Photoinduced electron transfer from chlorin $p_6$ to methyl viologen in aqueous micelles

Tushar Kanti Mukherjee, Padmaja P. Mishra, Anindya Datta *

Department of Chemistry, Indian Institute of Technology, Bombay Powai, Mumbai 400 076, India

Abstract

We report the effect of micellar encapsulation on the photoinduced electron transfer between chlorin $p_6$ and methyl viologen. In aqueous solutions, these molecules form contact ion pairs and the fluorescence quenching observed is mainly static in nature. The quenching efficiency increases markedly in SDS micelles and the mechanism changes partially to dynamic quenching. However, fluorescence quenching of all kinds are suppressed in CTAB and Triton X-100 micelles. This is explained in the light of dissociation of the contact ion pairs and the electrostatic attraction of MV$^{2+}$ by the headgroups of the surfactants.

1. Introduction

Aggregation and photoinduced electron and energy transfer in porphyrin based molecules have been studied extensively, in attempts to understand and mimic green plant photosynthesis and to develop efficient solar cells [1–6]. Recently, there has been a spate of activity in the field of PET in organized media [7,8] where the excited state dynamics differ largely from those in homogeneous solutions [9,10]. The motivation for the study of PET in porphyrinic systems in organized media stems from the urge to generate long-lived ion pairs, so that the energy produced thus can be used fruitfully. If the D–A distance is too large for the reactants to diffuse to each other during the excited state lifetimes, then PET is suppressed. On the other hand, if the distance is comparable to the van der Waal radius, then the back electron transfer is also ultrafast, leading to a very short-lived ion pair. The challenge, therefore, lies in the design of systems where this distance can be controlled in order to have an efficient forward electron transfer and a negligible back electron transfer. This goal can be achieved either by synthesis or by entrapment of the donor or acceptor in organized assemblies. The encapsulation effect of organized assemblies can bring the donor and the acceptor together and thus facilitate the forward electron transfer whereas their hydrophobic and hydrophilic microenvironments can provide differential solubilization to the ion pair formed, in case one of the products is more hydrophobic than the other, leading to the formation of solvent separated ion pairs and consequent suppression of the back electron transfer [11,12]. In the present study, we have investigated the effect of micelles on photoinduced electron transfer between chlorin $p_6$ and methyl viologen dication (MV$^{2+}$) (Fig. 1).

2. Experimental

Chlorin $p_6$ is prepared using literature procedure [3–5]. Methyl viologen dichloride and Triton X-100 (TX-100) (AR grade) from Aldrich have been used as received. Sodium dodecyl sulphate (SDS) and cetyl trimethyl ammonium bromide (CTAB) (AR grade) from...
Aldrich are recrystallized from methanol–water solutions. The concentration of chlorin \( p_6 \) used is 4 \( \mu \)M. The concentrations of SDS, CTAB and Triton X-100 are 14, 3 and 1 mM, respectively. The absorption and fluorescence spectra have been recorded on JASCO V570 spectrophotometer with 2 nm bandpass and a Perkin–Elmer LS-55 spectrofluorimeter with \( \lambda_{\text{ex}} = 401 \) nm, respectively. Fluorescence decays have been recorded on an IBH Fluorocube time resolved fluorescence spectrometer [13]. The fluorescence decays were fitted to biexponential functions by iterative deconvolution using the IBH DAS 6.0 software. Global analysis of the decays were performed using a homemade program.

3. Results and discussion

The absorption peaks of chlorin \( p_6 \) in water get red shifted and broadened with gradual addition of \( \text{MV}^{2+} \) (Fig. 2a), indicating ground state association due to their opposite charges [14]. Little, if any shift or broadening of the absorption peak is observed with addition of \( \text{MV}^{2+} \) to chlorin \( p_6 \) in 3 mM CTAB and in 1 mM TX-100 (Fig. 2b and c). In 14 mM SDS, the changes in absorption spectra on addition of \( \text{MV}^{2+} \) are less prominent than in bulk water, but are more prominent than in the other micelles (Fig. 2d). This indicates that the extent of contact ion pair formation is reduced substantially in micelles compared to neat aqueous solutions. The Stern–Volmer plot in water is linear (Fig. 3a). In CTAB and TX-100, the slope of the Stern–Volmer plot is zero, except for an initial small quenching in TX-100 up to a \( \text{MV}^{2+} \) concentration of \( 4 \times 10^{-5} \) M, (Fig. 3). These indicate a complete incorporation of chlorin \( p_6 \) in CTAB micelle, resulting in effective sequestering from \( \text{MV}^{2+} \), which resides in bulk water. In TX-100, chlorin \( p_6 \) may not be totally bound and \( \text{MV}^{2+} \) can initially quench the free fluorophore molecules. The most remarkable result is obtained with SDS, where a linear Stern–Volmer plot, with a steeper slope than that in neat aqueous solution, is obtained (Fig. 3a, Table 1). This is an indication of the changeover of the mechanism to a more efficient one. In SDS, where the association complexes are disrupted, the quenching mechanism might be predominantly dynamic in nature [15]. Interestingly, the \( K_{\text{SV}} \) is greater in SDS micellar media than in neat aqueous solutions, which is in contrast to some earlier observations [7,15,16]. The decrease in \( K_{\text{SV}} \) values in micelles is generally rationalized by a decreased mobility of incorporated quenchers and fluorophores. However, an increase in \( K_{\text{SV}} \) is also observed in certain cases. For example, an enhanced quenching of ruthenium complexes by \( \text{MV}^{2+} \) and \( \text{Cu}^{2+} \) is observed in SDS solutions, and is explained by the formation of clusters of the fluorophore with SDS, with which the oppositely charged quenchers associate easier [17]. In our experiment, since chlorin \( p_6 \) resides near the
negatively charged headgroups of SDS, this charged surface might offer electrostatic attraction to draw the MV$^{2+}$ ions towards the fluorophore. In order to gain a better insight to the situation, time resolved experiments have been performed.

The fluorescence decays of chlorin $p_6$ in water exhibit no change on addition of MV$^{2+}$ (Fig. 4a). This confirms that in water, only static quenching is operative and can be explained in the light of instantaneous electron transfer in the association complexes between MV$^{2+}$ and chlorin $p_6$ [14]. Dynamic quenching might be observed in micelles, where these association complexes are disrupted. However, there is no change in the fluorescence decays in CTAB or Triton X-100 micelles, indicating the absence of dynamic quenching by MV$^{2+}$ in these micelles. In SDS micelle, the fluorescence decays become faster with addition of MV$^{2+}$ (Fig. 4b), indicating the dynamic nature of quenching [15]. The decays are well fit to biexponential functions and the Stern–Volmer plots with average lifetime $\tau_{av} = \sum a_i \tau_i$ is shown in Fig. 5a. The Stern–Volmer constant is much smaller compared to that obtained from the steady state experiment (Tables 1 and 2). Similar discrepancies have been reported in some other studies of bimolecular processes in micelles [7]. We feel that this discrepancy arises out of the oversimplified model of data fitting. The analysis of multieponential fluorescence decays is by no means a trivial procedure and the results are strongly dependent on the model used to describe the system under investigation [18]. Several such models have been proposed so far [19–24]. For example, Gehlen and De Schryver [19] have investigated the ground state charge transfer complex between MV$^{2+}$ and pyrene in SDS by a model that allowed them to estimate all parameters related to the static and dynamic quenching processes. PET in micelles is often treated by the model proposed by Tachiya and coworkers [20,21], which involves immobile fluorophores and a migration of quenchers between the micelles and aqueous phase. In another model proposed by Almgren and Lofroth [22], the effect of polydispersity on fluorescence quenching in micelles is considered. In this context, a closer look at the fluorescence lifetimes of our system is required, with an appropriate model that is described below.

The fluorescence decay of chlorin $p_6$ in water is single exponential. In SDS, the decay becomes biexponential,

![Fig. 3. Stern–Volmer plots with fluorescence quantum yields ($\phi_0$) of chlorin $p_6$ in (a) water, 3 mM CTAB and in 14 mM SDS micelles and (b) water and 1 mM Triton X-100.](image)

![Fig. 4. Fluorescence decays in the presence and absence of 1 mM MV$^{2+}$ in (a) water and (b) 14 mM SDS. The instrument response functions (FWHM = 250 ps) are shown in dashed lines.](image)

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<th>Table 1</th>
<th>Values of $K_{SV}$ and $k_q$ from steady state experiments in different media</th>
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<td>$k_q$ (lit mol$^{-1}$ s$^{-1}$)</td>
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indicating that chlorin $p_6$ molecules experience two different kinds of environments in this microheterogeneous medium. Since no dynamic quenching is observed in bulk water, we can safely assign the dynamic quenching observed in SDS to PET between micelle-bound chlorin $p_6$ and methyl viologen. The micellar quenching model proposed by Tachiya yields unacceptable results and poor fits, probably because the migration of MV$^{2+}$ between aqueous and micellar phase is not significant and MV$^{2+}$ is mostly localized near the Stern layer of SDS micelle [23]. Moreover, chlorin $p_6$ in the Stern layer may not be totally immobile. Since the absorption spectra indicate a disruption of the ground state association complexes between chlorin $p_6$ and MV$^{2+}$, a model like that proposed by Gehlen and De schryver would also be inapplicable [19]. A more applicable model would be similar to those proposed by Tominaga and co-workers [24] or by Levstein and van Willigen [25]. Such a model would involve two kinds of fluorophores: one which are available for quenching by MV$^{2+}$ and the other, which are not. If this model is appropriate, then the decays would be biexponential. Only one component of the lifetime should exhibit a decrease on addition of MV$^{2+}$ and the other, corresponding to unavailable fluorophores, should remain unchanged. If the free-bound equilibrium of chlorin $p_6$ with SDS is unaltered by the addition of MV$^{2+}$, then the weightage of the components should remain unaltered as well. Thus, in this model, the only variable in the biexponential decay would be the shorter lifetime and it is this lifetime that should be used to construct the Stern–Volmer plot. A global analysis of the decays is required with the amplitudes and one lifetime as the global variables and the second lifetime as the local variable [26–28].

The results of the global analysis are shown in Table 3. The Stern–Volmer plot using lifetimes is shown in Fig. 5b. The plot is linear up to a MV$^{2+}$ concentration of 20 mM, but exhibits an upward deviation subsequently, indicating a breakdown of the model at such concentrations where the bound-free equilibrium of chlorin $p_6$ with micelles might be affected, as MV$^{2+}$ can cement the negatively charged SDS and chlorin $p_6$ at high concentration. However, the linearity of the Stern–Volmer plot up to 20 mM MV$^{2+}$ indicates the viability of the model till such concentrations. The $K_{SV}$ and $k_q$ values are $1140 \text{ M}^{-1}$ and $3.2 \times 10^{11} \text{ M}^{-1} \text{s}^{-1}$, respectively, which are higher than those obtained using the average lifetimes, but are still much lower than that obtained from the steady state data. The lower value of $K_{SV}$ obtained compared to the steady state analysis even with this model indicates that a large part of the quenching is still instantaneous in nature.

### Table 3

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<th>[MV$^{2+}$] $\times 10^{-5}$ (M)</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
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<td>1.38</td>
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The data were fit to a biexponential function with the amplitudes and the longer lifetime as global parameters and the first lifetime, $\tau_1$, as the local parameter.

### Conclusion

We have reported the effects of different surfactants on the PET between chlorin $p_6$ and MV$^{2+}$. The PET is totally static in water due to formation of contact ion-pairs between the fluorophore and the quencher. On addition of micelles, these contact ion pairs get disrupted. In the positively charged CTAB and neutral Triton X-100, quenching is suppressed as chlorin $p_6$ is incorporated in the micelle and MV$^{2+}$ is in the aqueous phase, thereby eliminating the chance of electron
transfer. In SDS, however, the negatively charged micellar surface attracts MV$^{2+}$ towards the chlorin $p_6$ ions and so, diffusion controlled PET is observed. The $K_{SV}$ obtained from time resolved data is significantly lower than those from the steady state results, indicating that a significant portion of the quenching process is instantaneous. Further experiments in the femtosecond time scale are required to investigate such instantaneous quenching. Microsecond to millisecond timescale studies also need to be performed to see whether the products of such PET are long-lived or not.

Acknowledgements

This work is supported by CSIR research Grant No. 01 (1851)/03/EMR-II to AD and UGC Junior Research Fellowship to TKM. The authors thank Ms. Jaya Bhatnagar for her participation in the initial stage of these experiments and Professor G. Naresh Patwari for some helpful comments.

References