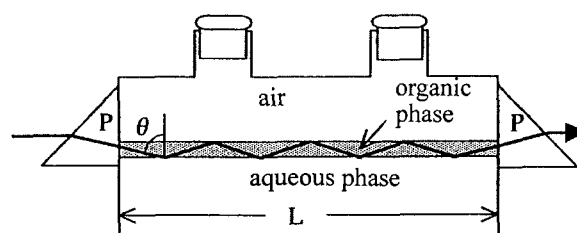


Figure 3 Schematic illustration of the multiple ATR method. L : light path length of optical cell, θ : angle of incidence greater than critical angle θ_c .

V_{org} and estimated integral number of reflections (stair-like dotted line).

The multiple ATR spectra of the aggregate adsorbed at the toluene/4M H_2SO_4 interface are shown in Figure 5, where the number of reflections was estimated using the relations given in Figure 4. The two bands at 473 and 720nm with some attendant bands were observed with the same band locations as in Figure 2. It is of note that the intensity of the two bands in the ATR spectrum, apart from the general discussion on the sensitivity of ATR method,³ was by far greater than that in the two-phase transmission spectrum. The intensity ratio of the 473nm band (as well as of the 720nm band) for 2, 3 and 4 reflections was about 2/3/4. On the other hand, the intensity of the other bands (at 419, 515, 548, 592, 648nm) corresponding to H_2TPP in the organic bulk phase was consistent, regardless of multiple reflections. This

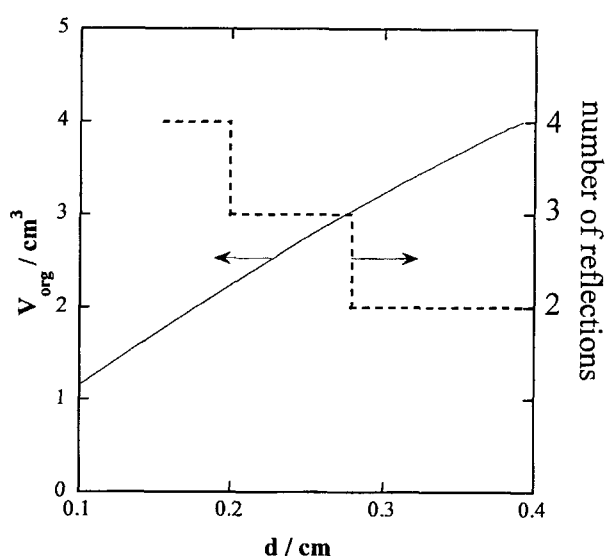


Figure 4 Relations among the thickness (d), the volume of organic phase (V_{org}) and integral number of reflections.

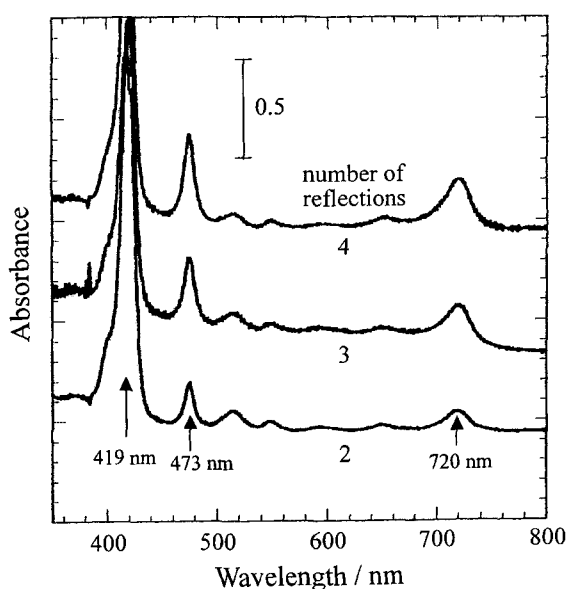


Figure 5 Multiple ATR spectra of the aggregate in the toluene-4M H_2SO_4 system. $[\text{H}_2\text{TPP}]_i = 1.6 \mu\text{M}$.

is to be expected because the sum of the reflected light-path length ought to be $L/\sin \theta$.

A further intensified spectrum of interfacial adsorbate would be observed, in principle, by increasing the L/d ratio. Therefore, the multiple ATR method could be useful to detect interfacial adsorbates having a lower molecular absorptivity than $10^5 \text{M}^{-1} \text{cm}^{-1}$ of porphyrins. In addition, full use can be made of its ability to observe only the spectrum of interfacial adsorbate produced from a hydrophilic solute in the liquid-liquid system where no absorption band exists in the organic bulk phase.

3.3 The ATR-ER method

The organic phase encountered in solvent extraction systems often contains a strongly light-absorbing solute. Hence the spectrum of interfacial adsorbate observed by both the double-phase transmission method and the ATR method may be considerably interfered with by the absorption bands of the organic solute, as illustrated by Figure 2 and Figure 5 with H_2TPP in the toluene-acidic aqueous solution system. In such a case, the external reflection (ER) method will be very useful.⁴ In this method, an incident light is projected obliquely toward the liquid-liquid interface from a lower-refractive index medium to a higher one, where the quantity of partial reflection light is detected depending on the interfacial concentration of adsorbate and on the angle of incidence. A simple device for the measurement of ER spectrum as well as ATR spectrum with a fixed angle of incidence is shown in Figure 6, where an optical cell ($L=2\text{cm}$, light path width=1cm) and a pair of right angle prism were used. In the toluene-4M H_2SO_4 system, the angle of incidence for ER condition (θ_{ER}) was estimated to be 73.0° and that for ATR condition (θ_{ATR}) to be 74.4° (as mentioned in 3.2). As can be seen from Figure 6, the absorption spectra of both organic and aqueous phases (A_{org} , A_{aq}), as well as the reflection spectra of liquid-liquid interface (ER, ATR) can be measured independently, by changing the height of an adjuster. Several such spectra are shown in Figure

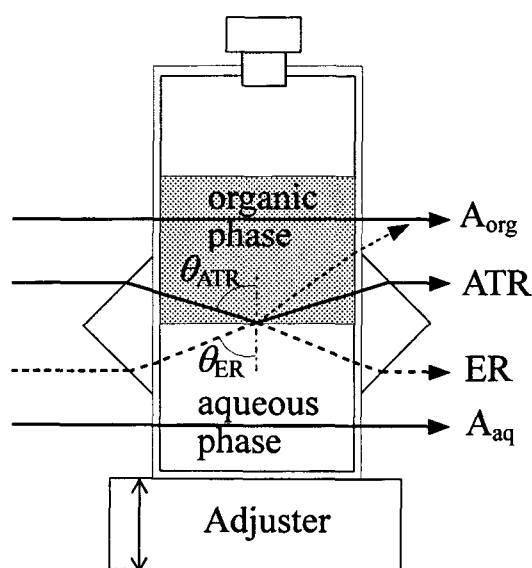


Figure 6 Schematic illustration of the ATR-ER method. The absorption spectra of both organic and aqueous phases (A_{org} , A_{aq}), as well as the reflection spectra of liquid-liquid interface (ER, ATR) can be observed independently, by changing the height of an adjuster.

7, relating to the interfacial adsorption of H_2TPP in the toluene-4M H_2SO_4 system ($[H_2TPP]_i = 2.3 \mu M$) with the same volume ($3cm^3$) of aqueous phase and of organic phase. It can be seen from Figure 7 that the ER spectrum was observed with three negative bands at 720, 473 and 412nm. The spectrum could not be interfered from the solute in the organic phase, since no ER band of H_2TPP was observed in the toluene-1M Na_2SO_4 system. Therefore, the spectrum of interfacial adsorbate itself has three main bands in the visible wavelength region. This was confirmed also by the ATR spectrum of adsorbate (ATR^{ad}) estimated by Equation (2).

$$A_{ATR}^{ad}(\lambda) = A_{ATR}(\lambda) - A_{org}(\lambda) / \sin \theta_{ATR} \quad (2)$$

where $A_{ATR}^{ad}(\lambda)$, $A_{ATR}(\lambda)$ and $A_{org}(\lambda)$ refer to the values of absorbance at the wavelength λ of ATR^{ad} , ATR and of organic bulk phase, respectively. The band locations of ATR^{ad} (thin gray line) agreed well with that of ER with a symmetrical pattern. Thus, a nearly pure spectrum of interfacial adsorbate itself could easily be observed by the ER method.

It is interesting that the Soret band (B-band) of aggregate appears in the two wavelength positions, 412 and 473nm: the former shows a blue-shift whereas the latter a red-shift as compared with the B-band (435nm) of monomeric species, $[H_4TPP^{2+}]$ in the aqueous phase. According to the discussion on the relationship between band-shift direction and form of aggregation,^{9,10} the next two cases may be feasible. (1) Mixture of *J*- and *H*-aggregates: The bands at 473 and 720nm belong to the B- and Q-bands of *J*-aggregate, respectively, while the 412nm band to the B-band of *H*-aggregate. (2) A zigzag stacking aggregate: Both red and blue shift can be arisen from one species. Nevertheless, we can not deny the possibility for only one species of *J*-aggregate, since our ER spectrum resembles the flow-induced dichroic spectrum of the *J*-aggregate of a water-soluble porphyrin, 5,10,15,20-tetra(4-sulfophenyl)porphyrin ($H_2TPPS_4^+$).¹¹ In the system, a diffuse absorption band is observed at 420nm together with sharp and intense absorption bands at 491 and 707nm, and it is considered that the three bands belong to one chemical species,

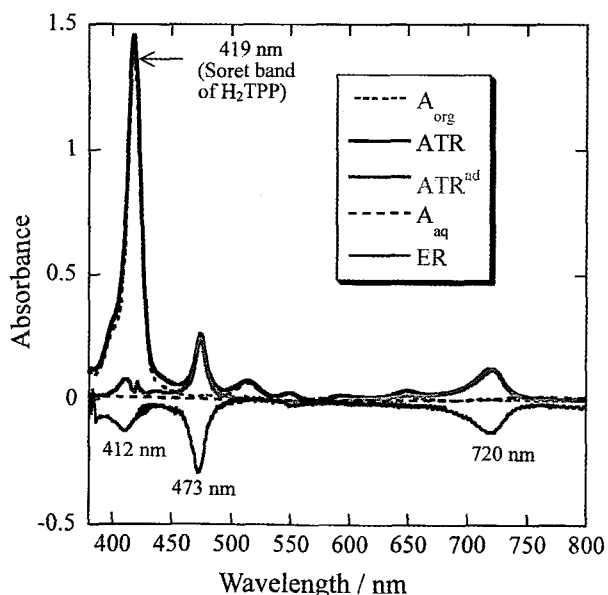
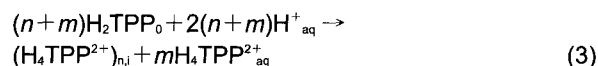


Figure 7 Several spectra relating to H_2TPP in the toluene-4M H_2SO_4 system. $[H_2TPP]_i = 2.3 \mu M$.

($H_4TPPS_4^{2+}$)_i, of a slipped face-to face stacking.

The feasibility of the appearance of some positive/negative bands in the polarized ER spectrum is shown by Hansen's approximate formulae in the literature.¹² For the measurement of polarized spectrum of interfacial species, a dichroic sheet polarizer was set in front of the detector. Thus, we could observe the *p*-polarized ER spectrum having two positive bands (473nm, 720nm) and a negative band (412nm), and directly study the qualitative orientation of interfacial adsorbate (supposing one species of *J*-aggregate) with the aid of the interface selection rule.⁵

Another application of ATR-ER method (illustrated in Figure 6) is described below. We studied the interfacial adsorption of the aggregate also in the dodecane-4M H_2SO_4 system. The mixture of the same volume ($3cm^3$) of acidic aqueous solution and dodecane solution in a Teflon test tube was shaken (250strokes/min) for 1h and then centrifuged (2500rpm) in a thermostated room at $298 \pm 2K$. All of the liquids were transferred into the prism-cell and allowed to stand for a prescribed time. A device similar to that in Figure 6 was assembled using a pair of 120° - 30° - 30° prisms for this system, where the incident angle for ATR spectrum was estimated to be of $\theta_{ATR} = 79.8^\circ (> \theta_c = 74.8^\circ)$. As a result, the Soret band at 416nm of H_2TPP disappeared completely from the A_{org} spectrum of dodecane phase, whereas three bands of the aggregate appeared in ATR spectrum with the same band locations as described for the toluene-4M H_2SO_4 system. In addition, an absorption band for $H_4TPP^{2+}_{aq}$ was observed at 435nm in the A_{aq} spectrum.¹³ Therefore, the protonation reaction of H_2TPP in the dodecane-4M H_2SO_4 system could be represented by



where all of the H_2TPP in dodecane phase was protonated to form an interfacial adsorbate ($H_4TPP^{2+})_{ni}$ and a monomeric aqueous species $H_4TPP^{2+}_{aq}$. Therefore, the ATR spectrum observed in this system should correspond to that of the interfacial adsorbate itself. It is important to determine the molecular absorptivity of $H_4TPP^{2+}_{aq}$, $\epsilon_{aq}^{435} (M^{-1} cm^{-1})$ for the stoichiometric analysis of interfacial adsorption. When the interfacial area $S (cm^2)$ is formed by the contact of two phases of same volume $V (cm^3)$, the interfacial concentration, $[H_4TPP^{2+})_i (mol cm^{-2})$, under our experimental conditions can be represented by

$$[H_4TPP^{2+})_i = 10^{-3}(V/S) \left\{ \frac{A_{soln}^{416}}{\epsilon_{soln}^{416} l_1} - \frac{A_{aq}^{435}}{\epsilon_{aq}^{435} l_2} \right\} \quad (4)$$

where A_{soln}^{416} and ϵ_{soln}^{416} refer to the absorbance of dodecane solution in concentration $[H_2TPP]_i$ measured with a 1cm cell ($l_1 = 1cm$) and the molecular absorptivity at 416nm ($\epsilon_{soln}^{416} = 4.33 \times 10^5 M^{-1} cm^{-1}$),³ respectively, and A_{aq}^{435} refers to the absorbance at 435nm of aqueous phase measured by the prism-cell ($l_2 = 2cm$). It is not so easy, however, to determine the value of ϵ_{aq}^{435} , because of the sparing solubility of H_2TPP in acidic aqueous solutions. In the dodecane-6M H_2SO_4 system with $[H_2TPP]_i = 0.244 \mu M$, we found that the interfacial adsorbate decreased whereas the aqueous species increased with elapsed time (h) as shown in Figure 8, though the dissolution equilibration was not attained even at 90 h. The plots of A_{ATR}^{720} and A_{aq}^{435} against A_{ATR}^{473} at each of the elapsed time were shown in Figure 9. It was found that the $A_{ATR}^{720}/A_{ATR}^{473}$ ratios decreased with elapsed time up to about 2h, and then maintained to a constant ratio thereafter. This strongly suggested that the interfacial adsorption state of H_4TPP^{2+} in the aggregate

changed from multilayer to monolayer, being accompanied by a change of ATR coefficient as described previously.¹³ In the monolayer adsorption state, the value of A_{ATR}^{473} (as well as that of A_{ATR}^{720}) must be proportional to the $[\text{H}_2\text{TPP}^{2+}]_i$. On the other hand, the values of A_{aq}^{435} at elapsed time over 3h linearly increased with decreasing A_{ATR}^{473} (as well as A_{ATR}^{720}). Using the four plots of A_{aq}^{435} at 3, 6, 19 and 90h, we obtained a linear approximation equation as

$$A_{\text{aq}}^{435} = 0.186 - 0.285 \times A_{\text{ATR}}^{473} \quad (r = 0.997) \quad (5)$$

under our experimental conditions ($[\text{H}_2\text{TPP}]_i = 0.244 \mu\text{M}$, $L = 2\text{cm}$). The value of A_{aq}^{435} at $A_{\text{ATR}}^{473} = 0$ was 0.186, which ought to be the absorbance of $\text{H}_2\text{TPP}^{2+}_{\text{aq}}$ with neither adsorbate nor solute in dodecane phase. Thus, the molecular absorptivity of $\text{H}_2\text{TPP}^{2+}_{\text{aq}}$ was obtained as $\epsilon_{\text{aq}}^{435} = 3.81 \times 10^4 \text{M}^{-1}\text{cm}^{-1}$, which was somewhat smaller than $\epsilon_{\text{soln}}^{416}$. The value of $\epsilon_{\text{aq}}^{435}$ could be used in Equation (4) for the estimation of $[\text{H}_2\text{TPP}^{2+}]_i$ in the dodecane-4M H_2SO_4 system, and also could be used for that in the other organic solvent-aqueous inorganic acid system, since the concentration of H_2TPP in the organic phase could be given by A_{org} spectrum whereas $\epsilon_{\text{aq}}^{435}$ should be consistent independently of the kind of inorganic acids.

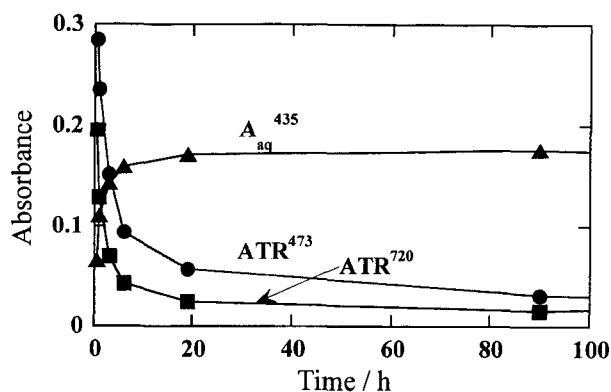


Figure 8 Absorbance change with elapsed time in the dodecane-6M H_2SO_4 system. $[\text{H}_2\text{TPP}]_i = 0.244 \mu\text{M}$.

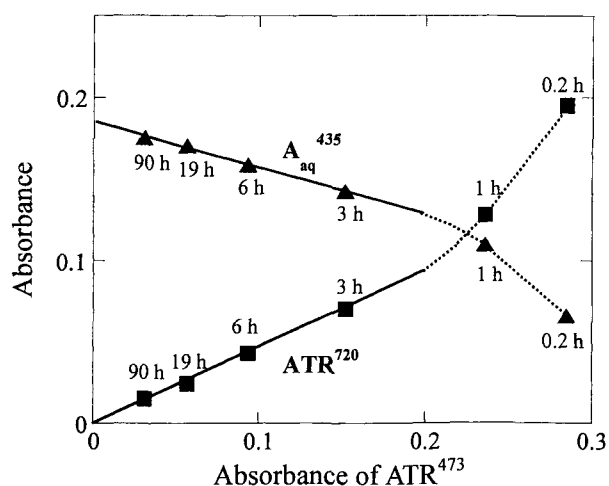


Figure 9 Absorbance plots of A_{ATR}^{720} and A_{aq}^{435} against A_{ATR}^{473} at each of the elapsed times in Figure 8.

4. Conclusion

Some simple devices comprised of an optical cell and prisms were proposed for direct spectroscopic measurement of the adsorbed species at the liquid-liquid interface, using a protonated *meso*-tetraphenylporphyrin as an interfacial adsorbate. The spectrum of adsorbate in aggregate form was effectively observed within the visible wavelength region by three kinds of the prism-cell assembly for (1) the double-phase transmission method, (2) the multiple ATR method and (3) the ATR-ER method. Particularly the last-mentioned method could be applicable widely and conveniently for the stoichiometric analysis of interfacial adsorbates. The characteristics of spectral appearance by each of the methods were described and discussed in detail.

Acknowledgements

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