Photophysical and Photochemical Properties of Pyranine/Methyl Viologen Complexes in Solution and in Supramolecular Aggregates: A Switchable Complex

E. B. de Borba, C. L. C. Amaral, M. J. Politi,* R. Villalobos, and M. S. Baptista*

Laboratório Interdepartamental de Cincética Rápida, Departamento de Bioquímica, Instituto de Química, Universidade de São Paulo, São Paulo, P. O. Box 26077, São Paulo, SP, 05599–970, Brazil

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The properties of a novel complex between pyranine (a photoacid and an electron donor species) and methyl viologen (an efficient electron acceptor, MV2+) in aqueous and in micellar solutions were determined. On the basis of the electrostatic driven force for pyranine/methyl viologen (pyranine/MV2+) complexation, the distribution of the complexed species could be manipulated using ionic micellar aggregates. This distribution permits control over competitive photochemical and photophysical pathways and therefore allowed maximization of electron- and proton-transfer capabilities. Pyranine/MV2+ complexes (for the acid and conjugated base pyranine species) were characterized by UV–Vis and fluorescence titrations. Pyranine/MV2+ photoredox reactions were investigated by monitoring the transients (laser flash photolysis) due to the solvated electron, the reduced (PO−) and oxidized (PO+•) forms of pyranine, and the semireduced methyl viologen (MV•). Ionic aqueous micelles (sodium dodecyl sulfate and cetyltrimethylammonium chloride) and anionic reversed micelles (sodium bis(2-ethylhexyl)sulfosuccinate) were used to disassemble the complex by attraction of one of its species by an oppositely charged micellar aggregate. Present findings demonstrate the formation of a complex and its manipulation, which may allow the development of a photocatalyst agent whose properties can be adjusted by the appropriate disposition of the complex partners in supramolecular aggregates.

Introduction

The search for photocatalyst agents aiming to efficiently promote charge separation with relatively high quantum yield is of major importance in photochemical studies. Among the most investigated photoredox couples are ruthenium complexes as excited-state electron donor and viologen derivatives as electron acceptor. Supramolecular assemblies where the photoredox pairs are spatially organized provide promising ways to efficiently realize energy conversion.5–7

One of the challenging issues in the field of supramolecular photochemistry is the ability to control the disposition of the photocatalyst groups. The use of electrostatic forces is certainly one way to realize spatial control and to change photochemical behavior; for example, ion pairs are known to exhibit distinct photochemical behavior compared with the independent constituents.8,9

Self-assembled thin films, which can present extraordinary photophysical and photochemical properties, are frequently constructed on the basis of electrostatic forces between the constituents.10,11 Micelles and reversed micelles are supramolecular aggregates that also are known to change photochemical behavior of specific photoredox systems.12,13 These aggregates promote concentration or exclusion of compounds in the micelle core or interface on the basis of hydrophobic or electrostatic interactions.1,2

Previously it has been shown that the conjugated base pair of the well-known photoacid 8-hydroxy-1,3,6-pyri
denium/sulfonate anion (pyranine) can undergo photooxidation yielding solvated electrons (es) upon intense laser excitation.14,15 Therefore one laser shot excitation of pyranine can generate electron and proton pulses that may in principle be harvested for hydrogen production. With this scenario we devise to develop a photoredox system with three characteristics: (a) It should lead to the ejection of H+ and e−; (b) the electron should be accepted by a good oxidant agent and should form a relatively stable radical species; (c) it should have the potential for being spatially organized to have its photochemical behavior controlled.

In this report pyranine and methyl viologen (MV2+)...
Photolysis. Effects of spatial organization provided by intermediate species were characterized by laser flash absorption and emission spectra and photochemical tolysis. Equilibrium constants were calculated by changes in photochemical properties of the pyranine/MV2 complexes and photochemical reaction routes were investigated.

**Materials and Methods**

Pyranine (Eastman Kodak) was used as received once no impurities were detected in thin-layer chromatography plates.17 MV2 (Aldrich) was recrystallized twice from cold acetone/methanol (85/15 v/v). Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was purified with activated charcoal and dried for 2 days under vacuum. Sodium dodecyl sulfate (SDS) and cetyltrimethylammonium chloride (CTACl) were obtained from Aldrich. Water was doubly distilled from an all-glass apparatus and was further purified via a MilliQ Milli-Q System. All other materials were of the best analytical grade available. Reversed micelles solutions were prepared and used in the same day.

Absorbance spectra were recorded in a Hitachi U-2000 spectrometer interfaced (RS-232C) to a 486 microcomputer for data manipulation and storage. Fluorescence spectra were recorded in a SPEX DM3000-F. Spectral data were further manipulated with a 386 GRAMS software (Galatica). Fluorescence lifetimes (τ) were determined in an LS1 Time-resolved fluorometer (PTI, Canada) using the 337-nm nitrogen line. τ values were obtained by standard deconvolution routines (PTI software) using Ludox (Dupont) for collecting the lamp profile, which in our setup presented a full width at half-maximum (fwhm) of 2–3 ns. For the determination of pyranine/MV2 association constants pyranine was held constant and MV2 was varied. Spectral data were obtained in 1-cm optical path length quartz cuvettes. The fluorescence quantum yield was obtained by comparing the corrected emission spectra of pyranine with that of quinine sulfate using the equation described by Demas and Crosby.18 Both pyranine and quinine solutions were excited at 350 nm and the spectra were measured and integrated from 390 to 700 nm.

Laser flash photolysis data were obtained with an Applied Photophysics system composed of a Nd:YAG laser (Spectron Laser System, U.K.) operating at 355 nm or 266 nm and delivering pulses with ~31.5 µJ/pulse and ~20-ns fwhm, a pulsed 150W Xe lamp, control electronics, and a Hewlett-Packard 54510B fluorometer (PTI, Canada) using the 337-nm nitrogen line. Data were handled using either CONTIN software (PTI) for line broadening and a custom software for data manipulation and storage. Fluorescence spectra were obtained using a 337-nm nitrogen line.

Photophysical and Photochemical Properties of Pyranine/MV2 Complex in Water. The formation of pyranine/MV2 complexes can be readily detected by recording the UV–Vis spectral changes in a solution of pyranine with the addition of MV2. Because pyranine has a ground-state pK_a around 7 (Scheme 1), the complexation was investigated at pHs where the dissociation equilibrium was displaced toward either one of the conjugated acid–base pair species. Figure 1 left and right display the complexation in aqueous solutions at pHs 3 and 11, respectively. Clearly in both media the spectra of pyranine for both the conjugated acid (Figure 1 left) or its base pair (Figure 1 right) gradually move toward longer wavelengths. Two isosbestic points in both spectra are also well apparent, that is, 335, 411 nm in acid and 355, 466 nm in basic media. Variation in the absorption as a function of MV2 concentration was treated using the Benesi–Hildebrand model and resulted in fairly linear plots (data not shown).22 The calculated complexation constants (K) are in the order of 10^4 and 10^5 M^-1 in acidic and basic media, respectively, and decrease with the increase in the ionic strength (Table 1).

Extinction coefficients (e) at the absorbance maxima of the complexes were calculated from the relation Δε = ε_complex − ε_pyranine − ε_MV^2+. Once MV2 is transparent in the visible region and ε_pyranine is readily obtained at the complex maximum absorption wavelength. Accordingly, in acid

**Scheme 1. Ground State Acid (POH) and Basic (PO−) Pyranine Species and Complexation Equilibria with Methyl Viologen (MV2+)**

[Diagram showing the reaction schemes]

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(16) The pyranine photoredox reactions can be represented using the full charge of the molecule:

\[ \text{PO}^+ + e^- \rightarrow \text{PO}^2^- \]

\[ \text{PO}^2^- + \text{PO}^+ + e^- \rightarrow 2\text{PO}^+ \]

To facilitate the visualization of the reduced and oxidized species as well as to go in accordance with the published literature (refs 14, 15, 20–25) we have decided to represent the above reactions as follows:

\[ \text{PO}^+ + e^- \rightarrow \text{PO}^+ \]

\[ \text{PO}^2^- - \text{PO}^+ + e^- \rightarrow 2\text{PO}^+ \]


equilibrium (quasi-equilibrium) in the order of occurrence of prototropic reaction of pyranine, which is conjugated acid at either pH in the absorption wavelength maximum (Figure 2). In the absence of MV2+ addition of MV2+ in the complexes result in fair linear relation (data not shown). On the other hand, analysis by the equation that considers the coexistence of static (Ks) and dynamic quenching (Kd) processes results in fair linear dependence (Figure 3). The values of Ks and Kd are collected in Table 1. Ks values obtained by analyzing the fluorescence data agree well with Ks values obtained by spectrophotometry. Kd values are in general 1 order of magnitude smaller.

Plotting the dependence of Ks and Kd on the ionic strength (μ) by using the Brønsted–Bjerrum limiting ionic activity coefficients and considering a 1:1 stoichiometry in the complexes result in fair linear relation (data not shown), which lends credence to the 1:1 assumption. The limiting values for the association constants obtained for μ = 0 are: Ks(basic) = 2.59 × 10^4 M^-1, Ks(acid) = 3.59 × 10^4 M^-1, Kd(basic) = 2.91 × 10^3 M^-1, and Kd(acid) = 1.23 × 10^3 M^-1.

As demonstrated by Gutman and co-workers, using a strong UV laser pulse (e.g., the third harmonic of a Nd: YAG laser), the photooxidation of pyranine caused by the absorption of a second photon during a typical flash excitation (about 20 ns in the present instrument) is observed. Shortly, photexcitation of pyranine leads to the appearance of the excited basic form of the dye (direct excitation or prototropic dissociation of the excited acid), which during its lifetime can absorb a second photon during a typical flash excitation or prototropic dissociation of the excited acid), yielding the pyranine anion radical (PO−) and e− (Scheme 2). In acid conditions the electron reacts with H+ and as well with pyranine ground-state, yielding the pyranine anion radical (PO−, reactions 1 and 2 in Scheme 2). In alkaline conditions the process involves mainly the generation of solvated electrons, and the reduced and oxidized forms of the dye. In the absence of oxygen the process is reversible and the attribution of the transients is as follows: PO− is a long-lived species and has an absorption band maximum at ~445 nm (ε445 ≈ 22 °C.

Table 1. Effect of Ionic Strength (μ) on Ground (Ks) and Excited (Kd)-State Association Constants of Pyranine/Methyl Viologen Complexes in Acid and Basic Conditions

<table>
<thead>
<tr>
<th>μ</th>
<th>Ks, spec. a</th>
<th>Kd, spec. a</th>
<th>Kd, alb. media (pH = 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0019</td>
<td>2.31e+4</td>
<td>2.22e+4</td>
<td>9.76e+2</td>
</tr>
<tr>
<td>0.0069</td>
<td>1.29e+4</td>
<td>1.57e+4</td>
<td>8.73e+3</td>
</tr>
<tr>
<td>0.021</td>
<td>7.24e+3</td>
<td>6.04e+3</td>
<td>6.68e+2</td>
</tr>
<tr>
<td>0.041</td>
<td>5.08e+3</td>
<td>3.86e+3</td>
<td>6.57e+2</td>
</tr>
<tr>
<td>0.062</td>
<td>2.33e+3</td>
<td>3.66e+3</td>
<td>5.61e+2</td>
</tr>
<tr>
<td>0.081</td>
<td>3.75e+3</td>
<td>3.42e+3</td>
<td>5.20e+2</td>
</tr>
<tr>
<td>0.101</td>
<td>2.42e+3</td>
<td>3.27e+3</td>
<td>4.02e+2</td>
</tr>
</tbody>
</table>

a Spec. and fluor. refer to the way Ks were calculated; see text. T = 22 °C.

media ε418 nm = 8230 ± 280 M⁻¹ cm⁻¹ and in basic condition ε483 nm = 11 500 ± 500 M⁻¹ cm⁻¹. The red shift observed at either pH in the absorption wavelength maximum associated with the decrease in for both pyranine species as well as the electron transfer from pyranine to MV2+ observed in the photooxidation studies (see below) suggest that these transitions have a CT character.

Effects on the fluorescence yield of pyranine due to the addition of MV2+ in the two selected pH are shown in Figure 2. In the absence of MV2+ the emission spectrum at pH 3 presents two unstructured transitions peaking at 445 and 510 nm that are assigned to the emission of the conjugated acid–base pair, respectively. The stronger emission at 510 nm compared to that at 445 nm shows the occurrence of prototropic reaction of pyranine, which is known to display an excited singlet state dissociation equilibrium (quasi-equilibrium) in the order of ~10⁻⁰.⁵ (see Scheme 2). At pH 11 the emission band centers at 510 nm and is simply due to the steady-state fluorescence emission of pyranine-conjugated base. Addition of MV2+ to either solution results in a strong fluorescence quenching. Treatment of the emission suppression data by standard Stern–Volmer analysis resulted in plots with upward curvature at high MV2+ concentration (data not shown). The other hand, analysis by the equation that considers the coexistence of static (Ks) and dynamic quenching (Kd) processes results in fair linear dependence (Figure 3). The values of Ks and Kd are collected in Table 1. Ks values obtained by analyzing the fluorescence data agree well with Ks values obtained by spectrophotometry. Kd values are in general 1 order of magnitude smaller.

Plotting the dependence of Ks and Kd on the ionic strength (μ) by using the Brønsted–Bjerrum limiting ionic activity coefficients and considering a 1:1 stoichiometry in the complexes result in fair linear relation (data not shown), which lends credence to the 1:1 assumption. The limiting values for the association constants obtained for μ = 0 are: Ks(basic) = 2.59 × 10^4 M⁻¹, Ks(acid) = 3.59 × 10^4 M⁻¹, Kd(basic) = 2.91 × 10^3 M⁻¹, and Kd(acid) = 1.23 × 10^3 M⁻¹.

As demonstrated by Gutman and co-workers, using a strong UV laser pulse (e.g., the third harmonic of a Nd: YAG laser), the photooxidation of pyranine caused by the absorption of a second photon during a typical flash excitation (about 20 ns in the present instrument) is observed. Shortly, photexcitation of pyranine leads to the appearance of the excited basic form of the dye (direct excitation or prototropic dissociation of the excited acid), which during its lifetime can absorb a second photon generating the photooxidized pyranine cation radical (PO−) and e− (Scheme 2). In acid conditions the electron reacts with H+ and as well with pyranine ground-state, yielding the pyranine anion radical (PO−, reactions 1 and 2 in Scheme 2). In alkaline conditions the process involves mainly the generation of solvated electrons, and the reduced and oxidized forms of the dye. In the absence of oxygen the process is reversible and the attribution of the transients is as follows: PO− is a long-lived species and has an absorption band maximum at ~445 nm (ε445 ~

43 000 M⁻¹ cm⁻¹). The short-lived PO⁻, whose formation is prevented by oxidants such as H⁺ and ferricyanide, has a maximum at 514 nm (ε = 25 000 M⁻¹ cm⁻¹), and the short-lived eₗ is observed at longer wavelengths (ε = 14 300 M⁻¹ cm⁻¹).¹³,¹⁴,²⁹

The effect of MV²⁺ in the photooxidation of pyranine was studied by monitoring the transient species by laser flash photolysis. Under 355-nm excitation only pyranine molecules are excited. The signal observed at 390 nm (Figure 4A) is thus simply that of depletion of pyranine due to the photooxidation cycle. Addition of MV²⁺ to provide 1:1.7 and 1:9.5 pyranine/MV²⁺ mole ratios (R) are accompanied, respectively, by the appearance of reduced viologen and disappearance of any detectable transient signal (notice that MV⁺ presents well-known absorption bands peaking at 390 and 617 nm with ε's of 36 000 and 9200 M⁻¹ cm⁻¹, respectively).³⁰ In parallel, by monitoring the signal at 617 nm the following features are observed (Figure 4B): (a) exponential decay of eₗ (absence of viologen) with a first-order rate constant of 8.3 × 10⁵ s⁻¹; (b) appearance of MV⁺ (1:1.7); and (c) suppression of the transient signal (1:9.5). It should be noticed that the rising time for the MV⁺ appearance observed at 390 or 617 nm resulted in an observed first-order constant of 2.0 × 10⁶ s⁻¹, in agreement with a process occurring within the lifetime of the eₗ decay. This suggests that the MV⁺ was formed through the reduction of MV²⁺ by the eₗ and, furthermore, that the complex pyranine/MV²⁺ is photoinactive.

The fluorescence quantum yield (φ) of pyranine in our instrumental setup in aqueous solution has a value of 0.82.²⁴,²⁵ In a large excess of MV²⁺, the φ is decreased to ~0 (Figure 4C, inset). Assuming that no other photochemical or photophysical process is taking place, this would lead to the conclusion that the fraction of absorbed energy delivered to the medium as heat (α) for the complex would approach 1 (α = 0.997). To check whether the excitation energy was being lost in the form of heat, TRTL transients of pyranine and pyranine/MV²⁺ complex were measured. This technique has the advantage of measuring directly the amount of heat deposited in the medium. In the absence of MV²⁺ the α value for pyranine was calculated to be 0.453 on the basis of its emission spectra (α = 1 − φ/φₑ). Where φₑ and φ are the excitation frequency and weighted average fluorescence frequency, respectively. It is important to comment that this α value includes, besides the amount of heat due to S₁ → S₀ nonradiative transition, the heat derived from higher S₂ states and even S₃ states since the excitation beam is fixed at 355 nm where S₁ and S₂ states start to overlap. As shown in Figure 4C, in the presence of a large excess of MV²⁺ there is an increase in the magnitude of the thermal lens signal of 2.3 times, leading to a α of 1.04. This measurement proves that the pyranine/MV²⁺ com-

{"footnotes":null}
plex loses the excitation energy in the form of heat upon 355-nm excitation (Figure 4C), in agreement with its photochemical inactivation.

Figure 4D shows the 390 nm \( \text{Abs} \) of a MV2\(^+\) solution with different amounts of pyranine added, using 266-nm excitation (at this wavelength both pyranine and MV2\(^+\) are excited, Scheme 2). In the absence of pyranine a relatively long-lived transient assigned to the semireduced form of MV2\(^+\) is observed. This signal arises from the excitation of MV2\(^+\) and its reduction probably by removal of an electron from water. By adding pyranine, clearly the signal augments and because for the signals with high \( R \) (traces labeled 2 to 5, \( R \) is 9.7, 3.2, 0.9, 0.45, respectively. Figure 4D inset shows \( \text{Abs} \) at 4 \( \mu \)s after the laser pulse as a function of \( 1/R \), for pyranine−MV2\(^+\) mixtures excited at 266 nm and measured at 390 nm (Milli-Q water).

Effect of Micelles and Reversed Micelles on Photophysical and Photochemical Properties of Pyranine and Pyranine/MV2\(^+\). The effect of increasing the concentration of direct micelles in a solution that has pyranine and excess of MV2\(^+\) is shown in Figure 5 for cationic micellar aggregates of CTACl (Figure 5A) and negatively charged ones of SDS (Figure 5B). In both cases disassembly of complex is observed, causing an increase in the fluorescence emission from pyranine. In CTACl the experiment was conducted at pH = 9.0, which leads to the following sequence of events: (a) The positively charged interface attracts pyranine and excludes MV2\(^+\), and (b) ground- and excited-state \( pK_a \)s of pyranine increase upon association with the micelle.\( ^{31} \) These effects are reflected in the appearance of POH emission (small band at \( 425 \) nm) and shifts in the emission wavelength maximum compared with the wavelength maximum observed in aqueous media. Anyhow the recovery of the pyranine emission is clearly observed. In SDS micelles an opposite effect is observed, that is, MV2\(^+\) is attracted to the interface and pyranine is excluded (Figure 5B). In the experimental condition (pH = 5) the overall effect is simply that of POH* and PO\(^-\) emission increase.

If the magnitude of fluorescence recovery observed for CTACl and SDS is compared, it is clearly seen that it is larger for CTACl; for example, at the surfactant concentration of \( 8 \times 10^{-4} \) M about 90% of fluorescence is recovered in the presence of CTACl and only about 30% is recovered in the presence of SDS. This effect is due to the high-affinity binding between the fourth charged pyranine and negatively charged SDS.

in water and that reversed micelles is smaller by 2 orders of magnitude than shown), suggesting the lesser importance of dynamic ever, the data did not fit well to this model (data not used is not known; however, a good estimate is that they presence of 0.2 M NaCl is 9 \(10^{-5}\) M, (a) 8 \(10^{-5}\); (b) 2.5 \(10^{-5}\); (c) 3.3 \(10^{-5}\); (d) 4.2 \(10^{-5}\); (e) 5 \(10^{-5}\); (f) 6 \(10^{-5}\); (g) 7.5 \(10^{-5}\); (h) 1.25 \(10^{-5}\); (i) 2.5 \(10^{-5}\); (j) 3 \(10^{-5}\); (k) 4 \(10^{-5}\); [acetate buffer] = 0.2 M, pH = 5. [pyranine] = 5 \(10^{-6}\) M; [MV\(^2+) = 1 \(10^{-4}\) M; \(\lambda_{exc} = 403\) nm.

CTACI monomers\(^{32}\) as well as to the smaller critical micelle concentration (cmc) of CTACI compared to SDS (1.3 and 8.1 mM in water for CTACI and SDS, respectively).\(^{33}\) The exact cmc values of these surfactants in the buffer solutions is not known; however, a good estimate is that they are around 1 order of magnitude smaller than the values observed in water; for example, the cmc of SDS in the presence of 0.2 M NaCl is 9 \(10^{-4}\) M.\(^{25}\)

Because reversed micelles have the ability to confine the components of the pyranine/MV\(^{2-}\) complex were investigated in AOT/isoctane/water reversed micelles.\(^{1,2,13,33}\) By keeping the water-to-surfactant molar ratio (W\(_0\)) and pyranine concentration constant and increasing the MV\(^{2-}\) concentration, a typical quenching profile of pyranine emission is observed (Figure 6). It is clear that the majority of the emission comes from the excited basic form of pyranine, demonstrating that the prototropic reaction is almost quantitative at this W\(_0\) value, in agreement with previous results.\(^{19,20}\) In addition to the emission suppression, changes in the absorption spectra are also observed, indicating the presence of dynamic quenching (Figure 6, inset A). K\(_q\) values were calculated using a Stern–Volmer plot (Figure 6, inset B). K\(_q\) values were shown to be 35 and 50 M\(^{-1}\) for W\(_0\) 25 and 11, respectively, showing that K\(_q\) in reversed micelles is smaller by 2 orders of magnitude than in water and that K\(_q\) decreases with the increase in W\(_0\). The suppression data were also treated using the model that considers both static and dynamic quenching; however, the data did not fit well to this model (data not shown), suggesting the lesser importance of dynamic quenching in reversed micelles.

The transient spectra of pyranine in aqueous (Figure 7A) and in reversed micelle solutions (Figure 7B) are significantly different. The transient spectra 1.5 \(\mu s\) after the laser pulse have in both cases maxima around 440 nm (assigend to the PO\(^{-}\) absorption). In the case of aqueous solution the transient spectra measured 5 \(\mu s\) after the pulse is quite different from that at 1.5 \(\mu s\) (Figure 7A), and this is interpreted as the reduction of PO\(^{-}\) by e\(_s\), forming PO\(^{2-}\) (Scheme 2, reaction 2). In other words the ΔA\(_s\)s measured at 5 \(\mu s\) after the pulse results from the positive contribution due to the PO\(^{2-}\) species and a negative component due to the PO\(^{-}\) bleaching (Figure 7A, inset). In the case of reversed micelle solutions the PO\(^{2-}\) transient spectra do not change with time (Figure 7B, 7A inset). This indicates that pyranine photoreduction is prevented in reversed micelles and also that the pyranine cation radical is a stable species within the measurement time course. Because no spectral shifts (absorption and fluorescence) were observed for either pyranine (at the experimental W\(_0\)), it is probable that it is located in the micelle core (recall that even PO\(^{2-}\) is a triply charged species). Another point to consider is that a low occupation number (less than 1% of the reversed micelles have a pyranine molecule) was used in the system, restring the photoreaction to the microenvironment of one specific reversed micelle.

The absorption of the e\(_s\) was also monitored in aqueous and reversed micelle solutions. The transient observed in aqueous solution at 617 nm (Figure 7B, inset) is due to the e\(_s\), which has a lifetime of \(\sim 1.2\) \(\mu s\). In the reversed micelle, however, only a small transient is observed, which can be understood if the lifetime of the solvated electron is smaller than the time resolution of our instrument (around 200 ns). This shortened e\(_s\) lifetime in AOT reversed micelles has been interpreted as due to the AOT quenching.\(^{33}\)

Indication of the photoreduction of MV\(^{2-}\) by pyranine in reversed micelle solution was obtained by laser flash photolysis. As shown above (Figure 4), both e\(_s\) and MV\(^{2-}\) absorb in the 600-nm region. In the absence of MV\(^{2-}\) the observed transient is basically due to the e\(_s\) transient...
(short-lived species). The nonreturn to the prepulse level in this transient signal has been observed before in deaerated aqueous solution and is probably due to the long-lived \( \text{PO}^+ \) species.\(^{14,15}\) In the presence of \( \text{MV}^{2+} \) (enough to have an average of 3 \( \text{MV}^{2+} \) molecules per reversed micelle) and keeping pyranine concentration constant, the magnitude of \( \Delta \text{Abs} \) at 617 nm is almost doubled (Figure 8), indicating the presence of \( \text{MV}^{2+} \) formed by photoexciting pyranine. At this condition pyranine molecules are partially complexed to \( \text{MV}^{2+} \), as can be seen by the emission

**Figure 7.** Laser flash photolysis transient spectra of pyranine in aqueous (A) and AOT reversed micelle (B) solutions measured 1.5 (●) and 5 µs (■) after the laser pulse. Insets A and B show the transients of the same aqueous and reversed micelle solutions monitored at 415 nm (A) and 617 nm (B). \([\text{AOT}] = 0.1 \text{ M} \quad (W_0 = 30), \quad [\text{pyranine}] = 1 \times 10^{-5} \text{ M}, \quad [\text{borate buffer}] = 0.02 \text{ M}, \quad \text{pH} = 10, \quad \text{laser energy} = 25 \text{ mJ/pulse}, \quad \text{RM is reversed micelle.}

**Figure 8.** Laser flash photolysis transients of pyranine (\([\text{pyranine}] = 4.6 \times 10^{-5} \text{ M}\) and pyranine/\( \text{MV}^{2+} \) (\([\text{pyranine}] = 4.6 \times 10^{-5}\) and \([\text{MV}] = 3.3 \times 10^{-7} \text{ M}\)) reversed micelle solutions.\(^\text{a}\) \(W_0 = 25, \quad \lambda_{\text{exc}} = 355 \text{ nm}, \quad \lambda_{\text{mon}} = 617 \text{ nm}, \quad \text{laser energy} = 25 \text{ mJ/pulse}.\) Inset: Pyranine emission spectra of the same solutions described above. \(\lambda_{\text{exc}} = 355 \text{ nm}, \quad [\text{HClO}_4] = 6.6 \times 10^{-4} \text{ M}.\)
spectra shown in Figure 8 inset. It is not possible to observe the rise time of MV\(^{++}\) due to the small \(e_1\) lifetime in AOT reversed micelles.

**Conclusion**

Photophysical and photochemical properties of pyranine and pyranine/MV\(^{2+}\) in aqueous and in reversed micelle solutions were measured. Association constants in aqueous solution as calculated by UV–Vis and fluorescence spectrometry, using 1:1 stoichiometry models for either acid or base pyranine species, are in the order of \(10^4\)–\(10^5\) M\(^{-1}\). Laser flash photolysis and TRTL data strongly suggest that upon 355-nm excitation the complexed pyranine returns to the ground state by internal conversion. However, the uncomplexed pyranine population is able to undergo its photocycle, ejecting a H\(^+\) and an \(e_1\) in solution and forming MV\(^{++}\). The complex pyranine/MV\(^{2+}\) acts as a photocatalyst itself when excited at 266 nm. The mechanism involved in the photocatalysis is related to the increase in the electron affinity of excited MV\(^{2+}\) that is able to abstract an electron from the complexed pyranine. Because of an electrostatic effect (MV\(^{2+}\) concentrates at the interface and pyranine in the micelle core), the complexation constant between POH and MV\(^{2+}\) in AOT reversed micelles is more than 2 orders of magnitude smaller than in aqueous media. A decrease in the \(e_1\) lifetime not allowing the photoreduction of ground-state pyranine (as observed in water) was observed in the absence of MV\(^{2+}\). In the presence of a large excess of MV\(^{2+}\), formation of MV\(^{++}\) was characterized. Therefore, the potential of reversed micelles to spatially organize the pyranine/MV\(^{2+}\) system, allowing proton- and electron-transfer reactions to occur, has been demonstrated. Efforts are being made to implement these solutions with hydrogen catalysts, such as platinum colloidal particles, to induce photostimulated hydrogen production, and to use the pyranine/MV\(^{2+}\) pair in the construction of thin films. It is important to note that MV\(^{++}\) is a reducing agent (\(E_{1/2} = -0.45\) V; MV\(^{2+}\)/MV\(^{++}\)) and PO\(^{++}\) is a good oxidizing agent (\(E_{1/2} = 1\) V; PO\(^{++}\)/PO\(^-\)), and both species are stable and separated at around 40 A (the approximated hydrodynamical radius of a reversed micelle at these conditions is 50 A, and the surfactant layer has thickness of around 10 A\(^1\) in the reversed micelle structure, showing the great photocatalyst potential that such a system has.

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