Heterogeneous Fluorescence Quenching Reaction between (5,10,15,20-Tetraphenylporphyrinato)zinc(II) and Methylviologen at Dodecane-Water Interface

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The heterogeneous fluorescence quenching reaction of (5,10,15,20-tetraphenylporphyrinato)zinc(II) (ZnTPP) in dodecane by methylviologen in an aqueous phase at the liquid-liquid interface was investigated by means of the centrifugal liquid membrane method. The quenching reaction could occur only in the presence of an anionic surfactant, sodium dodecyl sulfate (SDS). The quenching efficiency depended on the concentration of SDS in the aqueous phase with a maximum value of 13.5%.

The direct spectrophotometric method to determine the species adsorbed at the liquid-liquid interface has been required to study the solvent extraction system and the cell biology. Recently, the centrifugal liquid membrane (CLM) method was developed and the mechanism of the demetallation of (5,10,15,20-tetraphenyporphyrinato)zinc(II) (ZnTPP) at the liquid-liquid interface was investigated.[1] The CLM method can produce a two-phase liquid membrane system consisting of immiscible organic and aqueous phases in a rotating optical cell. It has high sensitivity for the interfacial species, because of a large specific interfacial area.

The fluorescence quenching and electron transfer (ET) reactions of porphyrin compounds, particularly in heterogeneous system, are very important as a model of the photosynthesis system.[2]

In this work, the CLM method combined with fluorescence spectrometry was applied to the investigation of the fluorescence quenching reaction between ZnTPP in an organic phase and a cationic quencher in an aqueous phase.

ZnTPP was prepared according to the method reported in the literature[3] and dissolved in dodecane which was highly purified by distillation after being washed with fuming sulfuric acid and sulfuric acid. The dichloride salt of methylviologen (MV^{2+}) (TCI, G.R.) as a quencher was dissolved in an aqueous solution in the presence of sodium dodecyl sulfate (SDS) (nacalai tesque, S.P.). Water was purified by a Millipore Milli-Q SP.TOC.

The CLM method can afford a stable ultra-thin two-phase liquid membrane by the centrifugal force produced by the rotation.[1] The organic solution, 0.100 cm^3, and the aqueous solution, 0.250 cm^3, were put into the cylindrical glass cell which was rotated at 10000 rpm by a high speed motor (Nakanishi Inc., NK-260) with a speed controller (Nakanishi Inc., NE-22E). The inner diameter and inner height of the cylindrical glass cell were 19 mm and 33 mm, respectively. The ultra-thin two-phase liquid membrane system was stable at the rotation speed above *ca.* 6000 rpm. In the present system, the dodecane solution was spread as an inner liquid membrane of 56 μm film thickness and the aqueous solution as an outer liquid membrane of 128 μm, respectively. The interfacial area between the two phases, S_i, was estimated as 19.6 cm^2 and the specific interfacial area, S_i/V_o, was calculated as 196 cm^{-1}. The thickness, d_o, and the specific interfacial area can be controlled within $42\ \mu m \le d_o \le 132\ \mu m$ and $78 \le S_i/V_o \le 245\ cm^{-1}$, respectively, by changing the organic phase volume, V_o. The fluorescence spectrum of the two-phase liquid membrane system was measured by a Perkin Elmer LS50B luminescence spectrophotometer with the optical arrangement as shown in Figure 1. All measurements were carried out in the thermostated room at 298±1.5 K.

Figure 2 shows typical emission spectra of the free base (H_2TPP), the diprotonated species (H_4TPP^{2+}) and ZnTPP, in the two-phase liquid membrane systems. The excitation wavelengths were the absorption maximum wavelengths, *i.e.*, 416 nm for H_2TPP and ZnTPP, and 466 nm for H_4TPP^{2+}. In the dodecane-hydrochloric acid system, H_2TPP is diprotonated at dodecane-water interface and H_4TPP^{2+} can exist only at the interface.[1] Thus, it was found that the emission spectrum of the interfacial species can clearly be measured by the CLM method. ZnTPP has two characteristic emission peaks at 642 nm, *Q*(0,1), and 596 nm, *Q*(0,0).[4] Experiments showed that the fluorescence quenching of ZnTPP took place in the presence of a large excess of MV^{2+} and a slight amount of SDS. The fluorescence quenching did not take place without SDS. ZnTPP is an extremely hydrophobic reagent, but specifically adsorbed at dodecane-water interface.[5] Since MV^{2+} is dissolved as a dication form in an aqueous phase, it is expected that the transport of MV^{2+} from an aqueous phase into a dodecane phase is negligible, no matter how the ion pair with SDS anions can be formed. Moreover, preliminary experiments showed that the fluorescence quenching of the free base, which is not adsorbed at dodecane-water interface, did not occur in the same condition. Therefore, it is suggested that the fluorescence quenching reaction of ZnTPP with MV^{2+} proceeds at dodecane-water interface.

MV^{2+} is well known as an effective fluorescence quencher for porphyrins by the function of an electron acceptor.[6] It is thought that the fluorescence quenching reaction in the present system results from the ET reaction from the singlet state of ZnTPP to MV^{2+} across the liquid-liquid interface.

$$\mathrm{ZnTPP_i} + h\nu \rightarrow \mathrm{ZnTPP_i^*} \qquad (1)$$

$$\mathrm{ZnTPP_i^*} + \mathrm{MV^{2+}{}_i} \rightarrow \mathrm{ZnTPP^{+}{}_i}\cdot + \mathrm{MV^{+}{}_i}\cdot \qquad (2)$$

The dependence of the relative quenching of emission on the concentration of SDS in an aqueous phase was evaluated from the

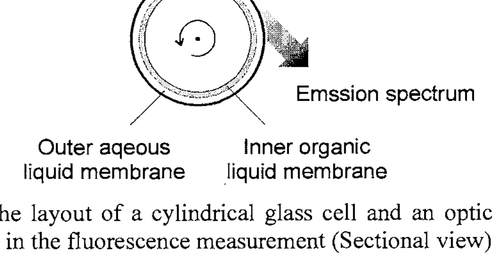

Figure 1. The layout of a cylindrical glass cell and an optical arrangement in the fluorescence measurement (Sectional view).

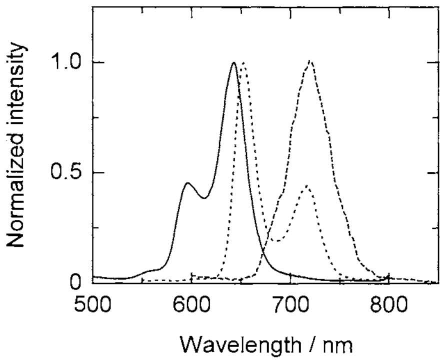

Figure 2. Typical emission spectra in the two-phase liquid membrane system. The solid, dotted and broken lines relate to ZnTPP, H_2TPP and H_4TPP^{2+}, respectively.

intensity change at 642 nm which was assigned to $Q(0,1)$ of ZnTPP. The relative quenched intensity plotted in Figure 3 was approximately constant value of 13.5% in the concentration region of SDS lower than *ca.* 10^{-5} mol dm^{-3}. This means that the interfacial concentration of ZnTPP quenched is 2.8×10^{-12} mol cm^{-2}. The addition of minute amount of SDS effectively quenched even in very low concentration, *i.e.*, less than 10^{-7} mol dm^{-3}. However, the relative quenched intensity was decreased by the increase of SDS concentration higher than 10^{-5} mol dm^{-3} and the quenching reaction was completely prevented in the higher concentration than *ca.* 5×10^{-5} mol dm^{-3}. Thus, the quenching reaction was controlled by the adsorption of SDS. In the absence of SDS, ZnTPP is adsorbed at the liquid-liquid interface, however, MV^{2+} dissolved in an aqueous phase can not be sufficiently provided to the interface. In the presence of SDS, the cationic quencher can be concentrated at the interface by the ion-association adsorption, and the fluorescence quenching reaction takes place. In the excess amount of SDS, the interface is occupied by the surfactant anions and the interfacial adsorption of ZnTPP is completely prevented. If it can be assumed that most of the surfactant molecules added into an aqueous phase is adsorbed at the liquid-liquid interface, the interfacial concentration of SDS can be estimated as 6×10^{-10} mol cm^{-2} in the case of 5×10^{-5} mol dm^{-3} SDS solution. This value is similar to the saturated interfacial concentration reported in the interfacial tension measurement, *i.e.*, 3.75×10^{-10} mol cm^{-2}.[7] Hence, the fluorescence quenching reaction could occur effectively in the concentration region of SDS less than 5×10^{-5} mol dm^{-3}.

The amount of ZnTPP adsorbed at the interface can be estimated from the interfacial adsorption constant defined as

$$K' = \frac{[\mathrm{ZnTPP}]_i}{[\mathrm{ZnTPP}]_o} \qquad (3)$$

where $[\mathrm{ZnTPP}]_i$ and $[\mathrm{ZnTPP}]_o$ denote the concentrations of ZnTPP adsorbed at the interface (mol dm^{-2}) and in the bulk organic phase (mol dm^{-3}), respectively. The value of K' was reported as 2.1×10^{-4} dm in the high-speed stirring experiment.[5] If all amount of ZnTPP at the liquid-liquid interface can be quenched by MV^{2+}, *ca.* 29% of the emission should be decreased in the present system. However, the experimental value of the relative quenched intensity of emission was 13.5%. The difference between the experimental and evaluated values should be ascribed to the limitation of the interfacial concentration of MV^{2+} and the short fluorescence life time of ZnTPP which was determined as $\tau = 2.3$ ns in dodecane by the natural fluorescence decay measurement.

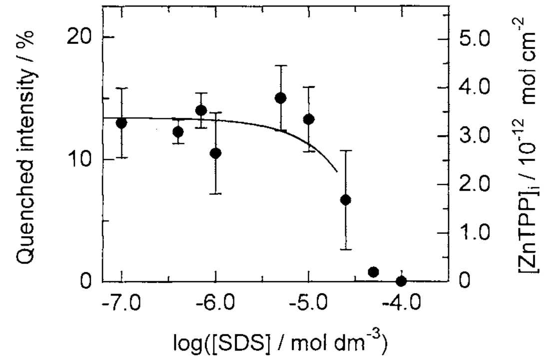

Figure 3. Plots of the relative quenched intensity of emission and the interfacial concentration of ZnTPP *vs.* the concentration of SDS in the aqueous phase. The concentrations of ZnTPP in dodecane and MV^{2+} in an aqueous solution were 4.1×10^{-6} mol dm^{-3} and 1.0 mol dm^{-3}, respectively.

In this study, the fluorescence quenching reaction at the liquid-liquid interface was measured in the presence of both an anionic surfactant and a cationic quencher. The presence of excess surfactant hindered the interfacial adsorption of ZnTPP. Therefore, the surfactant served as a catalyst for the heterogeneous fluorescence quenching reaction and an inhibitor for the interfacial adsorption of ZnTPP.

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