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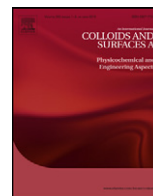
# Dye aggregation and influence of pre-micelles on heterogeneous catalysis: a photophysical approach

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## Dye aggregation and influence of pre-micelles on heterogeneous catalysis: A photophysical approach

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### ABSTRACT

Common cationic dyes used for laser and fluorescent probes present low solubility in water. In order to increase the dye concentration in aqueous solutions, anionic surfactant can be added. The strong interaction between anionic surfactant and cationic dye can affect drastically the dye absorption and fluorescence properties. Here we observed that the fluorescence of the species in aqueous solution is maximized at condition of complete micellization of surfactants at critical micelle concentration (CMC). In addition, combined measurements of absorption, emission and fluorescence lifetime provide fundamental information on the critical concentration of H-aggregates formation and monomer separation, induced by pre-micelles and homomicelles on different surfactant sodium dodecylsulphate (SDS) concentration. The experimental results show how to find precisely the critical concentration of H-aggregates by optical method in two different xanthene-derived molecules: rhodamine 6G and rhodamine B. The adequate transference of electron from excited dye to the conduction band of semiconductor (TiO<sub>2</sub>) promotes the creation of reactive species that provides the degradation of dye with advantage of use of irradiation in the visible region and strong photobleaching with direct exposure to the visible light irradiation in a scale of time of 10 min.

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### 1. Introduction

The use of laser dyes in aqueous solutions as fluorescent probes [1] represents an important biological application due to its low water toxicity if compared with several other organic solvents. But, on the other side, the solubility of laser dyes (such as rhodamine 6G and rhodamine B) in water is very low because of hydrophobic interactions between alkyl substituent [2] and water. In this case, dyes tend to aggregate in the form of dimers. In order to overcome this drawback, it is necessary to increase the solubility of organic dyes in aqueous solutions. One appropriate alternative is the introduction of an ionic surfactant with opposite charge relative to dye promoting the formation of dye–surfactant mixed micelles in the solution. Such process, extremely dependent on surfactant/dye ratio [3,4], need to be well characterized in order to be find the best surfactant and its concentration.

Relative to the interaction of oppositely charged surfactant/dye important regions can be cited: the critical micelle concentration (CMC), one above and other bellow the CMC. For instance, at low concentration of sodium dodecyl sulphate (SDS)

surfactant ( $C < CMC$ ), it is verified a strong interaction between surfactant and dye resulting in a sandwich of dye molecules between oppositely charged molecules of surfactant. This process reduces the influence of Coulombic repulsion and thermal agitation as a consequence of strong attractive force between the molecules resulting in a reduction in the distance of monomers, inducing the dimer formation [3,5], characterizing, consequently, a critical concentration named pre-micellar aggregation, which assumes values below the typical concentration of homomicelle aggregation [6]. The dimer formation is characterized by a large spectral change in the absorption spectrum around the main absorption peak in the visible spectrum (absorption decreases and a blue shifted shoulder appears), which characterizes the aggregation of dyes [6]. Relative to the dimerization, it is established that H (sandwich aggregates) and J (head-to-tail aggregates) [7] are possible conformation of dimers [8]. H-aggregates promotes hypsochromic shift in the absorption spectrum, representing weakly fluorescent species while the J-aggregates are fluorescent and provokes bathochromic shift [8].

Important applications can be cited for pre-micelles of dye/surfactant such as the enhanced energy transfer and the fast dye photodegradation using advanced oxidation processes (AOP). In the first case, the pre-micellar region takes advantage of the presence of more than one dye molecule per aggregate [9].

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The AOP is based on the insertion of a photocatalyst – in our case the titanium dioxide (a semiconductor with bandgap of 3.2 eV and 388 nm cut-off wavelength) in the media, being applied as a potential element in the photodegradation, since the interaction with UV radiation [10] promotes the separation of excited electrons and holes on the surface of semiconductor, providing a reaction with water that provides the creation of strong reactive radicals such as  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$ . The interaction of reactive species with dye produces water and mineral acids and the subsequent breakup of rhodamine molecules, with the efficient photodegradation of dyes dispersed in water. In this direction, Natarajan et al. [11] describe the use of UV-LEDs that provide degradation of rhodamine from the action of titanium dioxide. The optimized parameters were 1.6 g/L of catalyst, 62.6  $\mu\text{M}$  of rhodamine B and total exposure time in order of 180 min.

Sonocatalytic degradation of rhodamine B represents another interesting procedure in which the property of low penetrability of UV light in water is substituted by ultrasonic perturbation. Pang et al. [12], describe a reactor in which 2 g/L of  $\text{TiO}_2$  nanotubes degrades rhodamine B (50 mg/L) after 120 min.

Another important aspect to be considered is that increase in the catalyst amount increases the active sites and consequently the production of reactive radicals. The limitation is verified by turbidity induced by titanium dioxide in the solution that progressively blocks UV irradiation, minimizing the photoactivity of semiconductor.

In order to overcome these drawbacks, another important procedure that allows the pseudo-reduction of band gap and subsequent use of radiation in the visible region is based on the fast transfer from visible light excited chromophores of dye to the conduction band of  $\text{TiO}_2$  [13]. This process is extremely dependent on coupling between titanium dioxide and rhodamine B. In this direction, the use of selective transition metals [14] acting as dopants of titanium dioxide introduces advantages in the photocatalytic process. The introduction of transition metals reduces the recombination of generated electrons and holes and decreases the band gap of semiconductor or similarly creates intraband gap states allowing the photocatalysis with irradiation of light in the visible region.

The use of oppositely charged surfactant and dye introduces the advantage of sensitization of  $\text{TiO}_2$  from direct interaction of semiconductor and dimers of rhodamine B with the adequate energy transfer from excited dye to titanium dioxide, for instance, allowing the photocatalysis and, consequently, an efficient photodegradation of rhodamine B [15–19], reducing the bandgap from 3.2 eV to intermediate level from which the irradiation in the visible region promotes the excitation of electrons from excited dye to the conduction band of  $\text{TiO}_2$  with the electron–hole pair generation.

On the other side, above CMC, the surfactant promotes the dissociation of aggregates (postmicellar condition), increasing the electrostatic repulsion of dye molecules [20], forcing that molecular structures in the solution tends to be a distribution of homomices with monomeric form of dyes dispersed in the hydrophobic core of surfactant micelles. The shielding provided by micelles is confirmed from the measurement of the fluorescence signal (established as a 2.5-fold increase [2]), a direct consequence of additional rigidity of molecular structure, minimizing the rotational movement and thermal fluctuations of monomers dispersed in water [6]. Important applications, based on the enhancement of fluorescence of rhodamines, are described in the literature, such as the quantification of residues of chromophores (rhodamine B) in cosmetics [21]. The consequence of dye monomer encapsulation in the core of micelles is also noticed in measurement of fluorescent lifetime. Usually, the fluorescence lifetime increases and indicates that dye molecules are protected against water in the core of micelles [22].

Based on these concepts, we can see that determination of critical concentration of dimer/monomer formation represents an

important procedure that provides information about interaction of surfactant/dye and consequently applications to the mixed system (rhodamine/SDS) as described above. In this direction, we have analyzed the influence of SDS surfactant on the aggregation of rhodamine 6G and rhodamine B in aqueous solution on several optical properties, measuring the fluorescence (quantum yield), absorbance and fluorescence lifetime of dye/SDS solutions. The combination of these different experimental techniques allows obtaining precisely the critical concentration of surfactant that maximizes the dimer formation and/or the complete dissociation in monomers. The knowledge of critical concentration can be used to optimize the quantity of aggregates and/or isolated monomers for specific applications, such as environmental remediation and detection of dye residues, with implications on biological and medical applications, for instance. In this direction, we also have implemented a systematic study from which rhodamine B/SDS at different concentration interacting with titanium dioxide particles. It is reported [23] that in a specific combination of dye/surfactant/semiconductor (at pre-micellar condition) occurs the fast photodegradation of rhodamine B. Using this property we measured the efficiency of breakup (photodegradation) of organic dyes from measurement of absorbance and fluorescence of samples as a function of concentration of rhodamine B.

## 2. Experimental

### 2.1. Materials

Titanium dioxide was purchased from Aldrich, USA. The average particle size in nanopowder is 25 nm with purity of 99.7%, specific surface area of 200–220  $\text{m}^2/\text{g}$  and bandgap of 3.2 eV. Rhodamine B and rhodamine 6G were purchased from Vetec, Brazil and sodium dodecyl sulphate (SDS) with 99% purity was purchased from Aldrich, USA.

### 2.2. Analytical methods

Absorption spectra were recorded by use of a spectrophotometer (FEMTO model 800XI) in the range of 400–800 nm using a fused silica cuvette with a 1 cm of pathlength. Photoluminescence properties were studied by use of a PC1 spectrofluorimeter (ISS, USA) at  $25.0 \pm 0.1$  °C. The fluorescence spectrum was obtained with disposition of samples in a 5 mL fused silica cuvette with also 1 cm pathlength and excited at 310 nm (for both rhodamines), while the emission was recorded from 320 nm to 800 nm. All experiments were conducted in triplicates.

In order to measure the fluorescence lifetime of the samples, we used pulses with 70-ps at 532 nm and 100 Hz repetition rate from a frequency doubled Q-switched and mode-locked Nd:YAG laser. The laser pulse was focused into the sample with a lens with 12 cm focal length. The sample was placed in a 2 mm-thick fused silica cuvette. The fluorescence signal was collected perpendicularly to the excitation beam through a large core (1 mm diameter) optical fiber positioned close to the fluorescent spot. The optical fiber directed the fluorescence to a fast silicon detector ( $\sim 500$  ps rise time) to measure the fluorescence decay time. To remove the laser scattered light, we used a longpass filter (Schott OG550). The fluorescence signal is averaged and recorded in a 1 GHz digital oscilloscope. The measurement of the fluorescence signal takes approximately 1 min, basically due to the averaging process.

### 2.3. Experimental procedure

The standard concentration of both dyes (rhodamine 6G and rhodamine B) used in all of experiments was varied in the interval

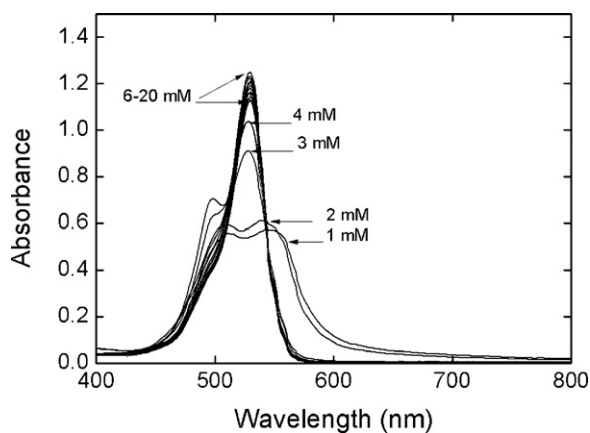


Fig. 1. Absorption spectra of rhodamine 6G dissolved in water with different concentrations of SDS.

$10^{-6}$ – $10^{-5}$  M in aqueous solution. Based on the fact that critical micelle concentration of SDS is 8.0 mM and pre-micelles of SDS/rhodamine B are verified at concentrations below the CMC, we established the range of 1–20 mM as a convenient interval of variation of surfactant concentration from which the analysis of response of monomers, pre-micelles and micelles interacting with dyes is favored. Relative to the second part of work (photodegradation of organic dyes) we have introduced semiconductor granules (titanium dioxide) in a concentration of 0.02 g/L, dispersed into aqueous solution containing dye and surfactant under dark condition, avoiding that additional process of photocatalysis can be initiated before complete dissolution of components. The process of solubilization is obtained after a few minutes under intense stirring. The photocatalytic reactor is composed by a 100 mL glass beaker containing aqueous solution of titanium dioxide/SDS/rhodamine B disposed at 30 cm from a 60 W halogen lamp. The distance from light source represents an important parameter in order to minimize thermal effects during photocatalysis.

The kinetics of photodegradation is mapped from measurement of absorbance and fluorescence of samples at fixed intervals of irradiation time, from which aliquots of sample at dark condition are subtracted for analysis and subsequently introduced in the media for posterior irradiation.

The calibration curve is obtained by measurement of characteristic peak of absorbance (at 547 nm) of aqueous solution containing SDS/TiO<sub>2</sub> and varying amount of rhodamine B/rhodamine 6G.

### 3. Results

#### 3.1. Interaction of dye/surfactant

As shown in Fig. 1, the absorbance of rhodamine 6G ( $10^{-5}$  M) aqueous solution at low concentration of surfactant (below 4 mM) is characterized by two peaks, which indicates that dyes are distributed in two forms, as monomers and dimers. The raising on SDS concentration induces an enhancement in the second peak ( $\sim$ 525 nm) when compared with the former, which can be identified, from this point, as a weak shoulder at ( $\sim$ 500 nm) for concentrations higher than 5 mM, allowing that a single peak prevails in the absorption spectrum.

A similar behavior (presence of shoulder and a peak at longer wavelength) also happens on rhodamine B aqueous solution. In order to analyze the ratio of monomer and dimer population with the SDS concentration, we deconvoluted the absorptions spectra using single Gaussian functions to fit the single absorption band related to the dimer signature. In Fig. 2, we show the dependency of absorption maximum associated with the dimer as a function of

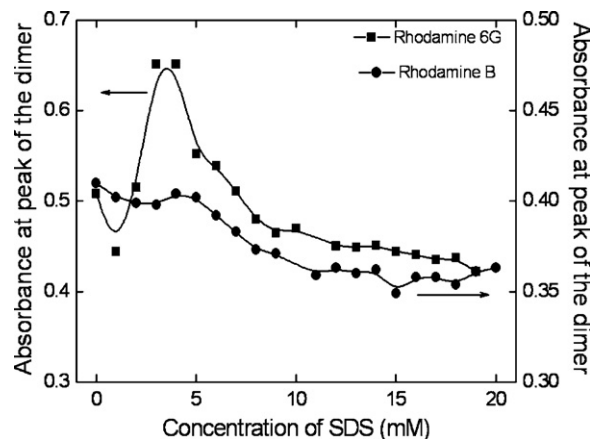


Fig. 2. Absorbance at the peak of the dimer as a function of SDS concentration for rhodamine 6G (square) and rhodamine B (circle).

surfactant concentration. In this figure, the behavior indicates that dimer formation increases until a concentration of 4 mM of SDS. After that, the intensity of band is progressively minimized. It is a strong indication that the maximum value in this curve characterizes the pre-micellar structures, since in this condition the aggregation is maximized.

Furthermore, additional information about the conformation of aggregates (H or J aggregates) can be addressed from measurement of the fluorescence signal of the samples.

In Fig. 3, one can observe that fluorescence of rhodamine 6G dissolved in water is strongly reduced in intensity, and a red shift is observed when the concentration of surfactant goes from 1 mM to 4 mM. It indicates that at approximately 4 mM of SDS, the maximum amount of the dimers is formed on the solution. On the other hand, when concentration of SDS is higher than 4 mM, the shift in the fluorescence spectrum basically stop to occur and the fluorescence intensity is strongly enhanced, indicating that dimerization and H-aggregates (typical weakly fluorescent species) are minimized in the bulk of solution and progressively substituted by dissolved monomers. Repeating the same experiment with rhodamine B aqueous solutions, it was verified a similar behavior on the fluorescence signal. Above this concentration, it is verified the same trend on the fluorescence enhancement.

This behavior can be better observed if we consider the area under the fluorescence spectrum for both dyes. As we can see in Fig. 4, the progressive reduction in the fluorescence signal is

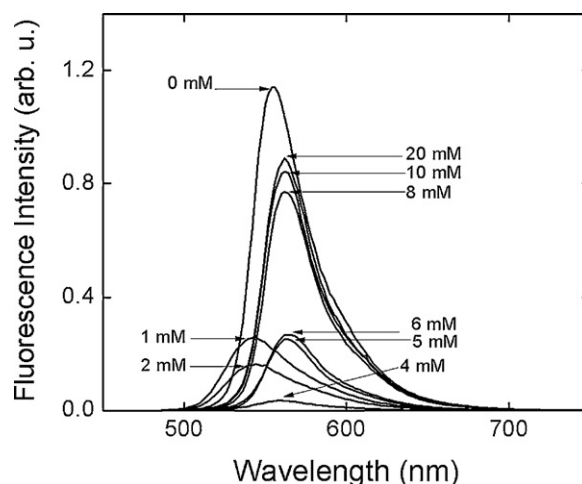
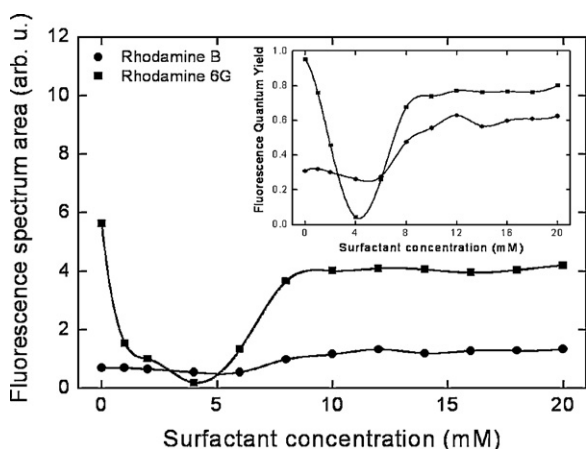


Fig. 3. Fluorescence of rhodamine 6G as a function of surfactant concentration.





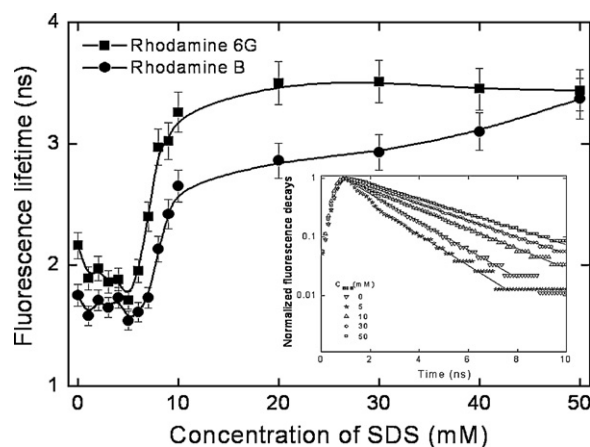
**Fig. 4.** Fluorescence spectrum area of rhodamine 6G (square) and rhodamine B (circle) as a function of surfactant concentration. The inset portrays the fluorescence quantum yield of both dyes as a function of surfactant concentration.

induced when the concentration of surfactant goes from 1 mM until 4 mM, where it reaches a minimum (complete dimerization of dyes) meaning pre-micellar structures. From this critical point, the fluorescence starts to increase reaching a constant plateau.

It happens because the electrostatic repulsion between similar molecules (surfactant) increases and homomicelles tends to be established, shielding and isolating the dye molecules from each other. In addition, once the dye molecules are surrounded by the micelles, its molecular structure becomes more rigid, reducing the vibrational modes and consequently the thermal effects. The consequence of this process is clearly observed in the plateau for concentrations higher than 8 mM (typical CMC of SDS). From this concentration, the population of monomers attain a maximum and the system is practically unaffected by inclusion of surfactant molecules. Moreover, from Fig. 4, one can notice that the minimum of the fluorescence signal (pre-micellar condition) for both dyes samples occurs between 4 mM and 6 mM for rhodamine 6G and B, respectively. It may be attributed as a consequence of the lower solubility of rhodamine B in water compared to rhodamine 6G, reducing the fluorescence quantum yield in the presence of low concentration of surfactant (below the limit of pre-micellization) as verified in the inset of Fig. 4. In this situation, it is important to verify that the fluorescence quantum yield of rhodamine B keeps practically constant for concentration smaller than 8 mM.

After this point, it is possible to observe an increase of approximately 2-fold on the fluorescence quantum yield, indicating the efficiency in the breakup of dimers provided by micelles of SDS. On the other hand, rhodamine 6G shows a little different behavior.

An alternative way to rationalize the behavior observed in the present study is by considering the fluorescence lifetime of the dye as a function of the surfactant concentration. Formation of dimers and/or aggregates tends to diminish the fluorescence lifetime. It occurs because the increase in the nonradiative pathways, occasioned by the coupling between the molecules. The measurement of the fluorescence lifetime also carries information about the critical concentration of mixed aggregates. The results can be visualized in Fig. 5 for both rhodamines. As can be seen, the minimum lifetime is obtained at concentrations in which the aggregation is maximized (condition of pre-micelles formation), which agrees with fluorescence and absorption spectra datas' previously discussed. On the other hand, when aggregates concentration is minimized by adding more SDS, the fluorescence lifetime starts to increase achieving a constant value between 3 ns and 3.5 ns. Again, it indicates that isolation provided by homomicelle decreases the non-radiative decays, optimizing the emission of dye by the radiative channel.



**Fig. 5.** Changes in the fluorescence lifetime of rhodamine B and rhodamine 6G in aqueous solution as a function of surfactant concentration. The inset depicts fluorescent decays of rhodamine B for different concentrations of SDS.

The process shows to reach saturation when the concentration of surfactant is in order or higher of micellization one, behavior that corroborates with the previous analysis. These lifetimes were obtained by adjusting a single exponential decay as can be seen on the inset of Fig. 5.

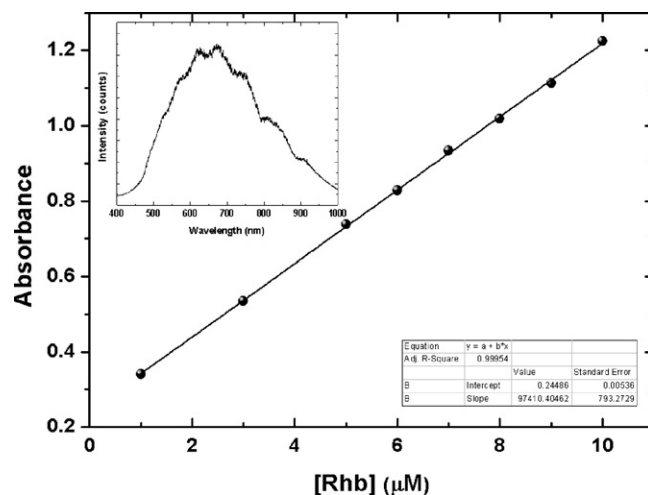
### 3.2. Photophysics of heterogeneous catalysis

Based on interesting results about aggregation of rhodamine B and SDS we explored the interaction of mixed system with a photocatalyst (titanium dioxide).

The amount of dispersed rhodamine B into aqueous solution in the presence of titanium dioxide and SDS was calculated from a calibration curve, as shown in Fig. 6, with variable amount of rhodamine B at fixed concentration of SDS and titanium dioxide (5 mM and 0.02 g/L, respectively).

With the use of light source (spectrum indicated in the inset of Fig. 6) we verified the effect of each component on the photocatalytic action of titanium dioxide from the measurement of absorbance at 547 nm and the use of calibration curve.

As we can see in Fig. 7, negligible results of photodegradation were obtained to the direct irradiation with light (visible region) in the solution containing rhodamine B. The same behavior was



**Fig. 6.** Calibration curve of rhodamine B into aqueous solution containing  $\text{TiO}_2$  (0.02 g/L) and SDS (5 mM) at condition of pre-micelles formation. In the inset is shown the spectrum of light source used in the experiment of photodegradation.

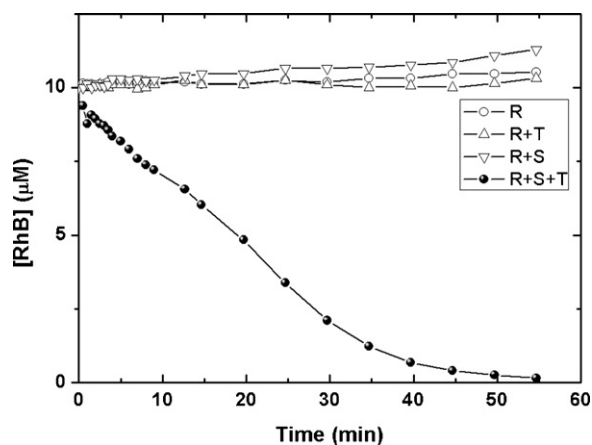


Fig. 7. Kinetics of photodegradation measured from absorption peak of RhB (R), RhB+SDS (R+S), RhB+TiO<sub>2</sub> (R+T), RhB+SDS+TiO<sub>2</sub> (R+S+T). ([RhB] = 10<sup>-5</sup> M, [TiO<sub>2</sub>] = 0.02 g/L, [SDS] = 5 mM) under continuous light incidence.

verified to the sample containing TiO<sub>2</sub> and rhodamine B, acting as a strong evidence that weak interaction of semiconductor and dye is established and photodegradation is activated only in the region of ultraviolet.

However, the introduction of surfactant at pre-micellar concentration in the presence of TiO<sub>2</sub> and rhodamine B induces a fast degradation process (as indicated in Fig. 7) that is a consequence of aggregation of dye molecules.

It is important to note in this point that additional processes such as self-degradation of dye, photocatalytic degradation of TiO<sub>2</sub> and degradation of SDS/rhodamine B aggregates introduce negligible contributions on the photocatalytic process induced by pre-micelles of SDS.

In order to clarify the contribution of SDS concentration on the photocatalytic process we studied the kinetics of photodegradation of rhodamine B with varying amount of SDS (0 mM, 3 mM, 5 mM, 10 mM and 15 mM), fixed concentration of TiO<sub>2</sub> (0.02 g/L) and rhodamine B (10<sup>-6</sup> M).

The results in Fig. 8 indicate that in the absence of surfactant and above the critical micelle concentration, the photodegradation is minimized while at pre-micellar condition (5 mM of SDS) the maximal rate of photodegradation is established in an indication that concentration of surfactant assumes a key role during photocatalytic process.

Another method to measure the photodegradation of rhodamines induced by titanium dioxide is performed from

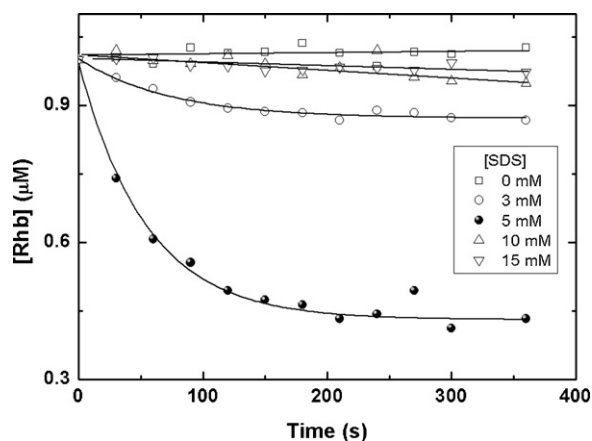


Fig. 8. Kinetics of photodegradation of rhodamine B ([RhB] = 10<sup>-6</sup> M) at fixed concentration of TiO<sub>2</sub> (0.02 g/L) and different concentrations of SDS.

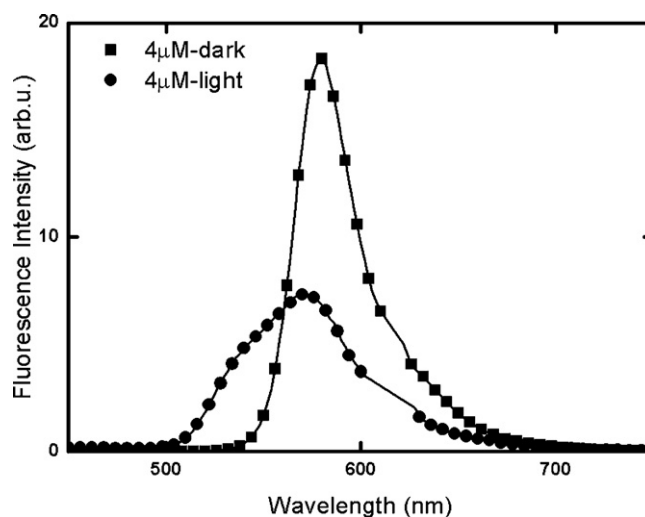


Fig. 9. Fluorescence of rhodamine B in the pre-micelles of SDS in the presence of TiO<sub>2</sub> at dark condition (square) and after irradiation with visible light during 10 min (circle).

monitoring of fluorescence intensity at 578 nm. The fluorescence signal was monitored in two different conditions: one is when the solution was kept in a dark condition without any interaction with light, and the other one is after irradiation with visible light. The analysis was realized with a fixed concentration of SDS (5 mM), titanium dioxide (0.02 g/L) and a variable concentration of rhodamine B from 0.5 μM to 5 μM. In this range of variation of chromophore concentration, it is possible to control the number of dimers enclosed in the hydrophobic environment of pre-micelles, allowing the direct control of distance between dye molecules and semiconductor particles. The sensitization of titanium dioxide as a function of number of dye molecules can be measured from the ratio of fluorescence peak of rhodamine B (verified at 578 nm) before and after the exposure to the visible light.

As we can see in Fig. 9 for sample with 4 μM of rhodamine B, it is verified a considerable reduction in the intensity of characteristic rhodamine B peak associated with a shoulder blue shifted, which characterizes the fluorescence of photodegraded residues. It is important to note that maximal photodegradation of rhodamine

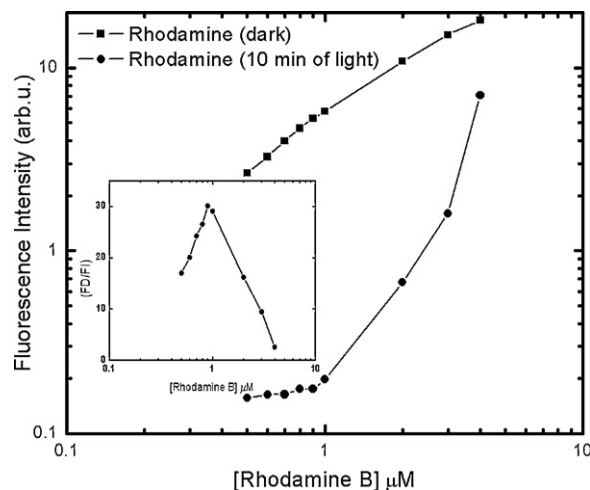
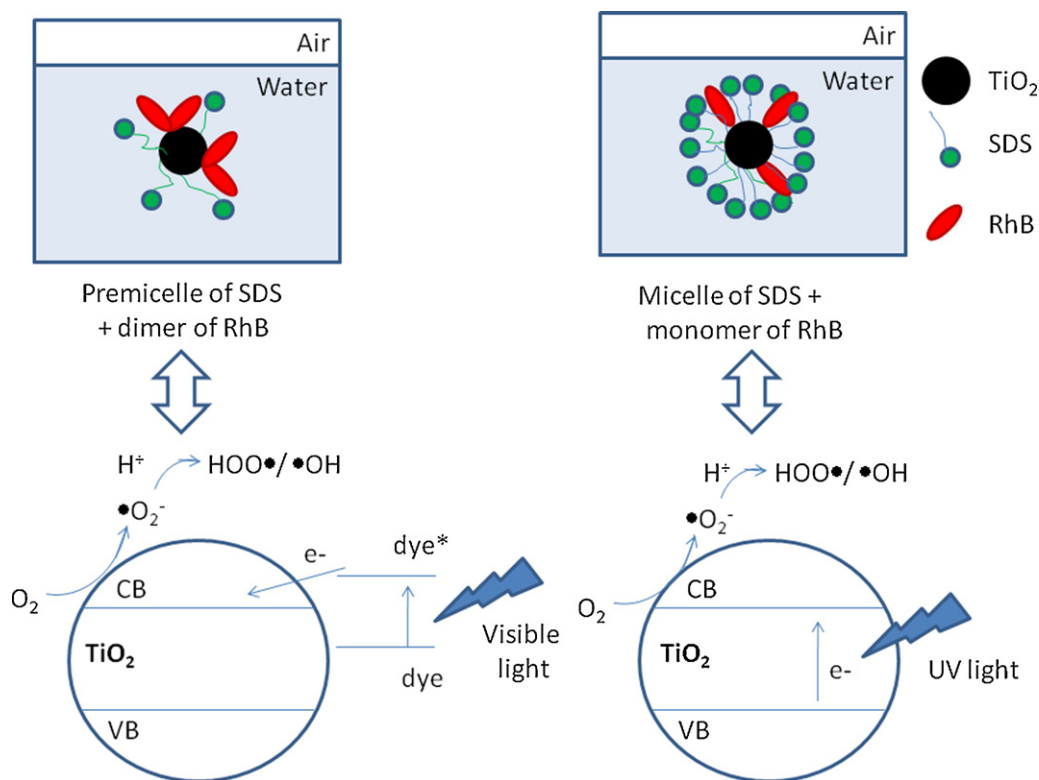


Fig. 10. Comparison between fluorescence at 578 nm of rhodamine + SDS system at dark condition (square) and rhodamine + SDS + TiO<sub>2</sub> after irradiation with visible light during 10 min (circle). The inset depicts the ratio between fluorescence at 578 nm of rhodamine B before (FD) and after (FI) the photodegradation promoted by visible light.



**Fig. 11.** Scheme of interaction of pre-micelles/TiO<sub>2</sub>/RhB (left side) and micelles/TiO<sub>2</sub>/RhB (right side) and corresponding energy band diagram for electron transfer in both cases.

B is obtained at condition of concentration of rhodamine B below 1  $\mu\text{M}$ , as indicated in Fig. 10. In this plot, we compare the fluorescence at 578 nm of rhodamine B+SDS at dark condition with the sample of rhodamine B+SDS+TiO<sub>2</sub> after 10 min of irradiation with visible light.

As we can see, the increase in the amount of rhodamine B in water at dark condition is accomplished by elevation in the level of fluorescence. After 10 min of irradiation with visible light, the fluorescence at 578 nm for all of samples is strongly reduced. By comparison of fluorescence of dye at dark condition (FD) and after illumination with visible light (FI) – inset of Fig. 10, it is possible to conclude that maximal efficiency in the photodegradation is established to the sample with 0.9  $\mu\text{M}$  of rhodamine B. In this case, the reduction in the fluorescence is in order of 30-fold.

Note that amount of titanium dioxide used in all experiments is extremely reduced (0.02 g/L) if compared with values reported in the literature [10–14]. The decrease in the photocatalyst concentration is associated with a strong reduction in the characteristic time for photodegradation, that is established from irradiation in the visible region.

Based on the previous results we can verify that inclusion of titanium dioxide nanopowder in the dye solution promotes strong interaction of pre-micelles/micelles of SDS and dimers/monomers of dyes as schematically described in Fig. 11. The low solubility of titanium dioxide, dimers of dyes and hydrophobic portion of surfactant tends to create a hydrophobic core inducing approximation of dimer and surfactant tail, resulting in a shielding effect from bulk water. This model is based on our results that indicate an optimal condition (pre-micelle concentration) from which sensitization of semiconductor surface is maximized, allowing the use of radiation in the visible region, providing consequently the degradation of rhodamine B in scale of minutes. Above CMC, the dimers concentration are minimized and shielding effect of micelles dominates,

enhancing the fluorescence of system and reducing the photocatalytic activity of semiconductor. An energy band diagram is also introduced below each scheme in Fig. 11, indicating the adequate use of visible light in the presence of pre-micelles and UV light in its absence, promoting the adequate photocatalytic degradation of dye.

#### 4. Conclusions

In summary, we demonstrated that pre-micellization and post-micellization represent two important processes in the interaction between oppositely charged dye/surfactant systems. In the case of rhodamine B/SDS and rhodamine 6G/SDS, the typical concentration of H-aggregates signature can be determined from the measurements of absorption spectrum, quenching in the fluorescence intensity and changes on the fluorescence lifetime.

The strong interaction of dye/semiconductor/surfactant verified at condition of pre-micellar concentration was conveniently applied as photocatalytic system. In this situation, an extremely reduced amount of titanium dioxide (in order of 0.02 g/L) is sufficient to provide the degradation of rhodamine B in scale of few minutes, which represents a fast process if compared with characteristic time reported in the literature.

In this case, the adequate transference of electron from excited dye to the conduction band of semiconductor represents a key role, promoting the creation of reactive species that provides the oxidation of dye with advantage of use of irradiation in the visible region. The maximal photodegradation in a period of 10 min of irradiation with visible light reduces the fluorescence of rhodamine B in 30-fold, in an indication that in this condition the electron transference between excited dye and semiconductor surface is optimized.

## References

- [1] B.E. Polat, S.C. Lin, J.D. Mendenhall, B. VanVeller, R. Langer, D. Blankschtein, Experimental and molecular dynamics investigation into the amphiphilic nature of sulforhodamine B, *J. Phys. Chem. B* 115 (2011) 1394–1402.
- [2] M. Fischer, J. Georges, Use of thermal lens spectrometry for the investigation of dimerization equilibria of rhodamine 6G in water and aqueous micellar solutions, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* 53 (1997) 1419–1430.
- [3] J.W. Park, H. Chung, Aggregation and dissolution of cationic dyes with an anionic surfactant, *Bull. Korean Chem. Soc.* 7 (1986) 113–116.
- [4] M. Bielska, A. Sobczynska, K. Prochaska, Dye–surfactant interaction in aqueous solutions, *Dyes Pigments* 80 (2009) 201–205.
- [5] H.M. Zhang, X.Q. Guo, Y.B. Zhao, D.Y. Wang, J.G. Xu, Study on the dimer–monomer equilibrium of a fluorescent dye and its application in nucleic acids determination, *Anal. Chim. Acta* 361 (1998) 9–17.
- [6] X.Q. Guo, Z.L. Zhang, Y.B. Zhao, D.Y. Wang, J.G. Xu, DNA-dye fluorescence enhancement based on shifting the dimer–monomer equilibrium of fluorescent dye, *Appl. Spectrosc.* 51 (1997) 1002–1007.
- [7] N.C. Maiti, S. Mazumdar, N.J. Periasamy, H-aggregates of porphyrin–surfactant complexes: time-resolved fluorescence and other spectroscopic studies, *J. Phys. Chem. B* 102 (1998) 1528–1538.
- [8] M. Arik, K. Meral, Y. Onganer, Effect of surfactants on the aggregation of pyronin B and pyronin Y in aqueous solution, *J. Lumin.* 129 (2009) 599–604.
- [9] H. Sato, M. Kawasaki, K. Kasatani, Energy-transfer between rhodamine 6G and pinacyanol enhanced with sodium dodecyl-sulfate in the premicellar region – formation of dye-rich induced micelles, *J. Phys. Chem.* 87 (1983) 3759–3769.
- [10] Z. Jing, Y. Song, F. Lu, W. Fei, Y. Mengqiong, L.B. Genxiang, X. Qian, W. Xiang, L. Can, Photocatalytic degradation of rhodamine B on anatase, rutile and brookite TiO<sub>2</sub>, *Chin. J. Catal.* 32 (2011) 983–991.
- [11] T.S. Natarajan, M. Thomas, K. Natarajan, H.C. Bajaj, R.J. Tayade, Study on UV-LED/TiO<sub>2</sub> process for degradation of rhodamine B dye, *Chem. Eng. J.* 169 (2011) 126–134.
- [12] Y.L. Pang, S. Bhatia, A.Z. Abdullah, Process behavior of TiO<sub>2</sub> nanotube-enhanced sonocatalytic degradation of rhodamine B in aqueous solution, *Sep. Purif. Technol.* 77 (2011) 331–338.
- [13] L. Pan, J.-J. Zou, X. Zhang, L. Wang, Water mediated promotion of dye sensitization of TiO<sub>2</sub> under visible light, *J. Am. Chem. Soc.* 133 (2011) 10000–10002.
- [14] M.A. Rauf, M.A. Meetani, S. Hisaindee, An overview on the photocatalytic degradation of azo dyes in the presence of TiO<sub>2</sub> doped with selective transition metals, *Desalination* 276 (2011) 13–27.
- [15] P. Qu, J.C. Zhao, L. Zang, T. Shen, H. Hidaka, Enhancement of the photoinduced electron transfer from cationic dyes to colloidal TiO<sub>2</sub> particles by addition of an anionic surfactant in acidic media, *Colloids. Surf. A: Physicochem. Eng. Aspects* 138 (1998) 39–50.
- [16] E.T. Soares, M.A. Lansarin, C.C. Moro, A study of process variables for the photocatalytic degradation of rhodamine B, *Braz. J. Chem. Eng.* 24 (2007) 29–36.
- [17] G.A. Epling, C. Lin, Photoassisted bleaching of dyes utilizing TiO<sub>2</sub> and visible light, *Chemosphere* 46 (2002) 561–570.
- [18] R. Libanori, T.R. Giraldo, E. Longo, E.R. Leite, C. Ribeiro, Effect of TiO<sub>2</sub> surface modification in rhodamine B photodegradation, *J. Sol–Gel Sci. Technol.* 49 (2009) 95–100.
- [19] D.L. Liao, G.S. Wu, B.Q. Liao, Zeta potential of shape-controlled TiO<sub>2</sub> nanoparticles with surfactants, *Colloids. Surf. A: Physicochem. Eng. Aspects* 348 (2009) 270–275.
- [20] H. Tajalli, A.G. Gilani, M.S. Zakerhamidi, M. Moghadam, Effects of surfactants on the molecular aggregation of rhodamine dyes in aqueous solutions, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* 72 (2009) 697–702.
- [21] C.C. Wang, A.N. Masi, L. Fernandez, On-line micellar-enhanced spectrofluorimetric determination of rhodamine dye in cosmetics, *Talanta* 75 (2008) 135–140.
- [22] P. Pal, H. Zeng, G. Durocher, D. Girard, R. Giasson, L. Blanchard, L. Gaboury, Spectroscopic and photophysical properties of some new rhodamine derivatives in cationic, anionic and neutral micelles, *J. Photochem. Photobiol. A: Chem.* 98 (1996) 65–72.
- [23] E.G.L. Oliveira, J.J. Rodrigues Jr., H.P. de Oliveira, Influence of surfactant on the fast photodegradation of rhodamine B induced by TiO<sub>2</sub> dispersions in aqueous solution, *Chem. Eng. J.* 172 (2011) 96–101.