

Effect of Diffusion on the Photoinduced Reaction between a Tetra-Anionic Porphyrin and Methylviologen Cation in Methanol

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The quenching of the fluorescence decay of electronically excited 5,10,15,20-tetraphenyl-21*H*,23*H*-porphinetetrasulfonate (TPPS^{4−*}) in the presence of methylviologen cations (MV²⁺) was measured at various ionic strengths in methanol. Analysis of the fluorescence decay curves revealed strong evidence for the presence of a second fluorescent species over the entire range of ionic strength used in this work, which is attributed to solvent-separated ion pairs (TPPS^{4−}—S—MV²⁺). Transient effects of the fluorescence decays were analyzed, and values for the effective reaction distance, R_{NH} , and the diffusion coefficients, D , were obtained. Diffusion coefficients were independently measured for TPPS^{4−} and MV²⁺ using the Taylor dispersion method. The values for D obtained by the analysis of the transient effect were found to be smaller than those for the sum of the diffusion coefficients of TPPS^{4−} and MV²⁺ obtained by the Taylor dispersion method and a possible explanation for this result is given.

1. Introduction

The kinetics of fast bimolecular chemical reactions in solution has been a subject of interest for many years.^{1–23} Diffusion-limited processes are of particular interest because of the many physical, chemical, and biological processes whose kinetics are influenced by diffusion. One class of reaction that is of special interest is that involving the transfer of an electron between an electronically excited fluorophore and a different ground-state molecule or ion, where the transfer of charge results in quenching of the fluorescence. The rate of rapid bimolecular electron transfer reactions in solution is governed to a large extent by the rate at which the reactants can diffuse to within a distance at which electron transfer can occur. In this case, the observed rate constant for the bimolecular reaction, $k(t)$, is predicted to be time-dependent,¹ leading to nonexponential decay kinetics often referred to as the “transient effect”.

Fluorescence quenching is the process of choice for studying such diffusion-influenced reactions because the time-dependence of the quenching rate constant is manifested in the nonexponential decay of the fluorescence from the fluorophore in the presence of the quencher. Fluorescence decay data measured using the technique of time-correlated single photon counting (TCSPC) for fluorophore solutions containing a known concentration of quencher, where both the fluorophore and quenching species are ionic, have been analyzed according to the equations for $k(t)$ derived by either Flannery²⁴ or Hong and Noolandi,²⁵ which are based on the Debye–Smoluchowski

model with the Collins–Kimball boundary conditions (DSCK model). The Hong–Noolandi expression is effectively a long-time approximation of the Flannery equation for $k(t)$, and has a form identical with that of the long-time approximation to the equation for $k(t)$ derived for diffusion-controlled bimolecular reactions in the absence of Coulombic interactions between the reactants. Although analysis of decay data according to these equations has its limitations, many results have been reported indicating that they provide a satisfactory description of the kinetics of diffusion-controlled bimolecular reactions between ions in solutions.

There have been a number of reported studies of electron-transfer quenching reactions involving various porphyrins and viologens.^{26–28} Previously, we studied^{29,30} the influence of diffusion on the fluorescence quenching of the tetra-anionic porphyrin, 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine-tetrasulfonate (TPPS^{4−}), by methylviologen cations (MV²⁺) in aqueous solutions as a function of ionic strength and temperature using the expression for $k(t)$ that was derived by Hong and Noolandi. More recently, we investigated the same donor–acceptor system in methanol³¹ and found that at low ionic strengths the double-exponential fluorescence decay suggests the formation of a loose or a solvent-separated ion pair, even for low quencher concentration. In the present work, we report further measurements on the latter system, but at higher ionic strengths, with effective reaction distances and diffusion coefficients obtained from the analysis of the transient effect. We have also measured the diffusion coefficients for TPPS^{4−} and MV²⁺ independently using a conventional method, and these results are compared with those obtained from the analyses of the transient effect.

2. Experimental Section

The tetrasodium salt of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphine (Na₄TPPS) was prepared by neutralization of

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H₄TPPS·2H₂SO₄·4H₂O (Dojin Laboratories) using NaOH. Methylviologen dichloride, MVCl₂·3H₂O (Tokyo Chemical Ind., >98%), was used as received. Some test measurements were made using MVCl₂ recrystallized twice from a methanol–acetone mixture, but the results were found to be essentially the same. Methanol (Wako Pure Chemical Ind., 99.7%) was stored in the presence of molecular sieves (Nacalai Tesque, 3A 1/16) and was distilled under nitrogen prior to use. Tetramethylammonium chloride (TMAC) (Tokyo Chemical Ind., GR, >98%) was dried in vacuum. Dissolved oxygen was removed by at least four freeze–pump–thaw cycles. The concentration of TPPS⁴⁻ used in this work (ca. 1 μM) was sufficiently low that no evidence of reabsorption or self-quenching effects was observed. The temperature of the sample was controlled at 25.0 ± 0.1 °C by a thermoregulated water bath.

The absorption spectra were recorded using a Hitachi 228A UV–visible spectrophotometer. The fluorescence and excitation spectra were recorded using a Hitachi F 2000 spectrofluorimeter. Fluorescence decays were measured using a time-correlated single photon counting apparatus. A stabilized picosecond light pulser (Hamamatsu Photonics PLP-02) emitting at 415 nm was used as an excitation source. Fluorescence photons from the sample were detected using a microchannel plate photomultiplier tube (Hamamatsu C2773). Signal pulses thus generated were routed through preamplifiers (Hamamatsu C5594 and Ortec 574), constant fraction discriminator (Ortec 473A), time to amplitude converter (Ortec 567), delay line (Ortec 425A), and a 100-MHz discriminator (Ortec 436) before finally being fed to a multichannel analyzer (Norland 5700). The light pulser had a pulse width of 20 ps and was operated at a repetition rate of 1 MHz with a total instrumental response function having a full-width at half-maximum of 80 ps. The fluorescence was detected at a wavelength of 600–700 nm using a short-wavelength cutoff glass filter (Toshiba R-60) and a long-wavelength cutoff glass filter (Koyo LS-700-F). For the present study all the fluorescence decays were measured with a time resolution of 25.6 ps/channel and 1024 channels were used to store a single decay or an excitation pulse profile.

Diffusion coefficients were measured using the Taylor dispersion method,^{32–35} which is also known as the chromatographic peak-broadening method. The concentration profiles after diffusion/dispersion were detected using a UV–visible detector (Hitachi, L-7420). Other details have been described elsewhere.^{36–39} Viscosities were measured by an Ubbelohde-type viscometer.

3. Theory

The time-dependent rate coefficient that was derived by Flannery²⁴ from the DSCK model for the quenching of an excited ionic fluorophore F* by an ionic quencher [Q] is given by

$$k(t) = a + b \exp(c^2 t) \operatorname{erfc}(ct^{1/2}) \quad (1)$$

where

$$a = \frac{\alpha_R \alpha_T}{\alpha_R + \alpha_T} \quad (2)$$

$$b = \frac{\alpha_R^2}{\alpha_R + \alpha_T} \quad (3)$$

$$c = \left(1 + \frac{\alpha_R}{\alpha_T} \right) \frac{D^{1/2}}{R^2} r_c \frac{\exp(r_c/R)}{\exp(r_c/R) - 1} \quad (4)$$

$$\alpha_R = k_{\text{act}} \exp(-r_c/R) \quad (5)$$

$$\alpha_T = \frac{4\pi r_c D N}{\exp(r_c/R) - 1} \quad (6)$$

In all these equations, R is the reaction distance, D is usually considered to be the sum of the diffusion coefficients of the reactants, k_{act} is the intrinsic rate constant for the reaction at a separation distance R , N is the Avogadro's number, and r_c is the Onsager distance given as

$$r_c = \frac{z_A z_Q e^2}{4\pi \epsilon_0 \epsilon k_B T} \quad (7)$$

Here, $z_A e$ and $z_Q e$ are the effective charges on the fluorophore and quencher respectively; ϵ_0 and ϵ are the dielectric constants of a vacuum and the reaction medium, respectively; k_B is Boltzmann's constant, and T is the temperature of the system.

At sufficiently long times, eq 1 can be approximated by the following equation, which was derived by Hong and Noolandi²⁵

$$k(t) = 4\pi D R_{\text{HN}} N \left[1 + \frac{R_{\text{HN}}}{\pi(Dt)^{1/2}} \right] \quad (8)$$

where

$$R_{\text{HN}} = \frac{r_c}{(1 + 4\pi r_c D N / k_{\text{act}}) \exp(r_c/R) - 1} \quad (9)$$

The parameter R_{HN} may be interpreted as an effective encounter distance at which the reaction proceeds with certainty.²⁵

The time dependence of [F*] in the presence of Q is given by

$$\frac{d[\text{F}^*]_t}{dt} = -[\text{F}^*]_t (\tau_0^{-1} + k(t)[\text{Q}]) \quad (10)$$

where τ_0 is the unquenched fluorescence lifetime of F*, $[\text{F}^*]_t$ is the concentration of F* at time t , and $[\text{Q}]$ is the concentration of the quencher. The function that is obtained for the time-dependent decay of fluorescence intensity, $I(t)$, upon substitution of eq 3 for $k(t)$ in eq 5 and then integration is

$$I(t) = I_0 \exp(-At - Bt^{1/2}) \quad (11)$$

where

$$A = \tau_0^{-1} + 4\pi D R_{\text{HN}} N [\text{Q}] \quad (12)$$

$$B = 8(\pi D)^{1/2} R_{\text{HN}}^2 N [\text{Q}] \quad (13)$$

4. Results and Discussion

The decay of fluorescence from the free-base tetra-anionic porphyrin (TPPS⁴⁻) in methanol, in the absence of the quencher methylviologen (MV²⁺), was found to be exponential with the fluorescence lifetime being approximately 12.5 ns for the entire range of ionic strengths studied, where the ionic strength was varied by the addition of TMAC. Figure 1 shows the fluorescence decay curves measured for TPPS⁴⁻ in methanol solutions containing 200 mM TMAC and various concentrations of MV²⁺. The distributions of reduced residuals that correspond to the best-fit curves calculated using either an exponential function or the function given by eq 11 are shown in the upper and lower panels of Figure 2, respectively. In the presence of MV²⁺ the decay cannot be described by a single exponential function, as demonstrated by the larger χ^2 . However the decays are found to be described well by the function given by eq 11.

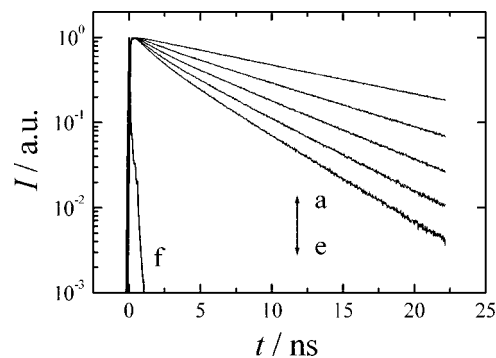


Figure 1. Fluorescence decay curves measured for TPPS⁴⁻ in 200 mM TMAC in methanol solution at MV²⁺ concentrations of (a) 0 mM, (b) 5 mM, (c) 10 mM, (d) 15 mM, and (e) 20 mM. Curve f is the instrument response function.

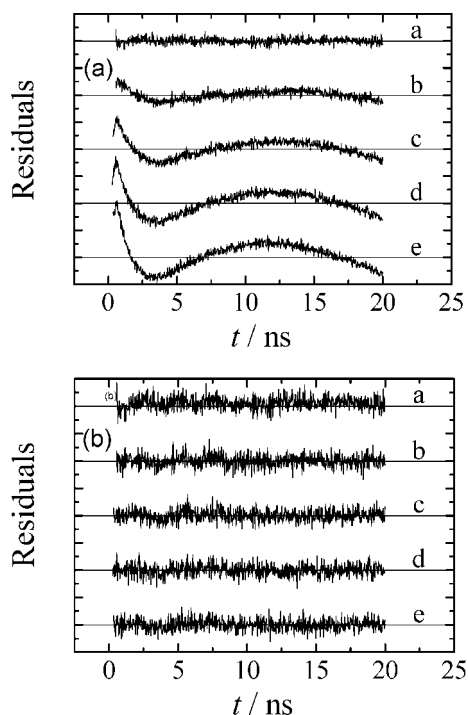


Figure 2. (a) Distributions of reduced residuals corresponding to the analysis of the fluorescence decay curves shown in Figure 1 using the single-exponential function. The corresponding values for the reduced χ^2 parameter are (a) 1.30, (b) 3.56, (c) 10.1, (d) 18.6, and (e) 26.7. (b) Distributions of reduced residuals corresponding to the analysis of the fluorescence decay curves shown in Figure 1 using the function given by eq 11. The corresponding values for the reduced χ^2 parameter are (a) 1.27, (b) 1.23, (c) 1.10, (d) 1.13, and (e) 1.09.

Analysis of the nonexponential decay curves according to eq 11 provides A and B values as a function of the MV²⁺ concentration. Plots of the recovered values of A and B as a function of MV²⁺ concentration are given in parts a and b of Figure 3, respectively. The good linear relationship supports our previous findings that, for sufficiently long times, the expression for $k(t)$ proposed by Hong and Noolandi provides a satisfactory description of the reaction kinetics for this ionic bimolecular fluorescence quenching reaction in solution. The R_{HN} and D values given in Table 1 were calculated using the slopes of the straight lines shown in parts a and b of Figure 3 and are plotted in parts a and b of Figure 4, respectively, as a function of TMAC concentration. As was reported previously for the reaction between these ions in aqueous solution,²⁹ the R_{HN} values tend to decrease progressively with the increasing ionic strength associated with increasing concentration of TMAC,

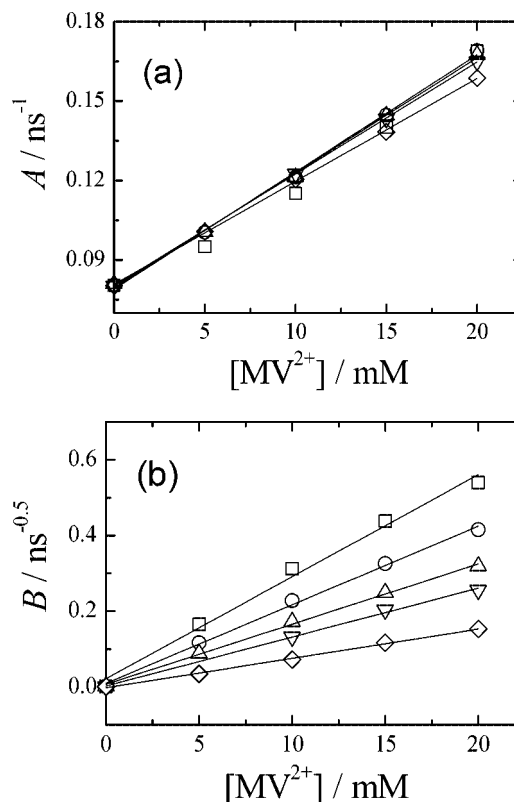


Figure 3. (a) Plots of A values of eq 11 vs MV²⁺ concentration and the corresponding lines of best fit calculated using eq 12 for TMAC concentrations of 150 mM (\square), 200 mM (\circ), 250 mM (Δ), 300 mM (∇), and 500 mM (\diamond). (b) Plots of B values of eq 11 vs MV²⁺ concentration and the corresponding lines of best fit calculated using eq 13 for TMAC concentrations of 150 mM (\square), 200 mM (\circ), 250 mM (Δ), 300 mM (∇), and 500 mM (\diamond).

TABLE 1: Results of Analysis of the Quenched Fluorescence Decay Curves of TPPS⁴⁻ by MV²⁺ in Methanol Solutions of TMAC at 25 °C According to Eq 11

[TMAC] (mM)	slope of A ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)	slope of B ($10^5 \text{ M}^{-1} \text{ s}^{-0.5}$)	D ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	R_{HN} (\AA)
150	4.44 ± 0.32	8.54 ± 0.44	0.228 ± 0.030	25.7 ± 1.5
200	4.43 ± 0.11	6.58 ± 0.22	0.271 ± 0.015	21.6 ± 0.6
250	4.34 ± 0.09	5.03 ± 0.13	0.315 ± 0.014	18.2 ± 0.4
300	4.23 ± 0.01	4.08 ± 0.13	0.349 ± 0.010	16.0 ± 0.4
500	3.89 ± 0.05	2.43 ± 0.06	0.440 ± 0.014	11.7 ± 0.2

reaching a limiting value of $11.7 \pm 0.2 \text{ \AA}$ when the concentration of TMAC reaches 500 mM. This observation of a limiting value for R_{HN} at sufficiently high ionic strength is attributed to the complete screening of the reactant charges resulting in the neutralization of the Coulombic interactions that exist between TPPS⁴⁻ and MV²⁺ in solutions of lower ionic strengths. The magnitude of this limiting value of R_{HN} in the present work is in good agreement with that obtained for this same reaction in aqueous solution of $10.7 \pm 0.6 \text{ \AA}$.²⁹ The values obtained for D in the present work display a gradual increase with increasing ionic strength. This is in contrast with the expectation that the D values should decrease to some extent with increasing ionic strength because of the increase in the viscosity.

We also measured diffusion coefficients for the TPPS⁴⁻ and MV²⁺ ions in methanol solutions containing TMAC using the Taylor dispersion method.^{32–35} Viscosities of the solutions and the diffusion coefficients are listed in Table 2 with the magnitude of the diffusion coefficients decreasing with increasing concentration of TMAC, as expected. Sums of the diffusion coefficients of TPPS⁴⁻ (D_{F}) and MV²⁺ (D_{Q}) are plotted in Figure 4b together

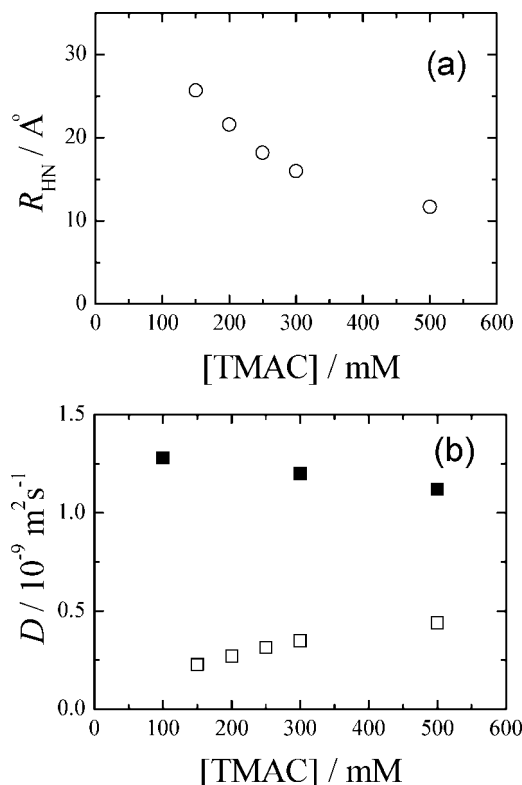


Figure 4. (a) Effective reaction radii obtained from the A and B values of eq 11 as a function of the TMAC concentration. (b) Diffusion coefficients obtained from the A and B values of eq 11 (□) and those ($D_F + D_Q$) obtained by using the Taylor dispersion method (■) as a function of the TMAC concentration.

TABLE 2: Diffusion Coefficients of TPPS⁴⁺ (D_F) and MV²⁺ (D_Q) in Methanol Solutions of TMAC at 25 °C Obtained Using the Taylor Dispersion Method

[TMAC] (mM)	η (mPa s)	D_F^a (10^{-9} m ² s ⁻¹)	D_Q^a (10^{-9} m ² s ⁻¹)
0	0.548	n.d. ^e	n.d. ^e
10	0.551 ^b	0.424 ^c	0.885 ± 0.012
50	0.560 ^b	0.420 ± 0.004	0.876 ^d
100	0.571 ^b	0.412 ± 0.006	0.870 ± 0.008
150	0.582 ^b	0.404 ^c	0.858 ^d
200	0.593 ^b	0.397 ^c	0.849 ^d
250	0.604 ^b	0.391 ^c	0.840 ^d
300	0.618	0.380 ± 0.002	0.823 ± 0.016
500	0.657	0.363 ± 0.010	0.800 ± 0.026
700	0.696	0.346 ± 0.006	0.779 ± 0.020
1000	0.771	n.d. ^e	n.d. ^e

^a Uncertainties quoted to two standard deviations. ^b Interpolated values calculated using the best-fit curve to the measured values of η : η / mPa s = 0.5488 + 0.2188 [TMAC]/M (correlation coefficient = 0.9989). ^c Interpolated values calculated using the best-fit curve to the measured values of D : $\log(D / 10^{-9} \text{ m}^2\text{s}^{-1}) = -0.603 - 0.891 \log(\eta/\text{mPa s})$ (correlation coefficient = -0.9982). See ref 38 for the function between D and η . ^d Interpolated values calculated using the best-fit curve to the measured values of D : $\log(D / 10^{-9} \text{ m}^2\text{s}^{-1}) = -0.198 - 0.559 \log(\eta / \text{mPa s})$ (correlation coefficient = -0.9963). ^e Values not determined.

with the values of D obtained from the analysis of the transient effect using eq 11. The values for D are found to be significantly smaller than those for the corresponding values of the sum $D_F + D_Q$. This result, together with the abovementioned unexpected trend of increasing D with increasing ionic strength suggests that, while acceptable statistical quality of fitting of the quenched fluorescence decay curves is obtained by using eq 11, the parameter values obtained suggest that analysis using this

equation provides an inadequate physical description of the kinetics of this reaction in the present systems.

We recently reported³¹ compelling evidence from fluorescence decay curve analysis for the existence of TPPS⁴⁺-S-MV²⁺ solvent-separated ion pairs (SSIP) in methanol solutions containing TMAC concentrations of up to 100 mM. At these lower ionic strengths (i.e., ≤ 100 mM TMAC), the fluorescence decay curves could not be fitted using eq 11, but a biexponential function was found to describe the kinetics of this system satisfactorily, where the two decay components were attributed to fluorescence from free TPPS⁴⁺ ions and TPPS⁴⁺-S-MV²⁺ SSIP. No evidence of ion-pair formation was found for these ions in aqueous solution, which clearly reflects the much stronger interaction between TPPS⁴⁺ and MV²⁺ in methanol compared with water due to the lower dielectric constant of methanol.

It is, therefore, proposed that the inability of eq 11 to provide physically realistic values for the parameters associated with the measured fluorescence decay kinetics at TMAC concentrations of 150 mM or greater is due to the contribution to the fluorescence signal from the TPPS⁴⁺-S-MV²⁺ SSIP. Therefore, the fluorescence decay curves measured in the present work were reanalyzed using the following equation

$$I(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-At - Bt^{1/2}) \quad (14)$$

in which the extra exponential term represents the fluorescence decay of the TPPS⁴⁺-S-MV²⁺ SSIP having a decay time of τ_1 . The values obtained for the fitted parameters using eq 14 are listed in Table 3. The shorter-lived component, τ_1 , is unlikely to be associated with the formation of a fluorescent excited-state complex, such as an exciplex or CT complex, because the steady-state fluorescence spectra show no evidence of the formation of a new fluorescent species and there is no detectable risetime in the time-resolved fluorescence measurements.

The values for diffusion coefficient, D , and the effective reaction distance, R_{HN} , obtained using eq 14 are listed in Table 4. The SSIP formation constant, K_{SSIP} , according to the equilibrium



is defined as

$$K_{SSIP} = \frac{[\text{SSIP}]}{[\text{TPPS}^{4+}]_{\text{free}} [\text{MV}^{2+}]_{\text{total}}} \quad (16)$$

where $[\text{MV}^{2+}]_{\text{total}} \approx [\text{MV}^{2+}]_{\text{free}}$ because $[\text{SSIP}] \ll [\text{MV}^{2+}]_{\text{total}}$. As discussed previously,³¹ K_{SSIP} can be related to the fitted pre-exponential factors through the following equation

$$K_{SSIP} [\text{MV}^{2+}]_{\text{total}} = \frac{I_1}{I_2} \quad (17)$$

In Figure 5, the values of I_1/I_2 from analysis using eq 14 (Table 3) are plotted as a function of $[\text{MV}^{2+}]_{\text{total}}$, with satisfactory linearity being found over the TMAC concentration range used in this work, and the corresponding values of K_{SSIP} are listed in Table 4. The K_{SSIP} values are plotted as a function of the TMAC concentration in Figure 6, where those values at ionic strengths of 100 mM or lower are taken from our previous work.³¹ As seen in Figure 6, the values for K_{SSIP} are seen to be continuous over the entire range of TMAC concentrations investigated, despite the different analysis performed on the fluorescence decay curves measured in these two concentration ranges, which provides good evidence that the models adopted in this work are physically reasonable.

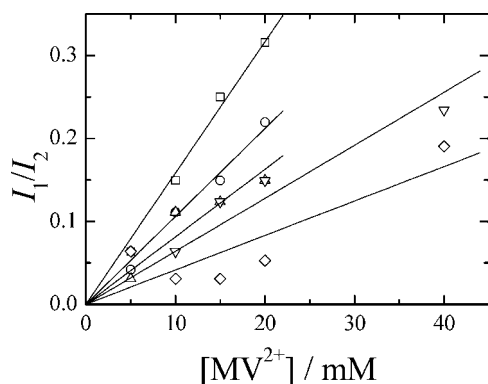
TABLE 3: Results of Analysis of the Quenched Fluorescence Decay Curves of TPPS⁴⁻ by MV²⁺ in Methanol Solutions of TMAC at 25 °C According to Eq 14

[TMAC] (mM)	[MV ²⁺] (mM)	A (ns ⁻¹)	B (ns ^{-0.5})	τ_1 (ns)	I_1/I_2	χ^2
150	5	0.110 ± 0.001	0.095 ± 0.010	1.31 ± 0.14	0.064	1.18
150	10	0.146 ± 0.002	0.157 ± 0.013	1.24 ± 0.06	0.149	0.98
150	15	0.185 ± 0.003	0.197 ± 0.017	1.19 ± 0.03	0.250	1.12
150	20	0.222 ± 0.003	0.247 ± 0.021	1.12 ± 0.02	0.316	1.02
200	5	0.109 ± 0.001	0.073 ± 0.001	1.53 ± 0.11	0.042	1.23
200	10	0.143 ± 0.002	0.114 ± 0.014	1.38 ± 0.08	0.111	1.06
200	15	0.174 ± 0.002	0.171 ± 0.014	1.24 ± 0.05	0.149	1.11
200	20	0.208 ± 0.003	0.203 ± 0.020	1.19 ± 0.03	0.220	1.07
250	5	0.106 ± 0.001	0.063 ± 0.007	1.91 ± 0.48	0.031	1.12
250	10	0.139 ± 0.002	0.069 ± 0.017	1.72 ± 0.09	0.111	1.17
250	15	0.167 ± 0.002	0.126 ± 0.017	1.42 ± 0.07	0.124	1.03
250	20	0.195 ± 0.002	0.168 ± 0.017	1.18 ± 0.05	0.149	1.04
300	10	0.132 ± 0.001	0.077 ± 0.008	1.79 ± 0.14	0.064	1.14
300	15	0.163 ± 0.002	0.092 ± 0.015	1.59 ± 0.10	0.124	1.07
300	20	0.189 ± 0.002	0.120 ± 0.017	1.38 ± 0.05	0.149	1.11
300	40	0.299 ± 0.005	0.230 ± 0.030	1.08 ± 0.03	0.235	1.08
500	5	0.102 ± 0.001	0.009 ± 0.007	3.68 ± 0.49	0.064	1.20
500	10	0.122 ± 0.001	0.059 ± 0.007	2.96 ± 0.62	0.031	1.12
500	15	0.145 ± 0.002	0.082 ± 0.016	1.61 ± 0.27	0.031	1.07
500	20	0.168 ± 0.001	0.104 ± 0.001	1.44 ± 0.05	0.053	1.09
500	40	0.265 ± 0.004	0.123 ± 0.026	1.25 ± 0.05	0.190	1.14

TABLE 4: Results of Analysis of the Quenched Fluorescence Decay Curves of TPPS⁴⁻ by MV²⁺ in Methanol Solutions of TMAC at 25 °C According to Eq 14

[TMAC] (mM)	slope of A (10 ⁹ M ⁻¹ s ⁻¹)	slope of B (10 ⁵ M ⁻¹ s ^{-0.5})	D (10 ⁻⁹ m ² s ⁻¹)	R _{HN} (Å)	K _{SSIP} ^d (M ⁻¹)
150	7.16 ± 0.21	3.8 ± 0.4	0.745 ± 0.078	12.7 ± 1.0	15.8
200	6.38 ± 0.11	3.2 ± 0.3	0.714 ± 0.052	11.8 ± 0.7	10.6
250	5.80 ± 0.13	2.5 ± 0.3	0.736 ± 0.077	10.4 ± 0.8	8.1
300	5.46 ± 0.11	1.9 ± 0.2	0.826 ± 0.086	8.73 ± 0.73	6.4
500	4.36 ± 0.07	1.8 ± 0.2	0.634 ± 0.062	9.09 ± 0.74	4.2

^d Values calculated according to eq 12.

**Figure 5.** The I_1/I_2 values in Table 3 as a function of the MV²⁺ concentration for TMAC concentrations of 150 mM (□), 200 mM (○), 250 mM (Δ), 300 mM (▽), and 500 mM (◇).

The recovered values for τ_1 (see Table 3) indicate that the fluorescence lifetime of TPPS⁴⁻ in the SSIP is much shorter than that of free TPPS⁴⁻ (12.4 ns³¹) despite the interaction between TPPS⁴⁻ and MV²⁺ in the SSIP being likely to be weak, especially at the higher TMAC concentrations (i.e., smaller K_{SSIP}). Although the stability of the ground-state solvent-separated complex may be relatively weak, it is not unreasonable to expect that the photoreduction reaction occurs between this loosely held pair via electron transfer through the intervening solvent molecule/s, since electron transfer is known to occur over such distances when there is a sufficiently large driving force, albeit with a slower rate than when the reactants are in physical contact. Our results are consistent with this situation, in which electron transfer that occurs in the SSIP on excitation

of TPPS⁴⁻ results in quenching of the fluorescence lifetime of TPPS⁴⁻ in the SSIP.

The R_{HN} values in Table 4 are plotted in Figure 7a and reach a limiting value of 9.1 ± 0.7 Å at a TMAC concentration of 500 mM, which, although somewhat smaller than that obtained from the analysis using eq 11, is still satisfactorily similar in magnitude to the limiting value for this reaction in aqueous solution. The D values obtained from analysis using eq 14 (Table 4) are larger than those obtained using eq 11 (Table 1) and are relatively independent of ionic strength, in contrast to the values obtained from analysis using eq 11. However, as seen in Figure 7b, the magnitude of the D values obtained from analysis using eq 14 are still substantially smaller than the values of the sum of the diffusion coefficients, $D_F + D_Q$, obtained using the Taylor dispersion method.

Scully and Hirayama reported²⁰ that use of the equation associated with the long-time approximation to analyze TCSPC fluorescence decay curves simulated according to the SCK model can lead to incorrectly inflated values of D if the decay curve contains insufficient counts in the channel of maximum intensity. This suggests that the discrepancy between the values for D and the sum $D_F + D_Q$ obtained in the present work is not due to an artifact associated with inadequate quality of the fluorescence decay data.

As we have noted previously,³⁸ the diffusion coefficient obtained from the analysis of the transient effect is that of the excited-state fluorophore, whereas that obtained by the conventional method is that of the ground-state fluorophore. However, it is unlikely that any difference between the diffusion coefficients of the fluorophore in these states can account for the magnitude of the apparent discrepancy between the diffusion coefficients, D , from analysis according to eq 14 and the diffusion coefficients measured using the Taylor dispersion method. A similar observation has been reported recently.^{40,41}

Another potential explanation for the apparent discrepancy is that the diffusion of F* and Q across the last layer of the solvent molecules to meet each other is slower than when they are diffusing at a remote distance.^{7,38,40-43} If molecules are diffusing collectively in a microscopic region, then it takes more time for F* and Q molecules to meet at the last moment after having diffused some distance. In this case, a correlation

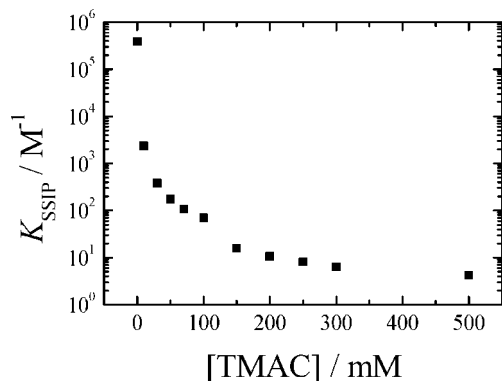


Figure 6. The values for the SSIP formation constant as a function of the TMAC concentration. The values at [TMAC] values of 150 mM or higher are from the present study (Table 4), whereas those at [TMAC] values of 100 mM or lower are from our previous work.³¹

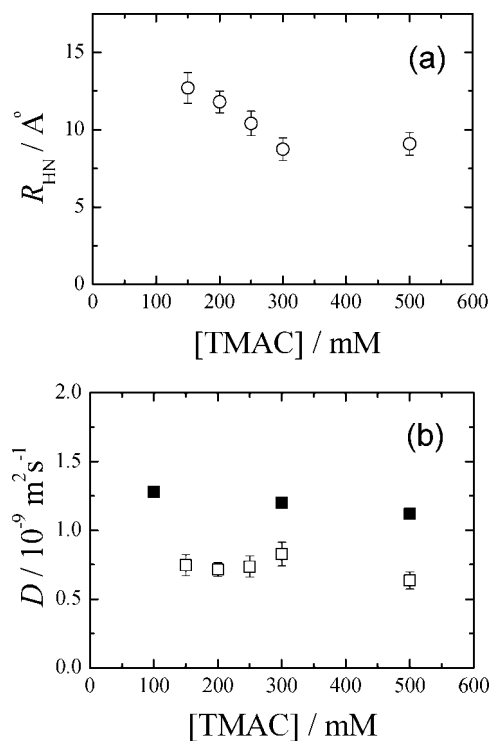


Figure 7. (a) Effective reaction radii obtained from the A and B values of eq 14 as a function of the TMAC concentration. (b) Diffusion coefficients obtained by the A and B values of eq 14 (\square) and those ($D_F + D_Q$) obtained by using the Taylor dispersion method (\blacksquare) as a function of the TMAC concentration.

would be expected to exist between the lifetime of the excited-state fluorophore τ_0 (or the diffusing time of F^* which is some fraction of τ_0), and the ratio between the D values obtained from the transient-effect analysis and those obtained from other methods reflecting macroscopic diffusion coefficient. The ratio for the present study, where $\tau_0 \sim 12$ ns, is 0.55–0.69 as obtained from the D values in Table 4 and the ($D_F + D_Q$) values in Table 2. In the case of 9,10-diphenylanthracene fluorescence quenched by maleic anhydride in acetonitrile, where $\tau_0 \sim 8$ ns, the ratio is 0.50.^{17,38} In the case of zinc tetraphenylporphine, ZnTPP, quenched by benzoquinone or tetrachlorobenzoquinone in acetonitrile or toluene, where $\tau_0 = 2.0$ ns, the ratio is 0.41–0.58.^{16,38} In the case of S_2 -deuterated xanthione in perfluoro-1,3-dimethylcyclohexane, where $\tau_0 = 0.53$ ns, the ratio is 0.34–0.42,⁴⁰ and in the case of S_2 -xanthione in the same solvent, where

$\tau_0 = 0.15$ ns, the ratio is 0.61–0.75.⁴⁰ Although in all cases the ratio is less than unity, there is no clear evidence of a correlation between the ratio of diffusion coefficients with either the fluorophore lifetime or the diffusing time of the excited-state fluorophore. Further study is required to establish whether there is any correlation between the ratio and other fluorophore-quencher combinations.

5. Conclusions

Analysis of the decay of fluorescence from $TPPS^{4-*}$ in the presence of MV^{2+} in methanol has revealed compelling evidence for the presence of a second fluorescent species over the entire range of ionic strength used in this work, which is attributed to the formation of solvent-separated ion pairs ($TPPS^{4-}-S-MV^{2+}$). In contrast, no evidence for the formation of solvent-separated ion pairs was found for these reactants in aqueous solution, and this difference is attributed to the lower dielectric constant of methanol. The values for the effective reaction distance, R_{HN} , were found to decrease with increasing ionic strength, reaching a limiting value that is similar in magnitude to the value found for this reaction in aqueous solution, suggesting that the magnitude of k_{act} for this reaction in these two solvents is comparable. The magnitudes of the diffusion coefficients D obtained from analysis of the transient effect in the fluorescence decays are significantly smaller than the sum of the macroscopic diffusion coefficients of $TPPS^{4-}$ and MV^{2+} measured using the Taylor dispersion method.

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