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Effect of detergents on the fluorescence from CdS-Q clusters prepared using variable excess Cd^{2+} concentrations

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Abstract

The effect of surfactants Triton X-100 (TX-100, neutral), cetyltrimethylammonium chloride (CTAC, cationic) and sodium dodecyl sulfate (SDS, anionic) on the intensity and lifetime of several fluorescence bands of Q-CdS clusters, which were prepared with variable excess Cd^{2+} concentration, was studied. The fluorescence intensity of the several clusters of Q-CdS is strongly increased by adding a little excess of Cd^{2+}. When more Cd^{2+} is added, a moderate increment of fluorescence intensity is observed and then, at higher excess Cd^{2+} concentrations, the fluorescence intensity remains nearly constant. The effect of the detergents on the fluorescence was found to depend on the excess of Cd^{2+} added to the cluster.

The quenching of the fluorescence from Q-CdS by CTAC and SDS render linear Stern–Volmer plots. The corresponding values of the Stern–Volmer constants (K_{sv}) are lowered when the excess cadmium concentration is increased.

For TX-100 the Stern–Volmer plots were non-linear for all the clusters with all the excess cadmium concentrations used. Two different zones, corresponding to different responses of the system in two concentration ranges are observed: the first one at TX-100 concentrations lower (zone I) and the second one at TX-100 concentrations higher (zone II), than 2×10^{-4} M, which is equal to the concentration of the polyphosphate used to stabilize the colloid. According to the experimental results, we believe that TX-100 quenching, for all the CdS clusters' fluorescence bands in the range of final cadmium concentration used for the experiments, is a polyphosphate-assisted process in zone I, while in zone II this assistence is not evident.

The fluorescence decay curves were also determined in all the cases. They were not altered, for any of the clusters, by the addition of TX-100 and SDS, pointing to static quenching processes in both cases. On the other side, the fluorescence lifetimes were shortened by the addition of CTAC, which is indicative that, at least in part, the quenching process is dynamic for this cationic detergent. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Q-CdS clusters; Triton X-100; CTAC; SDS

1. Introduction

The physicochemical processes ocurring at the interface between colloidal semiconductor Q clusters and liquid solution are of remarkable importance for both fundamental knowledge [1–5] and practical applications [6–10]. The properties of these particles are strongly dependent on the size of the clusters, due to quantum confinement effects [11,12] and on the conditioning of the clusters' surface [13,14], because of the relevance acquired by surface atoms in the nanometer size range when the surface/volume ratio increases greatly by decreasing the dimensions of the colloidal particles.

The semiconductor Q clusters can be prepared following several procedures, generally using a macromolecular stabilizer [15]. Sodium polyphosphate is one of them and it was previously used by Henglein and coworkers in early studies as a stabilizer to obtain Q-CdS particles in water solutions at several pH values. The fluorescence from these clusters can be activated by the addition of excess cadmium ion [16].

Experiences carried out with Q clusters of several semiconductors in the femtosecond time domain show that the charge carriers electron (e^-) and hole (h^+), generated by the absorption of a photon, migrate to the particle surface and are trapped into surface trap states in less than 1 ps [17–20]. The subsequent chemical reactions promoted by these semiconductor particles involve the transfer of some or both charge carriers in the interface to some species in solution, which is generally adsorbed onto surface sites [21,22]. On the other

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Table 1
Experimental conditions for the preparation of the clusters

Band (nm)	$[CdSO_4]_i$	$[(NaPO_3)_6]$	pH_i	$[H_2S]/[Cd^{2+}]_i$	τ_1	τ_2	τ_3	τ_4	$(Rel)_1$ (%)	$(Rel)_2$ (%)	$(Rel)_3$ (%)	$(Rel)_4$ (%)
460	4×10^{-4}	2×10^{-4}	8.3	1/2	6.4	66	241	553	2	15.6	51.8	30.6
481	2×10^{-4}	2×10^{-4}	8.7	Excess H_2S	8.2	53	170	589	2.7	37.7	45.1	14.5
559	2×10^{-4}	2×10^{-4}	10.5	1/1	4	37	172	765	5	19.8	47.7	27.5

side, many experiences are being carried out to sensitize colloidal semiconductors with dye molecules which absorb in the visible zone of the solar spectrum. These studies are motivated by the possibility of using these systems for solar energy conversion devices and also for the photodegradation of water-pollutant dyes. A charge-transfer process at the interface occurs here too, since the excited dye molecule transfers an electron to the conduction band of a semiconductor cluster [23–25].

Since water is the working solvent in many of the cases photoreactions involving semiconductor Q clusters and water-soluble ions or polar molecules are predominantly studied [26,27]. There is also the chance of using surfactants to incorporate to solution some species that are not water-soluble [28] or to enhance the interaction between the semiconductor particles and solutes that are not readily adsorbed onto the clusters' surface in the working conditions [29]. The study of the effect of detergents on these systems is then of remarkable importance, since they can alter the behavior of the charge carriers at the surface traps [30] and eventually they could undergo degradation following a charge-transfer process [31,32].

In a previous paper, we have reported the effect produced by tetraalkylammonium salts (R_4NCl) as analogue of the cationic surfactant cetyltrimethylammonium chloride (CTAC) and by alkylsulfate salts ($NaRSO_4$) as analogue of the anionic surfactant sodium dodecyl sulfate (SDS), on Q-CdS clusters that exhibit an isolated, either excitonic or trapped fluorescence band [33]. In this paper, we present a study of the effect on the fluorescence bands from Q-CdS, of several detergents: CTAC, SDS and Triton X-100 (TX-100, a non-ionic surfactant). The Q-CdS clusters were prepared using sodium polyphosphate as a stabilizer and the excess cadmium ion concentration was varied within a range.

2. Experimental details

2.1. Chemicals

Sodium polyphosphate (Merck, extra pure), sodium sulfide (Merck, p.a.), cadmium sulfate (Mallinckrodt, p.a.) and Triton X-100 (SigmaUltra) were used without further purification. Cetyltrimethylammonium chloride was a gift from Lever y Asociados, Argentina, and it was purified as previously described [34]. Sodium dodecyl sulfate (BDH) was washed with diethyl ether and recrystallized from ethanol.

2.2. Preparation of Q-CdS colloids

An aqueous solution of $CdSO_4$ containing sodium polyphosphate as stabilizer (initial concentrations for each cluster are given in Table 1) was de-oxigenated by nitrogen bubling for 30 min. Then a given quantity of $H_2S_{(g)}$, depending of the clusters to be prepared (see Table 1), was added while keeping the vessel hermetically closed. In nearly 2 min, the solution became pale yellow and then, after 10 min, the excess $H_2S_{(g)}$ was eliminated by nitrogen purging and pH was finally adjusted to its final value of pH=10.5. In this way, samples with single emission band with maximum wavelength at 460 nm (broad band), 481 nm. (excitonic band) or 559 nm (traps band) were prepared. These clusters emitted a very weak fluorescence that was greatly enhanced by the addition of excess Cd^{2+}.

Several solutions were prepared for each cluster, adding various excess Cd^{2+} concentrations to give several final cadmium concentrations ($[Cd^{2+}]_F$). The fluorescence intensity is strongly increased at low $[Cd^{2+}]_F$ and then, at $[Cd^{+2}]_F$ higher than 8×10^{-4} M, it tends to stabilize and form a plateau. This behavior is followed in all the cases and it is shown in Fig. 1 for the case of the excitonic band. The fluorescence intensity was nearly 20-fold increased, in the case of the 559 nm band and 200-fold increased in the 460 and 481 nm bands by this activation procedure. The addition of excess Cd^{2+} causes a blue shift fluorescence maximum of less than 20 nm in the case of the 559 nm band, less than 10 nm in the case of the 460 nm band and no shift was observed for the 481 nm band.

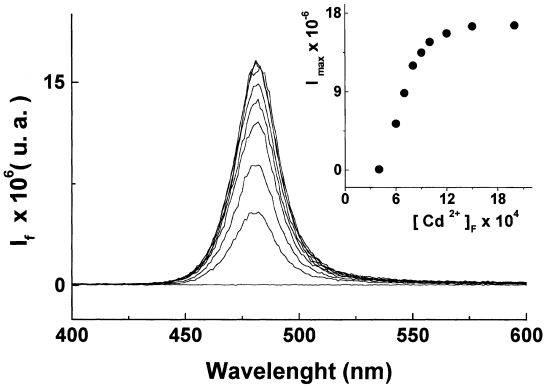

Fig. 1. Fluorescence spectra for the excitonic band with several excess cadmium concentrations. Fluorescence intensity at λ=481 nm (inset) as a function of final cadmium concentration.

A similar experiment was carried out on some of the samples but, instead of adding excess Cd^{2+} to activate the fluorescence with the pH set at 10.5, either NaCl, CTAC or TX-100 was added. Although both, CTAC and NaCl produced initially a linear increase of the clusters' fluorescence, this was of little significance when compared to that observed by the addition of excess Cd^{2+}. No activation of the fluorescence was detected by the addition of TX-100.

2.3. Quenching procedures

The quenching experiments with the several samples showing isolated fluorescence bands were carried out by adding a concentrated CTAC, SDS or TX-100 in Q-CdS solution to the corresponding Q-CdS clusters solution prepared with a given final cadmium concentration, which was constant for each quenching experiment. Quenching studies were done, for all the clusters and all the final cadmium concentrations used, at pH=10.5.

2.4. Apparatus

UV–Vis absorption measurements were performed with a Hewlett Packard HP 8452 A Diode Array Spectrophotometer. Stationary fluorescence experiments were carried out with an Spex Fluoromax spectrofluorometer. Fluorescence lifetime were measured with the time correlated single photon counting technique on an Edinburgh Instruments 0B900 equipment.

3. Results and discussion

The excitation and emission spectra for the isolated fluorescence bands from the several clusters are shown in Fig. 2. The weak fluorescence initially obtained was then greatly enhanced by the addition of excess Cd^{2+}, as it is shown in Fig. 1 for the case of the excitonic band with maximum emission wavelength at 481 nm. The corresponding fluorescence decay curves, which have different profiles for each one of the clusters, are shown in Fig. 3. It is clearly seen that in all the cases the decay does not follow a single exponential law. A fitting using four exponential terms renders a reasonable accord between the experimental data and the decay function. The four decay times and their corresponding weights are given in Table 1.

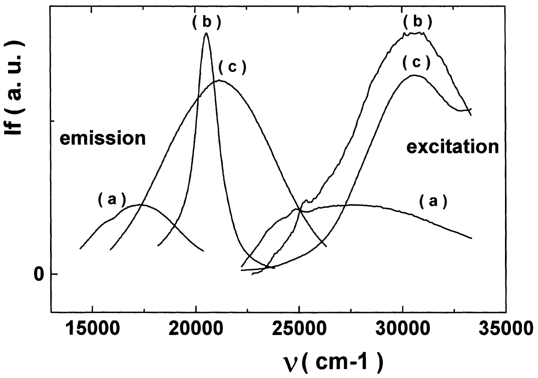

Fig. 2. Fluorescence excitation and emission spectra of the clusters: (a) traps fluorescence band (λ_{max}=559 nm); (b) excitonic band (λ_{max}=481 nm) and (c) broad fluorescence band (λ_{max}=460 nm).

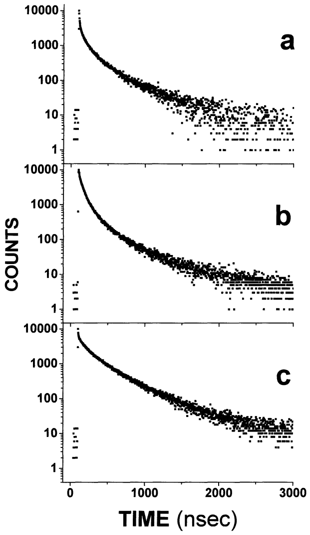

Fig. 3. Fluorescence decay profiles for: (a) traps fluorescence band (λ_{max}=559 nm); (b) excitonic band (λ_{max}=481 nm) and (c) broad fluorescence band (λ_{max}=460 nm).

We have studied the effect of the surfactants TX-100 (neutral), CTAC (cationic) and SDS (anionic) on the fluorescence from the above mentioned clusters of Q-CdS, in aqueous solutions with diverse concentrations of excess Cd^{2+}. The results obtained for each of the detergents are detailed below.

3.1. Triton X-100

As stated in Section 2, TX-100 does not produce any activation effect on the clusters' fluorescence. This is probably because TX-100 is a neutral detergent and the activation of fluorescence is effectuated by cations.

The Stern–Volmer plots were not linear for any of the clusters and for all the excess cadmium concentrations used in the experiments. As it can be seen in Fig. 4 for the case of the excitonic band, two different zones, corresponding to different responses of the system in two concentration ranges are observed: the first one at TX-100 concentration lower (zone I) and the second one at TX-100 concentration higher (zone II), than 2×10^{-4} M, which is equal to the concentration of the polyphosphate used to stabilize the colloid in all cases.

On the other hand, in order to understand the reasons for the existence of two quenching zones, we have carried out quenching experiments with clusters prepared using polyphosphate concentrations from 2×10^{-4} to 12×10^{-4} M, with the same initial $[Cd^{2+}]_i$ (2×10^{-4} M) and final $[Cd^{2+}]_F$ (8×10^{-4} M) in all the cases. The Stern–Volmer plots, shown

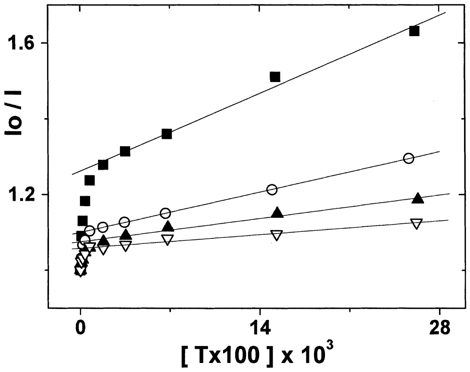

Fig. 4. Stern–Volmer plots for the quenching by TX-100 of excitonic band (λ_{max}=481 nm) prepared with several excess cadmium concentrations. $[Cd^{2+}]_F$: 4×10^{-4} M (■); 6×10^{-4} M (○); 8×10^{-4} M (▲) and 1.2×10^{-3} M(▽).

in Fig. 5, are nearly the same for polyphosphate concentrations of 4×10^{-4}–12×10^{-4} M, but the plot is different for polyphosphate concentration of 2×10^{-4} M. In the latter case, the quenching effect for a given TX-100 concentration is lower than that obtained with polyphosphate concentrations of 4×10^{-4}–12×10^{-4} M, except for high TX-100 concentrations, for which the quenching effect tends to reach a constant level for all the polyphosphate concentrations.

It is known that polyphosphate regulates the growing of CdS clusters, stabilizing them at a certain size and that the excess cadmium ion generates a given number of fluorescent sites on the clusters' surface (Fig. 1). The plots in Fig. 5 show that the fraction of the total fluorescence that is quenched at high TX-100 concentrations is nearly the same for all the polyphosphate concentrations, which means that the total number of fluorescent sites that are quenched is the same in all the cases. The difference between the clusters prepared with the several polyphosphate concentration is that for polyphosphate concentrations of 4×10^{-4}–12×10^{-4} M the total quenching fraction is almost attained in zone I, while for polyphosphate concentration of 2×10^{-4} M, the quenching fraction attained in zone I is much lower than the maximum and the remaining fluorescence fraction is quenched in zone II.

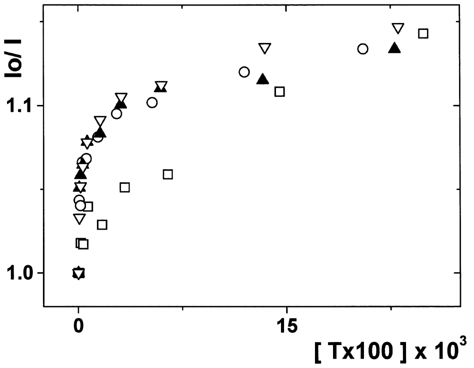

Fig. 5. Stern–Volmer plots for the quenching by TX-100 of the traps band (λ_{max}=559 nm) prepared with several polyphosphate concentrations. [PP]: 2×10^{-4} M (□); 4×10^{-4} M (○); 8×10^{-4} M (▲) and 1.2×10^{-3} M(▽). All the clusters prepared with $[Cd^{2+}]_F$=8×10^{-4} M.

According to the experimental results we believe that TX-100 quenching, for all the CdS clusters' fluorescence bands in the range of final cadmium concentration used for the experiments, is a polyphosphate-assisted process in zone I, while in zone II, this assistance is not evident. Furthermore, there is a polyphosphate concentration above which the maximum quenching assistence effect is obtained for some given experimental conditions of clusters formation which, for the case of Fig. 5 (excitonic band) appears to be 4×10^{-4} M.

We have also determined the fluorescence decay profiles at several TX-100 concentrations. No significative difference is observed between the decay curves, therefore, we conclude that the quenching is mainly static.

These experimental observations can be explained through a mechanistic scheme which is similar to that presented by us to explain the effect of tetraalkylammonium salts on the fluorescence of Q-CdS clusters [33], with Eq. (1) represents the adsorption of the TX-100 on the Q-CdS particles, assisted by polyphosphate (PP), that renders the static quenching observed in zone I:

$$\text{TX-100} + (\text{CdS})_{\text{ACT}}(\text{PP}) \overset{K_{\text{I}}}{\leftrightarrow} (\text{CdS})_{\text{ACT}}(\text{PP}) - \text{TX-100} \quad (\equiv P) \tag{1}$$

where $(\text{CdS})_{\text{ACT}}(\text{PP})$ represents the cluster formed in the presence of polyphosphate and activated with excess of Cd^{2+}. In order to simplify the notation, the cluster with TX-100 adsorbed $(\text{CdS})_{\text{ACT}}(\text{PP})-\text{TX-100}$, is indicated as P.

Eq. (2) represents the excitation of activated Q-CdS to give an electron-hole pair (h^+, e^-).

$$(\text{Cds})_{\text{ACT}}\,(\text{PP}) + h\nu \xrightarrow{I_a} (h^+, e^-) \tag{2}$$

A non-radiative process:

$$(h^+, e^-) \xrightarrow{k_d} (\text{CdS})_{\text{ACT}}(\text{PP}) \tag{3}$$

A radiative process:

$$(h^+, e^-) \xrightarrow{k_f} (\text{CdS})_{\text{ACT}}(\text{PP}) + h\nu \tag{4}$$

Finally, the adsorption of the TX-100 to the clusters' surface, at quencher concentration higher than polyphosphate concentration (zone II), rendering the static quenching observed in this concentration zone:

$$P + (\text{TX-100})_{\text{eq}} \overset{K_{\text{II}}}{\leftrightarrow} P - (\text{TX-100}) \tag{5}$$

where K_{I} and K_{II} represents the equilibrium constant for the association of the TX-100 to the clusters, with or without the assistance of polyphosphate, respectively. $(\text{TX-100})_{\text{eq}}$ represents the free TX-100 in solution, after Eq. (1) has reached a saturation.

Table 2
Stern–Volmer constants for the detergents and the bands with the several $[Cd^{2+}]_F$ used

Band	λ_{max} (nm)	Cd^{2+} (M)	CTAC	TX-100		SDS
				K_I[a]	K_{II}	
Broad	460	4×10^{-4}	39.9		3.9	7.0
Broad	460	6×10^{-4}	29.9	200	3.45	5.3
Broad	460	8×10^{-4}	26.6		2.2	4.65
Broad	460	12×10^{-4}	10.5		1.2	3.3
Excitonic	481	4×10^{-4}	79		14.3	20.3
Excitonic	481	6×10^{-4}	34.8	300	7.6	11.6
Excitonic	481	8×10^{-4}	29.2		4.1	10.5
Excitonic	481	12×10^{-4}	14.8		2.4	4.4
Traps	559	4×10^{-4}	31(57)		2.2	6.6
Traps	559	6×10^{-4}	19(29)	200	2.6	4.2
Traps	559	8×10^{-4}	12(15)		1.7	4.1
Traps	559	12×10^{-4}	9(9)		2.0	3.6

[a] Approximate value around which fluctuates K_I for the several excess cadmium concentrations used in the experiments.

The dependence of the fluorescence intensity upon quencher concentration is easily derived by consideration of the constants K_I or K_{II}, assuming that Eq. (5) occurs under conditions in which Eq. (1) reaches a saturation. The ratio of fluorescence intensities in the absence and the presence of quencher is then given, for both concentration zones, by the Stern–Volmer expression for static quenching.

$$\frac{I_0}{I} = 1 + K[\text{TX-100}] \tag{6}$$

Where K represents K_I or K_{II}. The values of these constants can be obtained from the slopes corresponding to zone I and zone II, respectively, in plots like the presented in Fig. 4. The values for all the cases studied are given in Table 2.

The values of K_I obtained from the plots for a given fluorescence band were nearly the same for all the final cadmium concentrations used. The reason for this may be that polyphosphate concentration is the same in all the samples. On the other side, the slope in zone II (K_{II}) for a given fluorescence band is lowered in all the cases when cadmium concentration is increased, as it is shown in Table 2 and Fig. 4.

3.2. CTAC

Since the sodium polyphosphate concentration used to stabilize the clusters was 2×10^{-4} M and the critical micelle concentration (CMC) for the cationic surfactant CTAC is 1.4×10^{-3} M, the experiments in this case were carried out with CTAC concentration higher than the CMC, to avoid precipitation when the detergent concentration equalizes the polyelectrolite concentration.

In the experiments that were carried out with constant final cadmium concentration lower than 8×10^{-4} M, the fluorescence was at first increased by the addition of CTAC and then, when more CTAC was added, the fluorescence was quenched (Fig. 6a). The initial rise of fluorescence is probably due to an activation effect produced by the cetyltrimethylammonium cation (CTA^+), as it was mentioned in Section 2. This effect was not observed when the experiments were carried out in solutions with constant final cadmium concentration higher than 8×10^{-4} M (Fig. 6b), because the activation effect of excess Cd^{2+} was nearly completed in this case. This is in accord with the observed dependence of the clusters' fluorescence intensity with the final cadmium concentration shown in Fig. 1 (inset), where it is evidenced a linear rise with cadmium concentrations lower than 8×10^{-4} M and a plateau with cadmium concentrations higher than this value.

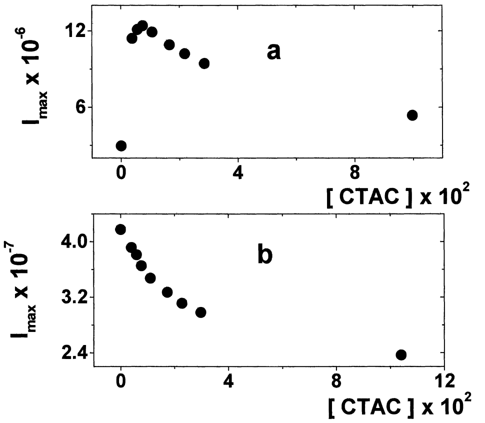

Fig. 6. Fluorescence intensity at λ=481 nm for the excitonic band, as a function of CTAC concentration: (a) $[Cd^{2+}]_F=4\times10^{-4}$ M and (b) $[Cd^{2+}]_F=1.2\times10^{-3}$ M.

Stern–Volmer plots were linear for all the final cadmium concentrations used in the experiments and for all the fluorescence bands, as it is shown in Fig. 7 for the quenching of trapped band. It is important to indicate that, for clusters with final cadmium concentration lower than 8×10^{-4} M, the Stern–Volmer plots were done considering as initial fluorescence intensity (I_0) that corresponding to the maximum in

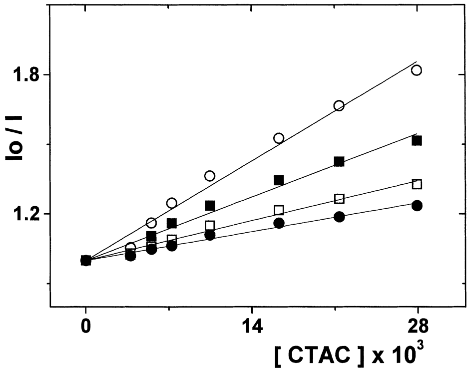

Fig. 7. Stern–Volmer plots for the quenching by CTAC of the traps band (λ_{max}=559 nm) prepared with several excess cadmium concentrations. $[Cd^{2+}]_F$: 4×10^{-4} M (○); 6×10^{-4} M (■); 8×10^{-4} M (□) and 1.2×10^{-3} M (●).

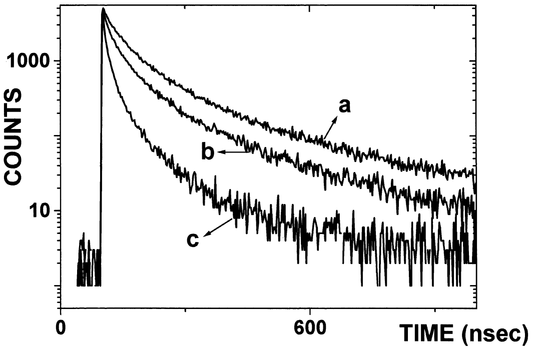

Fig. 8. Fluorescence decay profiles for clusters of the excitonic band (λ_{max}=481 nm) at several CTAC concentrations: (a) 0 M; (b) 2.94×10^{-3} M and (c) 1.03×10^{-1} M.

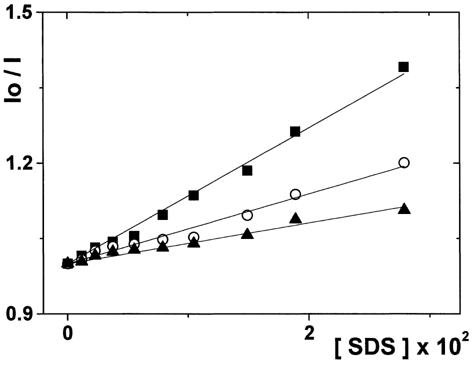

Fig. 9. Stern–Volmer plots for the quenching by SDS of the excitonic band (λ_{max}=481 nm) prepared with several excess cadmium concentrations. $[Cd^{2+}]_F$: 6×10^{-4} M (■); 8×10^{-4} M (○) and 1.2×10^{-3} M (▲).

Fig. 6a. The values of K_{sv}, obtained from the slopes of the straight lines in the plot, are given in Table 2. It must to be pointed that the activation of fluorescence by the CTA^+ cation does not protect the cluster surface as efficiently as Cd^{2+} cation does, since the subsequent quenching is more effective than that obtained with clusters which were activated only with cadmium. The difference is evidenced in Fig. 7, where the slopes are the highest when final cadmium concentrations are the lowest and also in Table 2, where the highest K_{sv} values are seen to be obtained for $[Cd^{2+}]$ lower than 8×10^{-4} M.

Time–fluorescence decay curves were also monitored for all the clusters, as a function of CTAC concentration, As can be observed in Fig. 8 for the case of excitonic band, fluorescence lifetimes are shortened when CTAC concentration is increased, suggesting that this quenching process is, at least in part, a dynamic one.

These experimental results can be explained through a mechanistic scheme similar to that presented for the case of quenching by TX-100, but considering that, in the experiments carried out with CTAC, the concentration of this surfactant was higher than the polyphosphate concentration, above the concentration range corresponding to zone I. In this mechanism, Eq. (1) represents the adsorption of the surfactant, assisted by polyphosphate, which could produce quenching of the fluorescence. However, since CTA^+ can activate the clusters' fluorescence, both effects could be acting in opposition, so that in the plots the existence of zone I, like that observed with TX-100, is not evident.

Furthermore, since CTAC changes the fluorescence decay profiles for all the Q-CdS clusters, we believe that the CTA^+ adsorbed on the clusters' surface through an adsorption equilibrium similar to that in Eq. (5), produces then a dynamic quenching process:

$$(h^+, e^-) + (CTA^+)_{ads} \overset{k_q}{\rightarrow} \text{dynamic quenching} \qquad (7)$$

A kinetic analysis renders a Stern–Volmer type equation, assuming that the concentration of $(CTA^+)_{ads}$ is proportional to the analytical CTAC concentration. The corresponding Stern–Volmer constants can be obtained from the slopes of the straight lines like those in Fig. 7 and they are given in Table 2.

3.3. SDS

As in the case of CTAC, an increase of the fluorescence is observed after the initial addings and a quenching effect with subsequent addition of SDS when the constant final cadmium concentration in the solution is lower than 8×10^{-4} M. This is possibly due to the action of sodium cation. At $[Cd^{2+}]_F \geq 8\times10^{-4}$ M, only the quenching effect is observed.

The quenching effect observed for all the fluorescence bands renders linear Stern–Volmer plots for all the final cadmium concentrations (constant) used, as it is shown in Fig. 9 for the excitonic band. The Stern–Volmer plots for clusters with final cadmium concentration lower than 8×10^{-4} M were taken, similarly to the CTAC experiences, considering as initial fluorescence intensity (I_0) that corresponding to the maximum of the fluorescence intensity versus concentration curve and plotted for the SDS concentration range above the corresponding to the that maximum. The Stern–Volmer constants, K_{sv}, obtained from the slopes in the plots are given in Table 2.

In summary, SDS follows the trend reported previously by us for sodium alkyl sulfates [33], suggesting that quenching is produced in this case by sodium cation.

4. Conclusions

Q-CdS clusters fluorescence is activated by excess Cd^{2+} cations. This is probably done through the formation of energetically stable surface traps, where the charge carriers can be stabilized. The fluorescence activation can be also attained with others cations, as it was reported by us in a previous paper for Na^+ [33] and it is confirmed by the experimental results presented herein for Na^+ from SDS and

CTA^+ from CTAC. In any case, the stabilization of charge carriers obtained by them is much less effective than that obtained by cadmium cations.

The experimental results show that, for any of the detergents and for all the clusters, the quenching effect is lowered by increasing the excess cadmium concentration. The reason for this can be that when the excess [Cd^{2+}] is increased, the number of traps generated on the surface is also increased, therefore the probability of an encounter of a quencher molecule with the electrons decreases for a given quencher concentration.

The values of Stern–Volmer constants quoted in Table 2 show that, for any of the surfactants used and for a given final cadmium concentration, the quenching is more effective in the case of the excitonic band. This trend is noteworthier for the cations, that is CTA^+ from CTAC and Na^+ from SDS. As described in Section 2 (Table 1); the clusters emitting the excitonic fluorescence band were prepared with excess H_2S. Although the excess H_2S was eliminated by nitrogen bubbling, before the addition of Cd^{2+} to activate the fluorescence, we believe that the quenching is more effective for this band probably because of some excess of sulfide anion on the clusters' surface, which can facilitate the access of the quencher, especially, if it is cationic.

With reference to the effect of each of the detergents, SDS follows the trend reported previously by us for sodium alkyl sulfates [33], suggesting that quenching is produced in this case by sodium cation. The quenching by TX-100 presents two concentration zones, we believe that the quenching in zone I is a polyphosphate-assisted process while in zone II this assistence is not evident CTAC presents an important difference with respect to SDS and TX-100: it modifies the fluorescence decay profiles for all the clusters, so that lifetimes are shortened when CTAC concentration is increased, suggesting that at least in part, the quenching process is dynamic Since CTA^+ activates the fluorescence from the clusters, we believe that CTA^+ can be modifying some surface traps or even creating new surface traps, This implies that CTA^+ interacts with the electrons and besides, since the quenching is dynamic, the interaction must be with electrons that are moving between traps.

According to the results obtained on the fluorescence quenching effect by any of the detergents on any of the clusters, which ranges from 10 to 40% depending on the excess cadmium concentration that was used, we believe that these surfactants can be used to solubilize organic substances in order to enhance its interaction with the clusters' surface, since the effect produced by these detergents on the fluorescence bands is meaningless and can be minimized by working at high excess cadmium concentrations.

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