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Photochemistry of a cyanine dye in reversed micelles

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Abstract

The effect of microenvironment on the existing state and spectral properties of a cyanine dye in different systems were investigated. Due to the space limitation and the polarity evolution of the water cell of reversed micelles, the optical behavior of the dye in reversed micelles was very different from in water and alcohol. The effect of surfactants with different charge on the interaction of a cyanine dye with AgCl nanoparticles in reversed micelles were also researched. The adsorption state of the dye on AgCl nanoparticles in reversed micelles was discussed. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Reversed micelles; Cyanine dye; AgCl nanoparticles

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1. Introduction

The formation of silver halide (AgX) nanoparticles in reversed micelles containing ionic or non-ionic surfactants have been reported [1–3]. However, it is difficult to use practically nano-sized particles of silver halide in photographic processes because of the poor photosensitivity and stability. Sensitizing dyes are used to extend the spectral response of AgX particles. Our group has studied the action of several dyes with Ag colloidal particles and AgCl nanoparticles in different systems, as well the effects of microenvironment on these events [4–7].

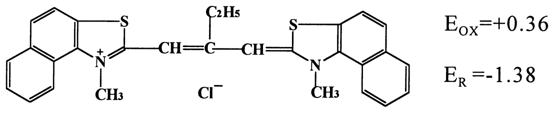
As a kind of sensitive dye, the interaction of cyanine dyes with AgCl nanoparticles is an important subject to be studied. This work will discuss the effects of the microenvironment of reversed micelles on the optical properties of a cyanine dye and explore the interaction between the cyanine dye and AgCl nanoparticles in reversed micelles.

2. Experiment

All chemicals were analytical grade reagents and used as received. AOT, bis(2-ethylhexyl)sulphosuecinate sodium salt and Triton X-45, octyl-phenoxy-polyethoxyethanol were obtained from Aldrich and Sigma Company, respectively.

The nanoparticles of silver chloride were prepared by mixing two individual reversed micelles both containing a surfactant solvent and an aqueous solution of either silver nitrate (0.25 mol dm^{-3}) or potassium chloride (excess 10% relatively to silver nitrate). The molar ratio of $[H_2O]/[surfactant] = \omega$ was controlled in 5 or 10 for the preparation of AgCl particles. The concentration of the surfactants was 0.2 mol dm^{-3}. The average diameter of AgCl particles was about 11.2 nm in the AOT system ($\omega = 10$) and 14.2 nm in the Tx-45 system ($\omega = 5$) determined by a Hitachi H-9000 high-resolution transmission electron microscope (TEM). The particles seemed spherical under TEM (see Fig. 1). The concentration of AgCl particles thus prepared was 4.3×10^{-3} mol dm^{-3}.

The structure of the cyanine dye used in the present work is shown below:



Dye I

The Dye I was dissolved in the aqueous solution of ethanol (50%), the concentration of the stem solution was 1×10^{-3} mol dm^{-3}. By measurements, the concentration of the Dye I was 1×10^{-5} mol dm^{-3}. The absorption spectra were measured with a Hitachi U-2001 spectrophotometer. The fluorescence spectra were measured with a Hitachi MPE-4 fluorescence spectrophotometer.

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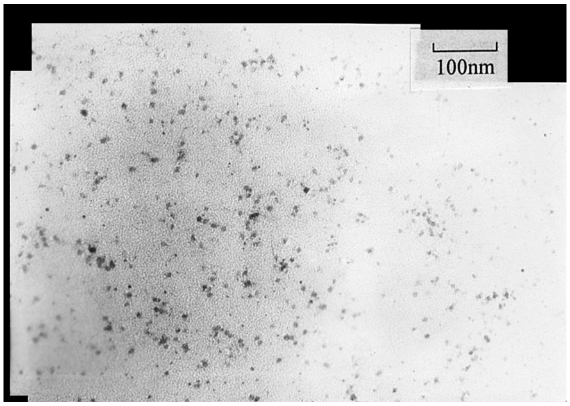

Fig. 1. The TEM photograph of AgCl nanoparticles in AOT reversed micelles The average diameter of AgCl particles was about 11.2 nm.

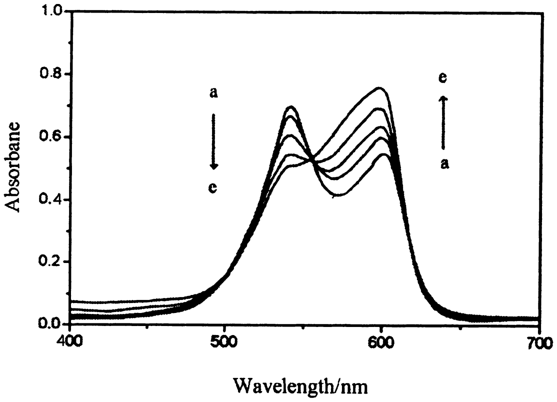

Fig. 3. The absorption spectra of the Dye I in AOT reversed micelles with changing $\omega = 1.4$(a), 2.9(b), 4.4(c), 6.4(d), 11.4(e).

3. Results and discussion

Fig. 2 shows the absorption of Dye I in the water/ethanol binary mixtures. The Dye I exhibited two absorption peaks in pure water solution located at 512 nm(strong) and 576 nm (weak). As increasing the content of ethanol, the peak at 512 nm showed red shifts and became weaker. Simultaneously, the peak at 576 nm became much stronger. When the content of ethanol was more than 40%, the peak at 512 nm became a small shoulder of the peak at 576 nm. The peaks at 512 nm and 576 nm correspond to H-aggregate state and monomer state of the dye, respectively, because the Dye I in pure water exists principally in the H-aggregate state and monomolecular state in ethanol [8]. The fluorescence of the Dye I in water and ethanol was so weak that they can be neglected.

As a comparison, the absorption spectra of the pure Dye I in reversed micelles were followed. As shown in Fig. 3, in AOT reversed micelles two absorption peaks at 542 nm and 598 nm for the Dye I were observed. The positions of the peaks are different from those in the aqueous solution. And as increasing ω from 1.4 to 11.4, the peak at 542 nm decreased and the peak at 598 nm increased. As noted in our previous work [7], there may be only one dye molecule in each water pool of reversed micelles. The probability that two dye molecules are contained in one water pool was very low, ca. 10^{-5} [7]. Therefore, the peaks at 542 and 598 nm could not be ascribed to the H-and J-aggregate formation as in water or ethanol.

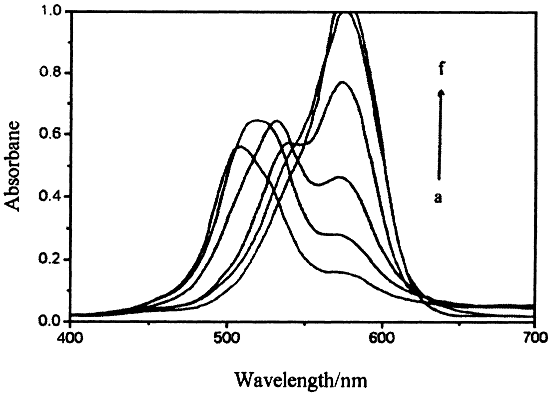

Fig. 2. The absorption spectra of the Dye I in water and alcohol. The content of alcohol(vol%): (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 100.

The fluorescence of the Dye I in the reversed micelles with different ω value was shown in Fig. 4, for $\lambda_{ex} = 595$ nm. As seen in Fig. 4, there was only one clear emission peak at 625 nm with a shoulder peak at a long wavelength. The weaker emission at 625 nm can be obtained, if the dye was excited at 535 nm. It can be concluded, therefore, that the dye in the reversed micelles existed in the molecular state absorbs light at 598 and 542 nm, and emits fluorescence at 625 nm.

As seen from the structure formula, the dye molecule has two plane parts linked by a methine chain. The molecule of the Dye I in ethanol solution extends freely, and the two planar parts should be conjugated through the hydrocarbon bridge. In this state, the whole molecule might be coplanar,

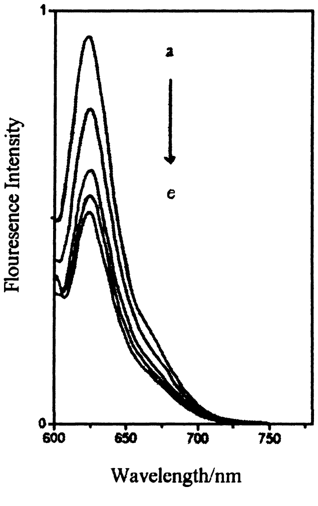

Fig. 4. The fluorescence of the Dye I in AOT reversed micelles with different ω. The conditions are the same as in Fig. 3.

and the π-electron is delocalized. When the dye molecule is pulled by an outside force, for example, a compressing force of the surfactant membrane of AOT, the methine chain will twist, the coplanarity of the molecule be broken, and the π-electrons be localized. Thus, there would be two kinds of monomolecular states for the Dye I in the reversed micelles, M_1 state corresponds to the coplanar molecule and M_2 state corresponds to the twisted molecule. M_1 state absorbs the light at 598 nm and M_2 state absorbs the light at 542 nm. The absorption peak of the M_1 state shows the red shift in comparison with that in alcohol solution owing to the microenvironment effects of the water pool of reversed micelles [7]. The compression force bigger is, the more is M_2 state. Therefore, there would be a balance between M_1 and M_2.

It has been carefully studied that the radius of the water pool for reversed micelles changes with the ω value [9]. The microenvironment change of water pools with ω may result in the evolution of absorption and fluorescence spectra of a molecule in the water pool. Duveneck et al. [10] found, if a molecule with low fluorescence efficiency was put into the cyclodextrin, the fluorescence efficiency became much higher. Enhancement of the rigidity of the fluorescent molecule could raise its fluorescence efficiency [11,12]. In the AOT reversed micelles, the state of the Dye I must be affected by the surfactant properties. With decreasing the radii of water pools, the molecular rigidity of M_1 state increased, and radiationless transition decreased, as a result, the quantum yield of the fluorescence increased markedly to compare with that in water or alcohol. All these factors make the Dye I in reversed micelles emit strong fluorescent as shown in Fig. 4.

When the ω value was small enough, with small radii of the water pool, the dye molecule in the water pool was compressed by the surfactant membrane and twisted. Thus, the planarity of the dye molecule was broken, the positive charge could not be in resonance between the two N atoms of the dye any more, and then the conjugated system was broken. Here, M_1 state changed to M_2 state. In the M_2 state the dye does not emit fluorescence. From Fig. 3 it can be seen that the absorption spectra of M_2 increased with decreasing ω. If the ω value is large, the water pool in the reversed micelles became larger, which is advantageous to keeping the Dye I in M_1 state, but the rigidity of the dye molecule became lower too. In this case, the molecule can move easily, therefore, radiationless transition increased, then fluorescence efficiency decreased. Thus, when the ω value became bigger, the absorption of M_2 state of the Dye I became weaker, the absorption of M_1 of the Dye I became stronger, but the fluorescence became weaker. This is identical with the result of our experiments (Figs. 3 and 4).

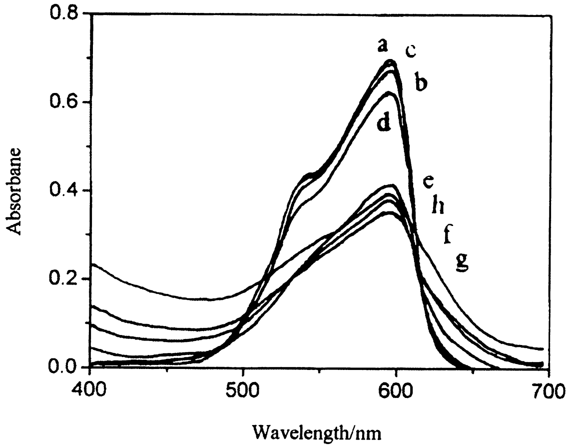

Fig. 5. The absorption spectra of the Dye I in AOT reversed micelles in the presence of AgCl nanoparticles. $[AgCl]/\times 10^{-4}\,mol\,dm^{-3} = 0(a)$, 1.09(b), 2.17(c), 3.26(d), 4.34(e), 6.51(f), 8.69(g), 13.03(h).

The absorption and fluorescence spectra of Dye I in AOT reversed micelles decreased in the addition of AgCl nanoparticles. As shown in Fig. 5, when the concentration of AgCl nanoparticles became higher than 2×10^{-4} mol dm^{-3}, the spectral absorption of the Dye I decreased. When the concentration was higher than 4.43×10^{-4} mol dm^{-3}, the decrease became slower.

Fig. 6 shows the fluorescence spectra of the same system in Fig. 5 excited by light at 535 nm. The tendency of the fluorescence spectral changes was identical with the absorption spectra in Fig. 5. The relative intensity of the fluorescence did not change markedly until the concentration of AgCl was more than 2×10^{-4} mol dm^{-3}. When the concentration of AgCl was higher than 6.51×10^{-4} mol dm^{-3}, the action of AgCl to the dye decreased.

In AOT reversed micelles, both the membrane of the surfactant AOT and AgCl nanoparticles are negativly charged, and the Dye I is a cationic dye. Therefore, there was a competitive attraction effect between the AgCl nanoparticles and the membrane of the AOT surfactant to the Dye I cations. When the concentration of AgCl is very low, less Dye I was adsorbed by the AgCl particles, thus there was no obvious change in the spectrum of the Dye I. When the AgCl

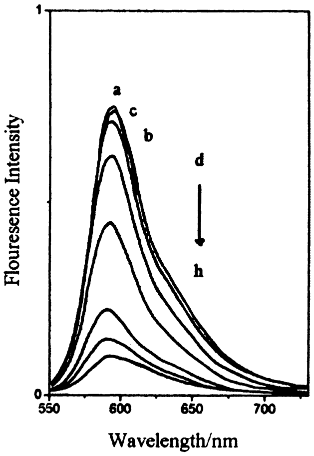

Fig. 6. The fluorescence quenching behavior of the Dye I in AOT reversed micelles by AgCl nanoparticles. $\lambda_{ex} = 535$ nm, The conditions are the same as in Fig. 5.

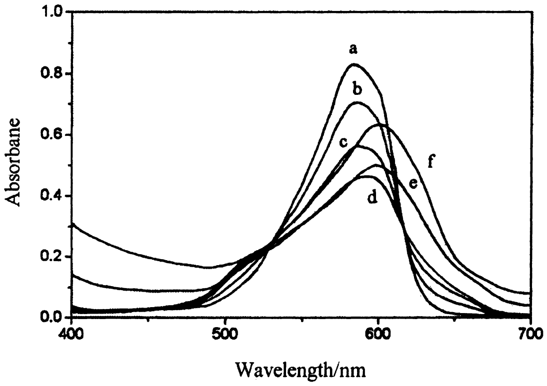

Fig. 7. The absorption spectra of the Dye I in Tx-45 reversed micelles ($\omega = 6.4$) in the presence of AgCl nanoparticles. [AgCl]/$\times 10^{-4}$ mol dm^{-3} = 0(a), 1.09(b), 2.17(c), 3.26(d), 5.43(e), 8.69(f).

concentration was high enough, AgCl nanoparticles adsorb effectively the dye. In this case, the absorption of the Dye I decreased and the fluorescence was quenched gradually.

Reckoning from the structure of the Dye I, the length, width and thickness of the Dye I molecule are 20, 7 and 4 Å, respectively. Therefore, if the dye orientation is flat-on the surface of AgCl particles, per molecule in a monolayer state would occupy 140 Å^2 and edge-on the surface, 80 Å^2.

In the AOT reversed micellar system the Dye I molecule could not orient end-on the surface of AgCl particles, it might adsorb around the surface of particles, because of the small volume of the water pool in the AOT system [5–7,9]. Based on the above supposition, the critical concentration of AgCl particles for complete adsorption of the Dye I, for the given concentration of 1×10^{-5} mol dm^{-3}, was about 6.0×10^{-4} mol dm^{-3}. In this case, the absorption of the free dye decreased to the lowest point and the addition of more AgCl particle can hardly influence the dye absorption. This analysis is consistent with the experimental results (Figs. 5 and 6).

As a comparison, same experiments in the Tx-45 reversed micellar system were done. The absorption spectrum of the Dye I in Tx-45 reversed micelles was similar as in the pure ethanol solution, but the peak showed a red shift to 586 nm, and the absorbance raised a little when the ω value became larger. The radius of the water pools in the Tx-45 reversed micellar system is generally larger than that in AOT reversed micelles at the same ω [13], and the Dye I may exist in M^1 state in Tx-45 reversed micelles.

In the Tx-45 system, there was no competitive attraction effect between AgCl particles and the membrane of the surfactant to the dye cations, since the Tx-45 is a nonionic surfactant. Therefore, the AgCl nanoparticles can adsorb the Dye I more effectively. Figs. 6 and 7 were the absorption and fluorescence spectra of the Dye I in the Tx-45 reversed micellar system containing AgCl of different concentration. The absorption of the Dye I decreased with increasing the AgCl concentration. The fluorescence of the Dye I was quenched gradually by AgCl.

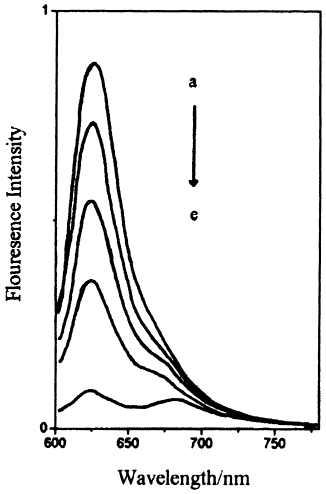

Fig. 8. The fluorescence quenching behavior of the Dye I in Tx-45 reversed micelles ($\omega = 6.4$) by AgCl nanoparticles. $\lambda_{ex} = 585$ nm, The conditions are the same as in Fig. 7.

The absorption at 510 nm in Fig. 7 probably was the H-band of the Dye I and the fluorescence of 684 nm in Fig. 8 may be related to the J-aggregate. The Tx-45 system was unstable compared with the AOT system. The Tx-45 reversed micellar system would be broken when the concentration of AgCl nanoparticles was higher, where the aggregates of the dye molecule would occur. Experiments showed here, when the Dye I was added to the system with high concentration of AgCl (ca. 4.34×10^{-3} mol dm^{-3}), after about 15 min, the system became turbid, the absorption at 684 nm increased clearly with the time, and the absorption for the monomolecule state of the Dye I decreased. All these showed that the system was broken and the J-aggregate produced. In this case, the dye can be adsorbed in H-aggregate or even J-aggregate on the surface of AgCl particles. As seen in Fig. 7, an absorption peak at 510 nm started to appear.

If the Dye I adsorbed flat-on the surface of AgCl particles in the Tx-45 reversed micelles system, a critical concentration of AgCl would be 7.6 × 10–4 mol dm^{-3}. Thus, the absorption and the fluorescence intensity of the Dye I would reach the lowest point. The experiments showed that, however, the critical concentration of AgCl would be $3.26 \sim 5.43 \times 10^{-4}$ mol dm^{-3} (Figs. 7 and 8, curve d and e). Obviously, the dye did not adsorb around the surface of the AgCl particles. The radii of the water pools in the Tx-45 reversed micelles was much larger than in the AOT system with the same ω [13], i.e. there would be enough room for one dye molecule in the Tx-45 water pool. Therefore, the dye molecule can adsorb orientation edge-on the surface of AgCl particles. Then the area occupied by one molecule would decrease to 80 Å^2, and the critical concentration would be 4.4×10^{-4} mol dm^{-3}. Clearly this is identical with the experimental results as showed in Figs. 7 and 8.

Comparing Fig. 6 with Fig. 8, it can be seen that the fluorescence was quenched much faster in the Tx-45 reversed micellar system than in the AOT reversed micellar system. As noted above, there was a competitive attraction effect between the AgCl nanoparticles and the membrane of AOT to the dye cations. So the AgCl nanoparticles in AOT reversed micelles can not effectively adsorb the dye and the quenching effect was weaker than in Tx-45 reversed micelles.

The energy of the highest occupied molecular orbital of the dye excited state is −3.04 eV [14] higher than the lowest energy level of the AgCl conduction band (−3.37 eV). The electron transition could occur between the excited state of the dye and the AgCl particles, it means that the fluorescence quenching of the Dye I by AgCl nanoparticles was caused by electron transfer.

4. Conclusions

As a microreactor, reversed micelles are used to research the photochemistry of a cyanine dye and the action the dye with AgCl nanoparticles. Due to different microenvironments, the Dye I emits strong fluorescence both in AOT and Tx-45 reversed micelles, while it emits very weak fluorescence in water or ethanol solution. The Dye I has two monomolecule states in the reversed micelles.

In AOT reversed micellar system the Dye I was adsorbed flat-on the AgCl nanoparticles surface, and there was a competitive attraction effect between the AgCl nanoparticles and the membrane of AOT to the dye cations. In Tx-45 reversed micellar system, the radius of the water pools were generally larger than that in AOT reversed micelles for a same ω, so the Dye I can orient end-on the surface of the AgCl nanoparticles.

In reversed micelles, the fluorescent of the Dye I was quenched by AgCl nanoparticles by the electron transfer mechanism.

Acknowledgements

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