

## Simple Devices for the Measurements of Absorption Spectra at Liquid-Liquid Interfaces

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Chemical reactions at liquid-liquid interfaces are an attractive subject in analytical sciences, especially in studies of solvent extraction, liquid membrane separation, counter current chromatography and ion-selective liquid membrane electrodes. The role of an interface in the solvent extraction of metal ions was demonstrated in our recent work where we employed a high-speed stirring method to gain advantages of an agitated system, a high specific interfacial area and promotion of mass transfer.<sup>1</sup> The principle of this method is as follows; when the specific interfacial area is large, interfacial adsorption of a solute can result in a significant decrease of the organic phase concentration. This concentration decrease can be measured spectrophotometrically after continuous phase separation by use of a Teflon phase separator.<sup>2</sup> This method was applied to measurements of extraction rates as well as to interfacial adsorption in various extraction systems. This is, however, an indirect method with respect to detection of interfacial adsorption. Consequently, a direct spectroscopic approach is desired to identify interfacially adsorbed species.

Among the methods proposed for measurements of absorption spectra at liquid-liquid interfaces, the total internal reflection method is thought most informative unless the organic phase contains strongly light-absorbing species.<sup>3</sup> Unfortunately, an organic phase encountered in solvent extraction usually contains colored species, and hence the application of this method is limited.

Two methods, an optical stir cell method and a Teflon capillary plate method, are proposed in this work for measurements of interfacial absorption spectra. Both devices were invented based on the same principle as the high-speed stirring method's; an increase in the specific interfacial area enlarges the proportion of the interfacial concentration. These methods were successfully applied to measurements of interfacial spectra of tetraphenylporphyrin (TPP) in a toluene/sulfuric acid

system.

### Experimental

*meso*-Tetraphenylporphyrin was from Dotite; it was used as received. Toluene (Wako, GR) was purified by fractional distillation. The concentration of sulfuric acid (Wako, GR) was determined by ordinary acid-base titrimetry.

The body of the optical stir cell was made of Pyrex glass. A quartz cell with 1 mm optical length was joined to the body, as shown in Fig. 1. The total volume of the cell was about 25 ml. A stirrer 17 mm in diameter with four blades each 7.5 mm in length and 5 mm in width was made of a solvent-resisting polymer resin (Gasukuro Kogyo). The stirrer was rotated by a small electric motor (Mabuchi RE-280) at a rate of 3400 rpm with a dc power supply of 1.5 V. Seven milliliters of TPP in toluene and the same volume of sulfuric acid were used in

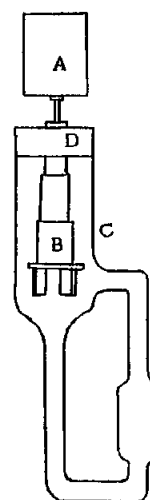


Fig. 1 Schematic drawing of the optical stir cell: (A) electric motor, (B) stirrer, (C) stir cell with 1 mm quartz flow cell, (D) Teflon cap.

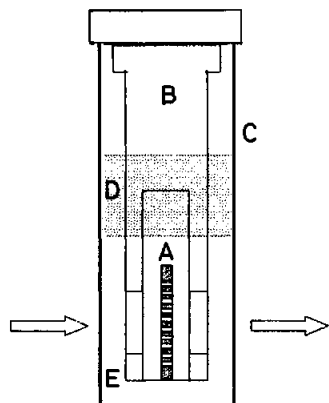


Fig. 2 Schematic representation of the Teflon capillary plate method: (A) Teflon capillary plate, (B) plate holder, (C) 10 mm quartz cell, (D) toluene phase, (E) aqueous phase.

each measurement. The stirred mixture was circulated through the 1 mm cell and the absorption spectra were recorded on an HP8452A photodiode array spectrophotometer.

The Teflon capillary plate was a small rectangular Teflon plate with capillary holes (Fig. 2). The dimensions of the plate were height 11.5 mm; width 7.5 mm; and thickness 1 mm, with 54 capillary holes of 0.6 mm diameter drilled in 9 rows $\times$ 6 columns. The distances between the adjacent centers of the holes were 1 mm. The plate was set in a plate holder and immersed slowly into the two-phase system of 0.6 ml TPP-containing toluene and 1.6 ml sulfuric acid in a 10 mm optical cell so as to fill the capillary holes with the organic phase, as illustrated in Fig. 2. By this procedure, a fresh liquid-liquid interface was created on both ends of each capillary hole. The absorption spectrum thus obtained is the sum of the absorption spectra of TPP at the two interfaces and in the bulk phase. The concentration of TPP in the acid solution was negligible. A JASCO UVIDEK 430 spectrophotometer was used for spectral measurements. All the operations were carried out in a room thermostated at  $25\pm 1^\circ\text{C}$ .

## Results and Discussion

### Optical stir cell method

Figure 3 shows a typical spectrum observed by the optical stir cell method for  $5.1\times 10^{-6}$  M TPP and 3.13 M sulfuric acid. Although noise distorted the base line, two distinct peaks at 420 nm and 472 nm are clearly observed. The spectra of the organic phase before and after the stirring showed only the 420 nm peak assignable to the neutral TPP in toluene. Therefore, the peak at 472 nm could be an interfacial species. This peak appeared at sulfuric acid concentrations above 2.6 M for a TPP concentration of  $5.1\times 10^{-6}$  M. The 472-nm absorbance increased when the TPP concentration was increased from  $2.0\times 10^{-6}$  M to  $1.0\times 10^{-5}$  M at a constant

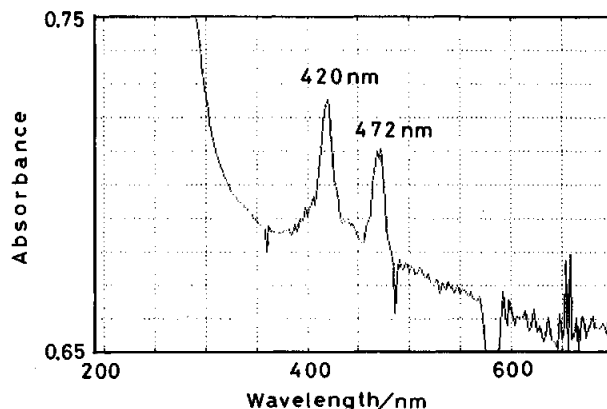


Fig. 3 Spectrum measured by the optical stir cell method for a mixture of  $5.1\times 10^{-6}$  M TPP in toluene and 3.13 M sulfuric acid.

sulfuric acid concentration of 3.13 M. The logarithmic plot of 472-nm absorbance against TPP concentration gave a straight line with slope of  $2.4\pm 0.1$ . In the highest concentration of TPP, a green film appeared at the interface after the stirring. The green film transferred onto a glass slide showed a absorption peak at 472 nm. The monomer of the diprotonated TPP has a peak at 440 nm.<sup>4</sup> In Fig. 3, there appears a slight peak around 440 nm. A monoprotated TPP is not observed in aqueous media.<sup>5</sup> These results suggest that the 472-nm species is the aggregate of the diprotonated TPP, produced at the surface of the toluene droplets. The aggregate may be a clathrate of  $\text{H}_2\text{TPP}(\text{HSO}_4)_2$ , as reported for  $\text{FeTPP}(\text{ClO}_4)(\text{H}_2\text{O})^6$  and  $\text{MnTPP}(\text{ClO}_4)(\text{H}_2\text{O})$  crystals.<sup>7</sup>

From the photographs of the dispersed mixture flowing downward through the 1 mm quartz cell, the mean diameter of the toluene droplets was estimated as  $0.89\pm 0.03$  mm.

### Teflon capillary plate method

Figure 4 shows a typical spectrum measured with the Teflon capillary plate for  $2.0\times 10^{-6}$  M TPP in toluene and 4.0 M sulfuric acid. The two peaks correspond to those in Fig. 3. Since the peak at 472 nm was detected neither in the toluene phase nor in the sulfuric acid phase, it can be ascribed to an interfacial species, most probably the aggregate of the di-cation. The absorbances at 420 nm and 472 nm are represented by;

$$A(420) = \varepsilon[\text{TPP}]_0 l \quad (1)$$

$$A(472) = 2\varepsilon'10^3 n[(\text{H}_2\text{TPP}^{2+})_n]_i \quad (2)$$

where  $\varepsilon$  and  $\varepsilon'$  are the molar absorptivities of TPP in toluene and  $\text{H}_2\text{TPP}^{2+}$  in the aggregate  $(\text{H}_2\text{TPP}^{2+})_n$ , respectively,  $[\text{TPP}]_0$  and  $[(\text{H}_2\text{TPP}^{2+})_n]_i$  are the TPP concentration in toluene (M) and the aggregate concentration at the interface (mol/cm<sup>2</sup>), respectively, and  $l$  is the thickness of the toluene phase (0.1 cm). The

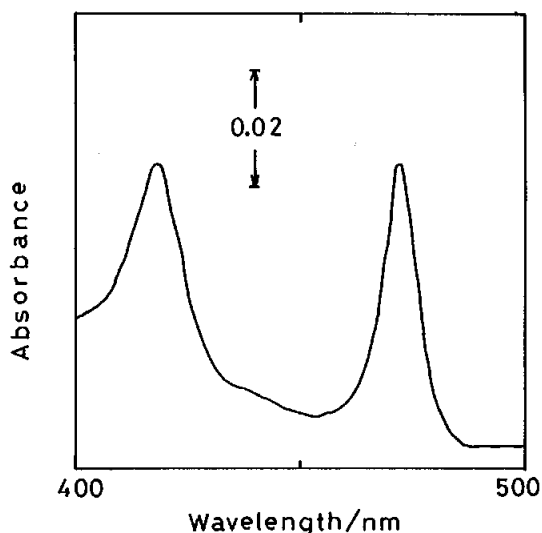


Fig. 4 Spectrum obtained by the Teflon capillary plate method for a system of  $2.0 \times 10^{-6}$  M TPP in toluene and 4.0 M sulfuric acid at 30 min after creation of the interface.

total amount of TPP in a capillary can be approximated by

$$[\text{TPP}]_{\text{init}}sl = [\text{TPP}]_0sl + n[(\text{H}_2\text{TPP}^{2+})_n]_i 2s \cdot 10^3 \quad (3)$$

where  $[\text{TPP}]_{\text{init}}$  is the initial concentration of TPP in toluene phase before contact with acid and  $s$  the area ( $\text{cm}^2$ ) of an interface. Hence, Eq. (2) can be rewritten as,

$$A(472) = \varepsilon'([\text{TPP}]_{\text{init}} - [\text{TPP}]_0)l \quad (4)$$

From Eqs. (1) and (4), the values for  $\varepsilon$  and  $\varepsilon'$  were estimated as  $4.2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  and  $3.4 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively.

## Summary

The two methods gave successfully the interfacial absorption spectra. The capillary plate method seems superior to the other in the simplicity of device, the stability of the interface and the reproducibility. The detection limit in this method can be improved by the use of multiple plates. The fraction of interface in a liquid-liquid system can be evaluated in terms of the specific interfacial area,  $a$ . The specific interfacial area for the stir cell is determined by the diameter of droplets,  $d$ , through the equation of  $a=6/d$ , which yields  $67 \text{ cm}^{-1}$  for the present system. On the other hand, the specific interfacial area for the capillary plate is determined solely by the thickness of the organic phase with the equation of  $a=2/l$ , which affords  $20 \text{ cm}^{-1}$  for the present case. Though the value of  $a$  of the optical stir cell is larger than the other, the spectrum observed in the stir cell method is seriously interfered with by refraction at the toluene droplet surface.

Further investigations on the interfacial reactions, including protonation and metal complex formation, are in progress in which the Teflon capillary plate method is being used.

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