

# Fluorescence quenching reaction of porphyrins in micelles: Ionic porphyrins quenched by nitrobenzene in ionic micelles

Makoto Takezaki, Toshihiro Tominaga\*

*Department of Applied Chemistry, Okayama University of Science, 1-1 Ridai-cho, Okayama 700-0005, Japan*

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## Abstract

Fluorescence decays have been measured for 5,10,15,20-tetraphenyl-21*H*,23*H*-porphinetetrasulfonate (TPPS<sup>4-</sup>) adsorbed on the surface of the cationic micelles, decyl-, dodecyl-, tetradecyl- and hexadecyl-trimethylammonium bromide at 25 °C, and 5,10,15,20-tetrakis{4-[*N*-(trimethyl)ammonio]phenyl}-21*H*,23*H*-porphine (TTMAPP<sup>4+</sup>) adsorbed on the surface of the anionic micelles, sodium decane-, dodecane-, and tetradecane-sulfonate at 55 °C, in the presence of nitrobenzene (NB). The fluorescence decay curves are well represented by a single exponential function. This is attributed to the shorter fluorescence lifetime of TPPS<sup>4-</sup> and TTMAPP<sup>4+</sup> compared with those of Ru complexes and pyrene, where non-exponential decays have been reported. The quenching rate constants in the micelles,  $k_m$ , have been obtained and the dependence of  $k_m$  on the surfactant alkyl chain-length is calculated to be 0.21–0.23 per methylene unit. These values are much smaller than the values for the distance-dependence factor for electron-transfer reactions, i.e. 1–1.5 per methylene unit. From model calculations, it appears that NB molecules are localized primarily in the peripheral region of the micelles rather than being uniformly distributed within the micelles. This phenomenon, together with the diffusion of NB molecules within micelles, results in the quenching reactions being quasi two-dimensional and causes the small chain-length dependency observed in this work.

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**Keywords:** Fluorescence quenching; Electron-transfer; Distance-dependence; Ionic micelle; Ionic porphyrin

## 1. Introduction

The study of electron-transfer fluorescence quenching reactions in micellar systems provides fundamental information that can assist in elucidating the mechanisms of model bio-reactions and bimolecular reactions in restricted systems. There have been many detailed studies and kinetics models developed for electron-transfer fluorescence quenching reactions in micellar systems [1–18]. The fluorescence decay curves for Ru complexes, pyrene and its derivatives in micellar systems are well described by the Tachiya–Infelta equation [1–9,19–21], which has been applied to a wide range of bimolecular reaction kinetics in micellar systems to determining micellar properties [19–21]. However, there

have been only a few reports of bimolecular reaction kinetics in micellar systems using fluorophores with relatively short lifetimes [14–18]. Furthermore, fluorescence quenching reactions involving porphyrins in micellar systems are not well understood.

We have reported previously the results of a study of the electron-transfer fluorescence quenching reaction for the anionic porphyrin 5,10,15,20-tetraphenyl-21*H*,23*H*-porphinetetrasulfonate (TPPS<sup>4-</sup>) adsorbed on the surface of Pt nanoparticles protected by cationic surfactants [22]. The surfactant chain-length dependence of the electron-transfer rate was found to be small for this reaction, which we interpreted as being due to the substantial penetration of the anionic porphyrin into the protecting surfactant layer. The study of the electron-transfer fluorescence quenching reaction for ionic porphyrins adsorbed on the surface of micelles in the presence of a quencher solubilized inside the micelles is necessary to gain a better understanding of redox reactions involving porphyrins in micellar systems.

\* Corresponding author. Tel.: +81 86 256 9565; fax: +81 86 252 6891.

*E-mail addresses:* [mtake@dac.ous.ac.jp](mailto:mtake@dac.ous.ac.jp) (M. Takezaki), [tominaga@dac.ous.ac.jp](mailto:tominaga@dac.ous.ac.jp) (T. Tominaga).

The fluorescence quenching reaction between porphyrins and nitrobenzene (NB) is known to be due to the electron-transfer mechanism [23,24]. In the present work, we have measured fluorescence quenching rates of TPPS<sup>4-</sup> adsorbed on the surface of a series of cationic micelles, and a cationic porphyrin, 5,10,15,20-tetrakis{4-[*N*-(trimethyl)ammonio]phenyl}-21*H*,23*H*-porphine (TTMAPP<sup>4+</sup>), adsorbed on the surface of a series of anionic micelles in the presence of NB solubilized in the micelles. Fluorescence quenching rate constants were determined and their dependence on the surfactant chain-length is discussed with the aid of model calculations.

## 2. Experimental

5,10,15,20-Tetraphenyl-21*H*,23*H*-porphinetetrasulfonic acid, disulfuric acid tetrahydrate (H<sub>4</sub>TPPS·2H<sub>2</sub>SO<sub>4</sub>·4H<sub>2</sub>O) (Dojin), 5,10,15,20-tetrakis{4-[*N*-(trimethyl)ammonio]phenyl}-21*H*,23*H*-porphine tetrakis(*p*-toluenesulfonate) (TTMAPP<sup>4+</sup>TS<sup>-4</sup>) (Dojin), NB (Wako, guaranteed reagent), sodium decane-, dodecane-, and tetradecane-sulfonate (C<sub>10</sub>SO<sub>3</sub>Na, C<sub>12</sub>SO<sub>3</sub>Na, and C<sub>14</sub>SO<sub>3</sub>Na) (Kanto Chemical, analytical reagent), and sodium dodecyl sulfate (NaDS) (Kanto Chemical, guaranteed reagent) were used without further purification. Decyl-, dodecyl-, tetradecyl-, and hexadecyl-trimethylammonium bromide (C<sub>10</sub>TABr, C<sub>12</sub>TABr, C<sub>14</sub>TABr, and C<sub>16</sub>TABr) (Tokyo Kasei, guaranteed reagent) were used after being kept below 1 Torr for 1–2 days. Water was doubly distilled. TPPS<sup>4-</sup> solutions were prepared by adding NaOH solutions to H<sub>4</sub>TPPS·2H<sub>2</sub>SO<sub>4</sub>·4H<sub>2</sub>O solutions.

Fluorescence decays were measured using an apparatus including a femtosecond laser system and a streak camera. The second harmonic of a femtosecond Ti:Sapphire laser (Spectra-Physics, Tsunami 3960, the wavelength of pulse ~ 800 nm, the fwhm of the pulse ~ 80 fs) pumped by the SHG output of a Nd:YVO<sub>4</sub> laser (Spectra-Physics, Millennia-V) was used to excite the porphyrins. The detected fluorescence was dispersed by a monochromator and measured using a streak scope (Hamamatsu, C4334). The fluorescence signals were averaged using a PC.

Fluorescence decay measurements were performed at 25 °C for TPPS<sup>4-</sup> and at 55 °C for TTMAPP<sup>4+</sup>. The surfactant concentrations were 200 mM (1 M = 1 mol dm<sup>-3</sup>) for all samples. The bulk NB concentrations were varied from 0 to 50 mM and the bulk concentrations of the porphyrins were ~ 1 μM.

## 3. Results and discussion

The fluorescence decay curves measured for TPPS<sup>4-</sup> adsorbed on the surface of C<sub>*n*</sub>TABr (*n* = 10, 12 and 16) micelles in both the absence and presence of 20 mM NB are shown in Fig. 1. The fluorescence decays for TPPS<sup>4-</sup> were also mea-

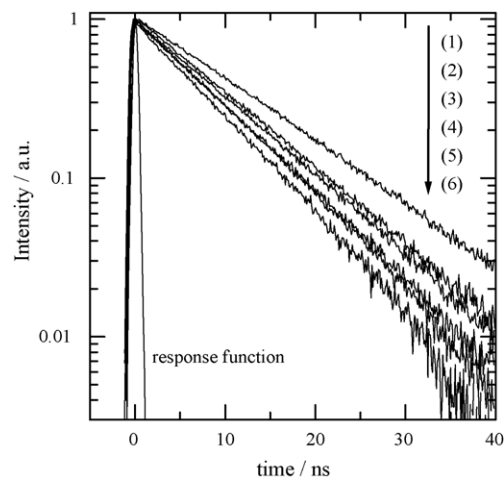


Fig. 1. Fluorescence decay curves for TPPS<sup>4-</sup> at 25 °C in (1) C<sub>10</sub>TABr, (2) C<sub>12</sub>TABr and (5) C<sub>16</sub>TABr and those in the presence of 20 mM NB in (3) C<sub>10</sub>TABr, (4) C<sub>12</sub>TABr and (6) C<sub>16</sub>TABr. All C<sub>*n*</sub>TABr concentrations are 200 mM.

sured in C<sub>14</sub>TABr, but are not shown in Fig. 1 for clarity. All decay curves are described well by the single exponential function:

$$I = I_0 \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where  $\tau$  is the decay time constant. In the absence of NB, TPPS<sup>4-</sup> fluorescence intensities decay more rapidly with increasing chain-length of C<sub>*n*</sub>TABr, and the fluorescence decay time constants in C<sub>10</sub>TABr and C<sub>16</sub>TABr are 11.4 and 7.8 ns, respectively (Fig. 1, curves 1 and 5). This decrease in lifetime is attributed to the TPPS<sup>4-</sup> fluorescence being quenched by Br<sup>-</sup> on the surface of the C<sub>*n*</sub>TABr micelles. The addition of NB increases the decay rates, which will be discussed later.

The fluorescence decay curve for TTMAPP<sup>4+</sup> adsorbed on the surface of C<sub>12</sub>SO<sub>3</sub>Na micelles is shown in Fig. 2 (curve 1). The TTMAPP<sup>4+</sup> fluorescence decay time in the absence of NB is virtually independent of surfactant chain-length, being in the range of 10.9–11.6 ns in the C<sub>*n*</sub>SO<sub>3</sub>Na solutions used in this work. Also shown in Fig. 2 is the effect of the addition of 20 mM NB on the fluorescence decay curves for TTMAPP<sup>4+</sup> adsorbed on C<sub>*n*</sub>SO<sub>3</sub>Na (*n* = 10, 12, 14) micelles (curves 2–4). In the presence of NB the TTMAPP<sup>4+</sup> fluorescence intensities decay more rapidly with decreasing length of the C<sub>*n*</sub>SO<sub>3</sub>Na chains. All decay curves are again described well by Eq. (1). If some fraction of the fluorophores were not adsorbed on the micellar surface, then the fluorescence decay curves would be expected to follow a double exponential function because fluorescence from the adsorbed fluorophores will be quenched to some extent by the NB molecules which localize in the micelles, whereas the fluorescence from any non-adsorbed fluorophores would be expected to be unquenched. The good fit of the decay curves to a single exponential function indicates that essentially all fluorophores are localized in the micelles.

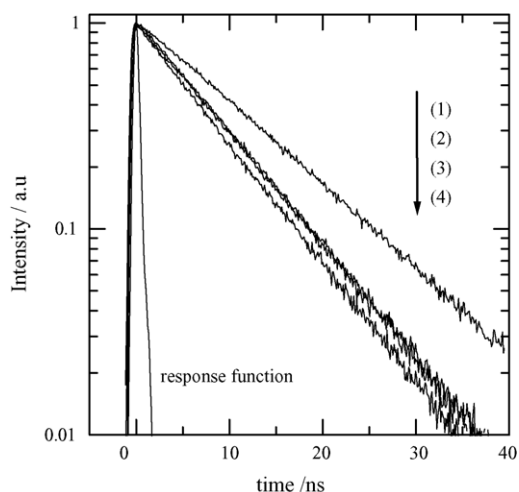


Fig. 2. Fluorescence decay curve for TTMAPP<sup>4+</sup> at 55 °C in (1) C<sub>12</sub>SO<sub>3</sub>Na and those in the presence of 20 mM NB in (2) C<sub>14</sub>SO<sub>3</sub>Na, (3) C<sub>12</sub>SO<sub>3</sub>Na and (4) C<sub>10</sub>SO<sub>3</sub>Na. All C<sub>n</sub>SO<sub>3</sub>Na concentrations are 200 mM.

For fluorophores with long lifetimes such as Ru complexes and pyrene at low quencher concentrations in micelles [1,3–9,19–21], fluorescence decay curves have been reported to be well described by the Tachiya–Infelta equation [2,3]:

$$I(t) = I_0 \exp \left[ q \{ \exp(-k_m t) - 1 \} - \frac{t}{\tau_0} \right] \quad (2)$$

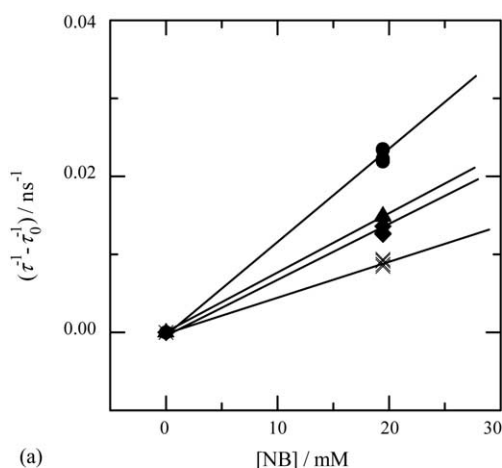
where  $q$  is the average number of quencher per micelle,  $\tau_0$  the decay time in the absence of NB, and  $k_m$  a micellar quenching rate constant. The derivation of Eq. (2) includes the assumption that the distribution of the quencher in micelles obeys a Poisson distribution. In the present cases of the TPPS<sup>4-</sup> + NB/C<sub>n</sub>TABr, TTMAPP<sup>4+</sup> + NB/C<sub>n</sub>SO<sub>3</sub>Na and TTMAPP<sup>4+</sup> + NB/NaDS systems, however, the fluorescence decays cannot be described satisfactorily by Eq. (2). If the product of  $k_m$  and  $\tau_0$  is much smaller than 1, then Eq. (2) reduces to Eq. (3):

$$I(t) \approx I_0 \exp \left[ - \left( qk_m + \frac{1}{\tau_0} \right) t \right] \quad (3)$$

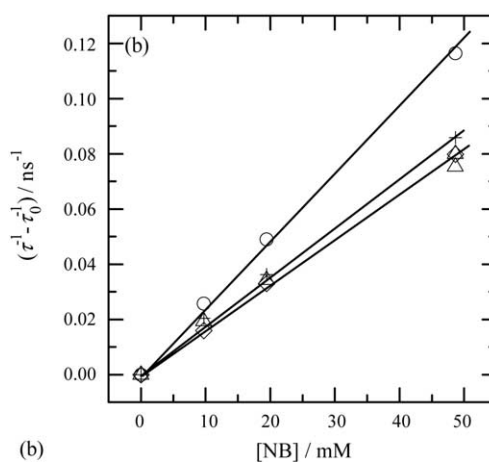
In this case, the decay function becomes a single exponential function.

The quenching rates,  $1/\tau - 1/\tau_0$  are plotted as a function of the bulk NB concentration, [NB], in Fig. 3. The  $(1/\tau - 1/\tau_0)$  ( $=qk_m$ ) values are proportional to the bulk NB concentration, and increase with decreasing alkyl chain-length. To obtain the  $k_m$  values, it is necessary to estimate the  $q$  values. Because the  $(1/\tau - 1/\tau_0)$  values are proportional to the bulk NB concentration, we assume that all NB molecules are simply solubilized in the micelles and that the micellar aggregation numbers,  $N$ , and micellar sizes are independent of the NB concentration. The number of NB molecules per micelle,  $q$ , was calculated using Eq. (4):

$$q = \frac{[\text{NB}]}{[\text{M}]} \quad (4)$$



(a)



(b)

Fig. 3. Fluorescence decay rates as a function of the bulk NB concentration: (a) TPPS<sup>4-</sup> in C<sub>10</sub>TABr (●), C<sub>12</sub>TABr (▲), C<sub>14</sub>TABr (◆) and C<sub>16</sub>TABr (×). (b) TTMAPP<sup>4+</sup> in C<sub>10</sub>SO<sub>3</sub>Na (○), C<sub>12</sub>SO<sub>3</sub>Na (△), C<sub>14</sub>SO<sub>3</sub>Na (◇) and NaDS (+).

where [M] is the micellar concentration, which was estimated using Eq. (5):

$$[\text{M}] = \frac{[\text{S}] - \text{cmc}}{N} \quad (5)$$

where [S] is the total surfactant concentration and cmc the critical micelle concentration. The [M] values were calculated using the literature values for cmc and  $N$  [19,25–27], which are listed in Table 1. Fig. 4 shows the quenching rates,  $1/\tau - 1/\tau_0$  ( $=qk_m$ ), plotted as a function of the  $q$  values. The fluorescence quenching rate constants,  $k_m$ , were calculated from the slopes of the lines in Fig. 4 and these values are also listed in Table 1.

The magnitude of  $k_m$  is more than an order of magnitude smaller than the  $1/\tau_0$  values which are in the range of  $(0.8\text{--}1.3) \times 10^8 \text{ s}^{-1}$ . The  $\tau_0$  values for the ionic porphyrins are one to two orders of magnitude smaller than those for Ru complexes, pyrene and its derivatives, whose decay curves can be described by Eq. (2) but not by Eq. (3). The observed

Table 1  
Micellar properties and quenching rate constants

	cmc (mM) <sup>a</sup>	<i>N</i> <sup>a</sup>	<i>k<sub>m</sub></i> (× 10 <sup>6</sup> s <sup>-1</sup> ) <sup>b</sup>
C <sub>10</sub> SO <sub>3</sub> Na	41 [25]	40 [26]	9.5
C <sub>12</sub> SO <sub>3</sub> Na	10 [27]	52 [27]	5.7
C <sub>14</sub> SO <sub>3</sub> Na	2.6 [27]	80 [26]	4.0
NaDS	8 [19]	64 [19]	5.2
C <sub>10</sub> TABr	65 [19]	39 [19]	4.0
C <sub>12</sub> TABr	15.3 [19]	55 [19]	2.6
C <sub>14</sub> TABr	3.6 [19]	70 [19]	1.9
C <sub>16</sub> TABr	0.9 [19]	89 [19]	1.1

<sup>a</sup> Values for cmc and aggregation numbers were taken from the literatures shown in square brackets.

<sup>b</sup> Quenching rate constants for TTMAPP<sup>4+</sup> + NB in anionic micelles and TPPS<sup>4-</sup> + NB in cationic micelles.

single exponential decays are attributed to the small values of the product of *k<sub>m</sub>* and  $\tau_0$ .

In Fig. 5, the logarithm of the *k<sub>m</sub>* values are plotted as a function of the surfactant chain-length, *n*, and these values are seen to decrease linearly with increasing alkyl chain-length. The fluorescence quenching reaction of the porphyrins with NB is due to electron-transfer [23,24] and electron-transfer rates are known to decrease exponentially with increasing reaction distance between reactants, *r* [28–30]. Therefore, *k<sub>m</sub>* can be expressed as:

$$k_m = k_0 \exp(-\beta r) \quad (6)$$

where *k<sub>0</sub>* is the reaction rate at *r*=0 and  $\beta$  a distance-dependence factor. From the study of fluorescence quenching reactions, Murata et al. [31] have reported  $\beta$  values ranging from 0.8 to 1.2 Å<sup>-1</sup> (or 1–1.5 per methylene unit assuming 1.25 Å per methylene unit). From analysis of the transient effect in fluorescence quenching reactions [31,32], transient-absorption and fluorescence decay measurements [33–38], and current measurements using a gold electrode [39–43],

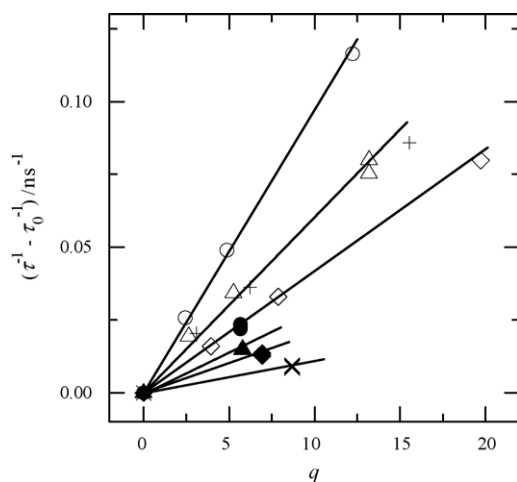


Fig. 4. Fluorescence decay rates as a function of the number of NB molecules per micelle for TPPS<sup>4-</sup> in C<sub>10</sub>TABr (●), C<sub>12</sub>TABr (▲), C<sub>14</sub>TABr (◆), C<sub>16</sub>TABr (×); and for TTMAPP<sup>4+</sup> in C<sub>10</sub>SO<sub>3</sub>Na (○), C<sub>12</sub>SO<sub>3</sub>Na (Δ), C<sub>14</sub>SO<sub>3</sub>Na (◇), NaDS (+).

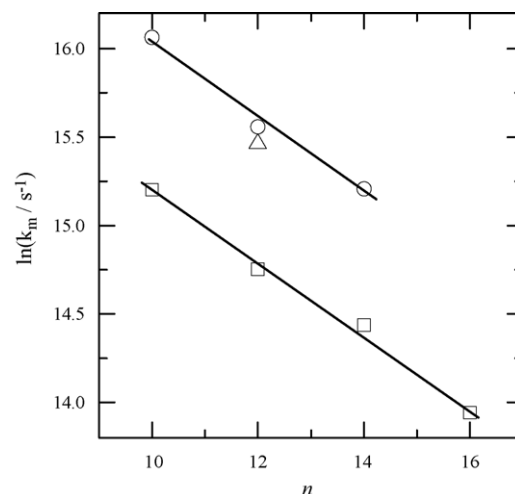


Fig. 5. Fluorescence quenching rate constants, *k<sub>m</sub>*, as a function of the surfactant chain-length, *n*. TTMAPP<sup>4+</sup> + NB/C<sub>*n*</sub>SO<sub>3</sub>Na (○), TTMAPP<sup>4+</sup> + NB/NaDS (Δ), TPPS<sup>4-</sup> + NB/C<sub>*n*</sub>TABr (□).

the  $\beta$  values are calculated to be in the range of 0.8–1.8 per methylene unit.

If the NB molecules are solubilized only in the core of the micelle, then the chain-length dependence of *k<sub>m</sub>* would be expected to be approximately 1–1.5 per methylene unit. From the slopes in Fig. 5, the chain-length dependences are calculated to be 0.23 and 0.21 per methylene unit for the TPPS<sup>4-</sup> + NB/C<sub>*n*</sub>TABr and TTMAPP<sup>4+</sup> + NB/C<sub>*n*</sub>SO<sub>3</sub>Na systems, respectively. The chain-length dependences for the present systems are more than a factor of 4 smaller than the literature values. In the case of Pt nanoparticles stabilized by C<sub>*n*</sub>TACl, we reported [22] a chain-length dependence value of 0.45 per methylene unit for the electron-transfer from excited TPPS<sup>4-</sup> adsorbed on the stabilizing layer surface to the Pt metal core. This smaller value was interpreted as being due to the penetration of TPPS<sup>4-</sup> into the cationic surfactant layers [22]. Because the chain-length dependence values for the present systems are about half that for the TPPS<sup>4-</sup>-Pt nanoparticle system, their small magnitude cannot be interpreted as being solely due to the penetration of the porphyrins into micelles.

In order to better understand the possible reasons for the small chain-length dependences, model calculations were performed based on the following assumptions: (1) one fluorophore is adsorbed on the micellar surface and one quencher is solubilized in the micelle; (2) the quenching rate constant, *k<sub>m</sub>*, is given by Eq. (6), where *r* is in units of Å,  $\beta$  is 1 Å<sup>-1</sup>, and *k<sub>0</sub>* is one per step; (3) the radii of the micelles do not change as a result of solubilization of a quencher molecule; (4) the fluorophore moves randomly on the micellar surface at the diffusion coefficient, *D<sub>F</sub>* = 1 × 10<sup>-11</sup> m<sup>2</sup> s<sup>-1</sup>, and the quencher inside the micelle diffuses at *D<sub>Q</sub>* = 1 × 10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup>. Lengths of the surfactants, including the head group, were calculated using the MM2 method, and are 13, 16, 18, 21 and 23 Å for octane-, decane-, dodecane-, tetradecane-, and hexadecane-sulfonate, respectively. Calculations were

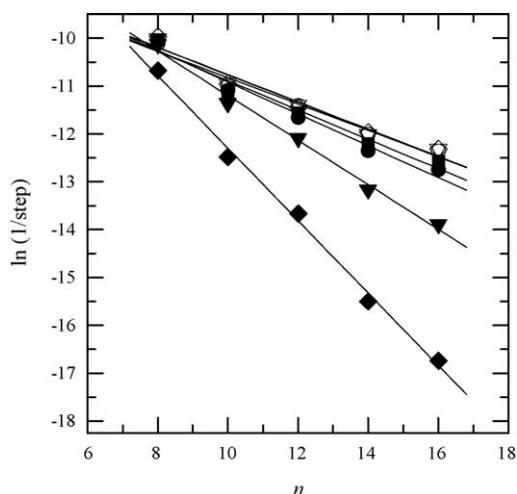


Fig. 6. Dependence of reciprocal number of steps on the surfactant chain-length from model calculations. NB molecules are assumed to be solubilized in the core whose radius is 1.0 (■), 0.8 (●), 0.66 (▼) and 0.5 (◆) times the micellar radius, or in the shell whose thickness is 0.2 (○), 0.33 (▽) and 0.5 (◇) times the micellar radius.

performed as follows. Operation 1: initial positions of reactants are generated. Operation 2: quencher is moved by a distance  $(2D_Q\Delta t)^{1/2}$  within a micelle and fluorophore is moved by  $(2D_F\Delta t)^{1/2}$  on the same micellar surface in random directions. Operation 3: if a generated random number is less than or equal to  $\exp(-\beta r)$ , quenching reaction is taken to have occurred. Otherwise return to the operation 2. Operation 4: return to operation 1. The  $\Delta t$  value was 10 fs. The number of times of operation 2, which we will call the step numbers, required to react were calculated and averaged over 10,000 different initial distributions for each surfactant chain-length.

At first, the initial positions of the quencher were assumed to be uniformly distributed all over the entire micelle, and the steps required to react were calculated. Reciprocals of the average number of steps, which are proportional to the quenching rate, are plotted in Fig. 6 (see data points represented by ■). The reciprocal numbers of steps decrease with increasing chain-length, and the chain-length dependence is calculated to be 0.31 per methylene unit. Next, we assumed that a micelle consists of a core and a shell and that the quenchers are located either only in the core or only in the shell. The

step numbers were calculated changing the radii of the core, and the reciprocal number of the steps are shown in Fig. 6 (closed symbols). The calculated chain-length dependences for quenchers distributed within the core of 1.0, 0.8, 0.66, 0.5, and 0.3 times the micellar radii,  $r_m$ , are 0.31, 0.33, 0.46, 0.76, and 1.15 per methylene unit, respectively. (The results for the core of 0.3 times  $r_m$  are not shown in Fig. 6.) With decreasing core-radius, the chain-length dependence increases, and at 0.3 times  $r_m$ , the chain-length dependence is  $0.92 \text{ \AA}^{-1}$ , which is close to  $1 \text{ \AA}^{-1}$  or 1.25 per methylene unit at the limit of infinitely small core without diffusion. Also shown in Fig. 6 are the results for quenchers distributed only within the shell (open symbols). For the shell thickness range from 0.5, 0.33, 0.2 and 0.1 times of  $r_m$ , the chain-length dependences are 0.29, 0.28, 0.27 and 0.27 per methylene unit, respectively. (For clarity, the results for the shell thickness of 0.2 times of  $r_m$  are not shown in Fig. 6.) The chain-length dependences decrease, although slightly, with decreasing thickness of the shell. This calculation suggests that NB molecules are solubilized mostly in the peripheral region of the micelles, and this is consistent with spectroscopic studies showing that aromatic compounds are solubilized in the palisade layer of micelles [44–50]. The calculations using 10 times smaller  $D$  values increase the step numbers, but the calculated chain-length dependences did not change.

The above results of the model calculation show that the NB molecules solubilized near the micellar surface and close to the excited porphyrins are mainly responsible for controlling the reaction rate. The difference in the chain-length dependences determined from experiment (0.21–0.23 per methylene unit) and calculation (0.27 per methylene unit) may reflect that the porphyrins are more or less penetrated into the micelles but are not only located in the surface as assumed in the calculation. As was described previously, the  $k_m$  values were obtained from the slopes of the plots in Fig. 4, where the reaction rates are plotted as a function of the quencher concentration  $q$  in molecule per micelle. In order to compare the  $k_m$  values at the same surface concentration of the quencher in molecule per unit surface area, values of  $k_m S$  ( $S = 4\pi r_m^2$ ) were calculated and are listed in Table 2. The chain-length dependence of  $k_m S$  is much smaller than that of  $k_m$ , but the  $k_m S$  values still decrease slightly with increasing surfactant chain-length. This fact suggests that the

Table 2

Experimental quenching rate constants,  $k_m$ , micellar radius  $r_m$ ,  $k_m$  normalized by micellar surface area,  $k_m S$ , and  $k_m$  normalized by micellar shell volume,  $k_m \Delta V$

	$k_m^a$ ( $\times 10^6 \text{ s}^{-1}$ )	$r_m$ (nm)	$k_m S$ ( $\times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	$k_m \Delta V^b$ ( $\times 10^{-20} \text{ m}^3 \text{ s}^{-1}$ )
C <sub>10</sub> SO <sub>3</sub> Na	9.5	1.6	3.1	4.4
C <sub>12</sub> SO <sub>3</sub> Na	5.7	1.8	2.3	3.8
C <sub>14</sub> SO <sub>3</sub> Na	4.0	2.1	2.2	4.2
C <sub>10</sub> TABr	4.0	1.6	1.3	1.9
C <sub>12</sub> TABr	2.6	1.8	1.1	1.7
C <sub>14</sub> TABr	1.9	2.1	1.1	2.0
C <sub>16</sub> TABr	1.1	2.3	0.7 <sub>3</sub>	1.5

<sup>a</sup> From Table 1.

<sup>b</sup>  $\Delta V$  is the shell volume of the 1/10 thickness of the micellar radius.

reaction is not a perfect two-dimensional surface reaction either. Other factors to be considered are the facts that the diffusivity of NB molecules decreases with increasing surfactant chain-length and that the degree of penetration of the porphyrins into the micelles becomes smaller with increasing surfactant chain-length. Also shown in Table 2 are  $k_m$  values normalized to micellar shell volume,  $k_m \Delta V$ , where  $\Delta V = V\{1 - (1 - p)^3\}$ ,  $V = 4\pi r_m^3/3$ , and  $pr_m$  the thickness of the shell. The  $k_m \Delta V$  values are less dependent on the surfactant chain-length. However, further study is necessary to clarify the effect of the chain-length on the diffusivity of the solubilize and the degree of penetration of porphyrins into micelles.

#### 4. Summary

The electron-transfer reaction rate constants were determined for the TPPS<sup>4-</sup> + NB/C<sub>n</sub>TAB and TTMAPP<sup>4+</sup> + NB/C<sub>n</sub>SO<sub>3</sub>Na micelle systems. The fluorescence decay curves measured can be described well by a single exponential function because of the short unquenched decay time-constants of these porphyrin molecules and the slow quenching rate. Values for the micellar quenching rate constant,  $k_m$ , were obtained, and  $\ln k_m$  values were found to decrease linearly with increasing surfactant chain-length. The chain-length dependency is as small as 0.21–0.23 per methylene unit. The model calculations show that quencher molecules are localized in the peripheral region of micelles. The quencher being preferentially localized in the peripheral region of the micelles, together with the fact that the quencher diffuses, results in the small chain-length dependencies obtained in this work.

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