The study on energy transfer mechanism between fluorescein sodium and eosine Y in micelles of cationic surface active agent

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ABSTRACT

In this paper, the condition of energy transfer between acidic fluorescent dyes in micelles of Cetyl trimethyl ammonium bromide or Hexadecyl pyridinium bromide was investigated. It was indicated that in the micelles which were formed by cationic surface active agent with dyes embedded, the effective energy transfer between anionic dyes could occur. When the concentration of cationic surface active agent reached to certain value, the energy transfer could occur. The model of energy transfer between dyes in micelles and laws of it were deduced.   © 2012 Trade Science Inc. - INDIA

KEYWORDS

Energy transfer;
Fluorescein sodium;
Eosine Y;
Model;
Fluorescence spectra;
Cationic surface active.

INTRODUCTION

There are many reports about fluorometry with Fluorescein sodium and Eosine Y. These dyes had strong fluorescence, but the wavelength difference of optimal excitation and emission wavelength were too small. So in order to avoid interferes of rayleigh scattering light, generally we didn't chose the optimal excitation wavelength of dyes which cause the decrease of sensitivity in practical application[1-9]. Energy transfer fluorescence analysis was with high sensitivity and excellent repeatability. In energy transfer fluorescence analysis, the generation of acceptor's fluorescence depended on the donor's florescence, which not only assured maximum emitting of the acceptor's fluorescence but could avoid the interfere of Rayleigh scattering light[10]. There were reports on the research and application of energy transfer between cationic dyes in micelles of anionic surface active agent (Dodecyl benzene sodium sulfonate)[11,12]. The application of surfactants in

fluorescence analysis was also wide[13-18]. But the researches about the rela- tionship between the efficiency of energy transfer and critical micelle concentration (cmc) and about the model of energy transfer have been not reported. According to the phenomena of the energy transfer between Fluorescein sodium and Eosine Y in different kinds of surfactants, we concluded that the effective energy transfer could occur only in the micelles whose charges were opposite to dyes.

EXPERIMENTAL

Apparatus

All fluorescence spectra were recorded with a Shimadzu RF-540 fluorescence spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer; Absorption was measured with an UV-VIS recording spectrophotometer (UV-265 Shimadzu Japan). All pH measure-

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ments were made with a pHS-3C acidity meter (Leici, Shanghai).

Chemicals

Fluorescein sodium and Eosine Y (EY) was purified according to the standard method[19]:5.0×10^{-4} mol/l as stock solutions. The working solution concentrations of EY and Fluorescein sodium were 5.0×10^{-5} mol/l and 5.0×10^{-6} mol/l respectively.

Surfactant standard solutions: Cetyl trimethyl ammonium bromide (CTAB): 5.0×10^{-3} mol/l; Hexadecyl pyridinium bromide (CPB): 5.0×10^{-3} mol/l; Dodecylbenzene sodium sulfonates (DBS): 5.0×10^{-3} mol/l; Sodium dodecyl sulfate (SDS): 0.01 mol/l; Trtion X-100 solution: 2.0×10^{-3} mol/l.

Above reagent were all analytical purity grades. Water for experi-ments was all deionized water.

Procedures

To 10 ml colorimetric cylinder, chemicals added in following order: 1.0 ml Fluorescein sodium of 5.0×10^{-6} mol/l, 0.5 ml EY of 5.0×10^{-5} mol/l, 1.2 ml CTAB of 5.0×10^{-3} mol/l, shook harmoniously, lay aside for 30 min. The fluorescent intensity of the solution was measured at $\lambda_{ex}/\lambda_{em} = 470/556$ nm against reagent blank prepared in the same way.

RESULTS AND DISCUSSION

The reaction between cationic surface active agent (Cass) and dye monomer

The reaction between EY and CASS was similar to that of Fluorescein sodium and CASS, because the structure of acidic dye Fluorescein sodium was similar to EY's. So we chose EY as an example to present the reaction between dye monomer and CASS of different concentrations, seen from Figure 1. It was demonstrated that (we divided the reaction course into four parts): (1) in the dilute solution of CASS, the fluorescence of aqueous EY solution was quenched (F, $\lambda_{ex} = 522$ nm, $\lambda_{em} = 540$ nm) gradually with the ioncomplex formed between EY and CASS, in this region, the concentra tion of CASS was no more than 1.0×10^{-6} mol/l. (2) When EY was fully formed no fluorescent ioncomplex, the fluorescence of the solution disappeared completely (the CASS concentration range: 1.0×10^{-6} mol/l ~ 1.6×10^{-4} mol/l). (3) with

the concentration of CASS increased, when CASS was gathered more and more in the solution and the micelles was more and more and appeared a new fluorescence peak ($\lambda_{ex}/\lambda_{em} = 537/566$ nm), the fluorescent intensity was stronger and stronger (the CASS concentration range: 1.6×10^{-4} mol/l ~ 9.0×10^{-4} mol/l). (4) When the concentration of CASS reached to certain value, the fluorescent intensity which reached to the maximum and kept stable was unchanged with the increasement of CASS's concentration. In this region, the concentration of CASS was more than 9.0×10^{-4} mol/l. The critical micelle concentration (cmc) of CTAB and CPB was 9.0×10^{-4} mol/l and 9.2×10^{-4} mol/l respectively[20]. It was indicated that when the concentration of CASS was more than cmc, the fluorescent intensity which reached to the maximum and kept stable.
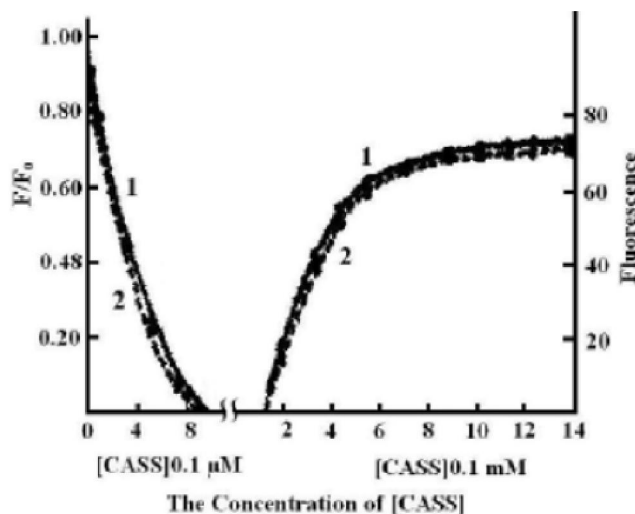

Figure 1 : The course of florescence quenching and generation of new fluorescence 1. CPB 2. CTAB

The influence of surfactants on the efficiency of energy transfer system

The fluorescence spectra in water phase and absorption spectra in medium of CTAB between Fluorescein sodium and EY were shown in Figure 2 and 3 respectively. It was presented that the emission wavelength of Fluorescein sodium and EY were 522 nm and 540 nm in Figure 2. From the absorption spectra of EY, we knew the maximum absorption wavelength of EY (520 nm) was 2 nm less than Fluorescein sodium's emission wavelength, which provided the precondition of energy transfer between Fluorescein sodium (donor) and EY (acceptor). The absorption spectra (Figure 3) of mix system were only the dyes added simply and no new peak appeared

there was no reaction between them. It was also indicated that the course of energy transfer didn't depending on the reaction of donor and acceptor; we chose 470 nm as an excitation wavelength, at which the absorbance of EY was close to zero, in that case, it could be assured that there was Fluorescein sodium's strong fluorescence generated and EY unexcited.

The fluorescence spectra of mix system were shown in Figure 2. It was demonstrated that the fluorescence spectra of mix system in aqueous water was simple addition, the energy transfer couldn't occur. Keep the concentration of dyes unchanged, with the increasement of CASS's concentration; the energy transfer occurred, seen from Figure 4. When the concentration of CASS

was 6.0×10^{-4} mol/l, the efficiency of energy transfer (η) reached to the maximum, but when the concentration of CASS went on increasing; the efficiency of energy transfer began to decrease, seen from Figure 5. According to the critical micelle concentration (cmc) of CTAB and CPB, we knew the maximum efficiency of energy transfer (η_{max}) was at about 2/3 cmc. When surfactants were anionic surface active agents (SDS, DBS) and non-ionic surface active agent (Trtion X-100) with concentration being 2/3 cmc respectively, there was no energy transfer phenomenon. The critical micelle con- centration (cmc) of SDS, DBS and Trtion X-100 were 8.7×10^{-3} mol/l[21], 1.2×10^{-3} mol/l[22], 3.1×10^{-4} mol/l[23] respectively.
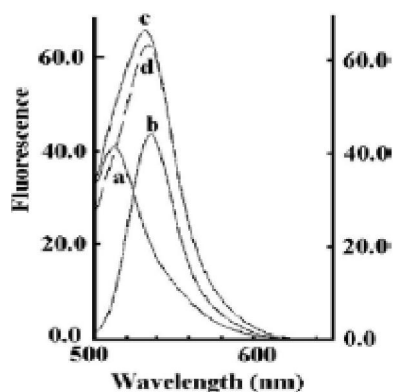

Figure 2 : Fluorescence spectra of dyes monomer in water phase: (a) fluorescein sodium, (b) EY, (c) the mixture of fluorescein sodium and EY, (d) a+b. Fluorescein sodium: 5.0×10^{-7} mol/l; EY: 2.5×10^{-6} mol/l
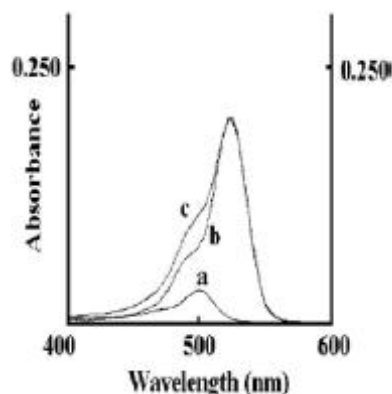

Figure 3 : Absorption spectra of dyes monomer in medium of CTAB: (a) fluorescein sodium, (b) EY, (c) the mixture of fluorescein sodium and EY. CTAB: 6.0×10^{-4} mol/l; fluorescein sodium: 5.0×10^{-7} mol/l; EY: 2.5×10^{-6} mol/l
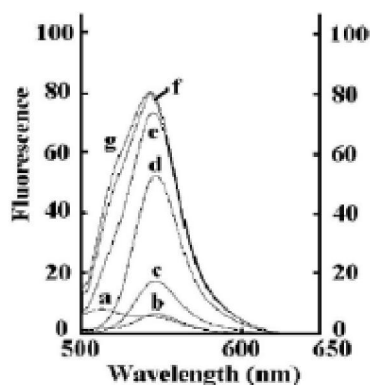

Figure 4 : Influence of CASS on energy transfer system:from (a) to (g):the concentration of CTAB (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4) $\times 10^{-3}$ mol/l; luorescein sodium: 5.0×10^{-7} mol/l; EY: 2.5×10^{-6} mol/l

The influence of fluorescein sodium and ey's concentration on the efficiency of energy transfer
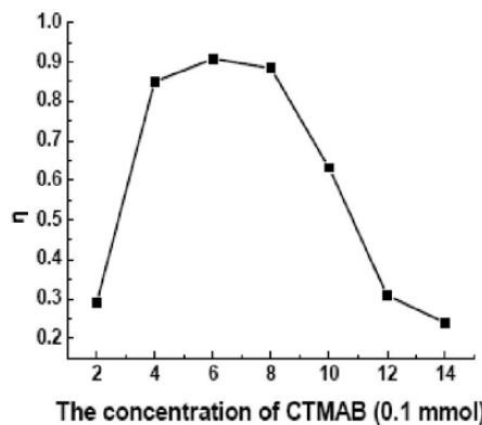
In the CASS's concentration which the efficiency of

Figure 5 : Influence of CASS's concentration on the efficiency of energy transfer: fluorescein sodium: 5.0×10^{-7} mol/ l; EY: 2.5×10^{-6} mol/l

energy transfer (η) was the maximum, keep the concentration of Fluorescein sodium unchanged, with the change the concentration of EY we studied the influence of Fluores-

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cein sodium and EY's concentration on the efficiency of energy transfer, seen from Figure 6. It was indicated that the efficiency of energy transfer reached to the maximum when the molar ration between Fluorescein sodium and EY was 1:3 to 1:7. So we chose 1:5 as optimal molar ratio, 1.0 ml 5.0×10^{-6} mol/1 Fluorescein sodium and 0.5 ml 5.0×10^{-5} mol/l EY as optimal value.

In the course of energy transfer, the efficient of energy transfer (η) can be calculated by formula l[24]:

$$\eta = 1 - (F_d/F_{do}) \tag{1}$$

where, F_d: the fluorescent intensity of donor in the presence of acceptor, F_{do}: the fluorescent intensity of donor without acceptor.
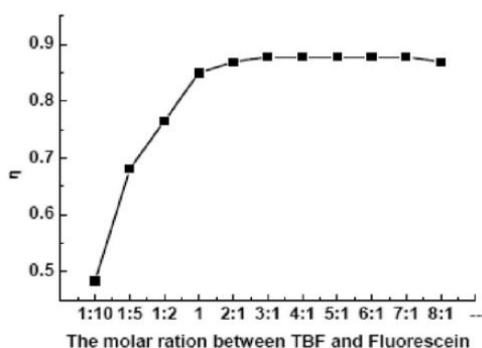
Figure 6 : Influence of fluorescein sodium and EY's concen tration on the efficiency of energy transfer

The model of energy transfer

When the ioncomplex was completely formed between acidic dyes and CASS with the increasement of CASS's concentration, the fluorescence of the system disappeared and the energy transfer couldn't occur; when the concentration of CASS reached to certain value but not to the cmc, the aggregation number of CASS was small, parts of CASS began to be gathered and formed micelles, the charges of hydrophobic ioncomplex was neutralized, which was easy to be extracted by micelles. When the ioncomplex entered into the micelles, it was probably that the mixture micelles among Fluorescein sodium, EY and original micelles because of rearrangement. Here the terminal hydrophilic group of dyes which would faced to water layer was influenced by positive electric field of micelles, the solid parts of big conjugate system would be in the core of micelles' hydrophobic group. In this microenvironment of micelles, dyes was in the hydrophobic environment which was formed by long carbon chain of alkyl, because of narrow space of them and polar medium, which made Fluorescein sodium and EY closer and the

energy transfer occurred, seen from Figure 7. When the concentration of CASS reached to certain value, the efficiency of energy transfer (η) was the maximum, but the fluorescent intensity of acceptor didn't reached to maximum, and if the concentration of CASS went on increasing, the fluorescent intensity was unchanged. When the concentration of CASS was excess cmc, the molecular number of dyes in micelles was decreased oppositely, here the micelles of the system was very close, which made parts of dyes molecular was piled out to the layer between micelles and water, the dyes molecular piled out was in completely polar medium and the efficiency of energy transfer (η) decline. The effect of CASS's spike was dominant and peak was blue shifted, the fluorescence peak of acceptor was changed from 556 nm to 540 nm, the peak at 540 nm was fluorescent peak of ioncomplex between EY and CTAB, the appearance of this peak indicated that the deduce that parts of dyes molecular was piled out to the layer between micelles and water was correct, seen from Figure 4. When surfactants were anionic surface active agents (SDS, DBS) and nonionic surface active agent (Trtion X-100) respectively, there was no energy transfer phenomenon. It was proved that the model of energy transfer was dependable.
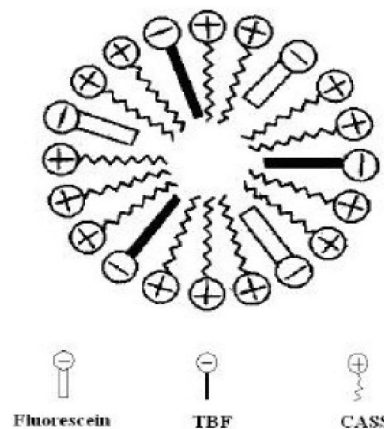
Figure 7 : Model of energy transfer

CONCLUSION

The conditions that the effective energy transfer could occur between dyes in dilute solution were: (1) the difference between donor's emission wavelength and acceptor's absorption wavelength was little as possible. (2) The medium was surfactants whose charges were opposite to

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dyes'. (3) The efficiency of energy transfer (η) reached to maximum when the surfactants' concentration value was about 2/3 cmc. (4) The acceptor's fluorescent intensity depended on the assistant influence of the efficiency of energy transfer (η) and surfactants' spike, so when the fluorescent intensity of acceptor was maximum, the concentration value of surfactants may be not 2/3 cmc. (5) The energy transfer mechanism between the dyes which the charges were opposite was awaited to research.

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