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Dyes and Pigments 67 (2005) 223–228

DYES and PIGMENTS

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Studies on aggregation of AOT and NaDEHP via the energy transfer between AO and RB molecules

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Received 6 June 2004; received in revised form 12 August 2004; accepted 3 December 2004
Available online 25 February 2005

Abstract

The aggregation behaviours of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and sodium bis(2-ethylhexyl)phosphate (NaDEHP) solutions are studied via the energy transfer of acridine orange (AO) and rhodamine B(RB) molecules. The approximate apparent energy transfer efficiency (ϕ_a) of the dye molecules reaches its maximum value when the concentrations of AOT and NaDEHP are far lower than their cmc. This might be caused by the formation of surfactant–dye mixtures. The anionic surfactants (SDS, AS, AOT and NaDHEP), cationic surfactant (CTAB) and nonionic surfactant (Triton-X-100) are chosen to investigate the effect of the structure of surfactant on the ϕ_a between AO and RB molecules. The results indicate that the effective energy transfer may occur in the anionic surfactant systems and it is not obvious in the nonionic and cationic surfactant systems.

Keywords: AOT; NaDEHP; AO; RB; Energy transfer

1. Introduction

The surfactant system is a good model for simulating the biological system [1]. Different kinds of aggregates, such as the regular micelle, the reversed micelle, the microemulsion, the liquid crystal and so on can be formed due to the special characters of the surfactants. The aggregate state of the molecules at the interface of the lipid–water in the cell membrane of the simulation system can be obtained with the aid of the dye molecules. The micelle formed by ionic surfactants, as a particle with charges, can work in the separation charges, which plays a key role in the transition of photo-energy to electro-energy [2]. The energy transfer between different dye molecules in the surfactant solutions has attracted much attention in the recent years [3–8]. The investigation on the energy transfer of the dye molecules in the micelle system provides much useful information on the structure of the micelle.

At present the studies about the energy transfer between two dye molecules in the single-chain surfactants and polymer/surfactants have been carried out [7,9,10], while the effect of the double-chain surfactants on the energy transfer of the dye molecules has not been observed until now. Sodium bis(2-ethylhexyl)phosphate (NaDEHP) and sodium bis(2-ethylhexyl)sulfosuccinate (AOT) are important surfactants used in studies on chemical reaction and enzyme activity, liquid–liquid extraction of proteins, sol–gel preparation, nanoparticle preparation, hydrometallurgy and the nuclear industry [11–16]. They contain the same hydrophobic chains but the different polar headgroups. The aggregation behaviours of them in the apolar solution are violently different, even reverse [17–19]. The aggregation behaviours of the two surfactants have been studied by the surface tension measurement, computer simulations, the fluorescence

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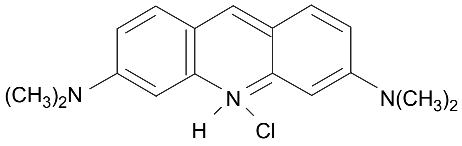
doi:10.1016/j.dyepig.2004.12.004

spectroscopy and the dynamic light scattering (DLS) and the results suggest that small aggregates are more readily formed by NaDEHP molecules than AOT molecules and the interaction between AOT and poly(vinylpyrrolydone) (PVP) is stronger than that between NaDEHP and PVP molecules [20–22]. The present paper aims to further investigate the differences of aggregation behaviours between AOT and NaDEHP in the aqueous solution via the energy transfer from AO molecule to RB molecule in the double-chain surfactants.

2. Experimental section

2.1. Materials

AOT was purchased from Fluka Corp. AO, RB, bis(2-ethylhexyl)phosphate (HDEHP, C.R.), sodium dodecyl sulfate (SDS), sodium alkyl sulfonate (AS), cetyltrimethyl ammonium bromide (CTAB) and Triton-X-100 were bought from Shanghai Chemical Corp. (China). The preparation of NaDEHP was described in previous paper [20].



AO

2.2. Sample preparations

The solutions of AOT (0.03 M) and NaDEHP (0.1 M) are prepared and have been diluted to the required concentration in the experiment. AO and RB solutions (10^{-4} M) are prepared. The solution is obtained by putting suitable amount of surfactant, dye and water into the tube and shake to clear.

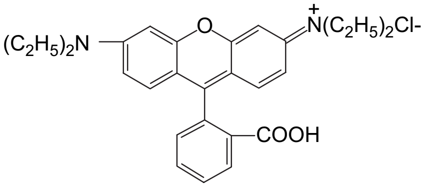
2.3. Fluorescence spectra measurements

Fluorescence spectra were recorded on F-4500 FL Spectrophotometer. The optimal excitation and the maximum emission spectra of AO and RB molecules obtained by continuously scanning the excitation and the emission spectra are 493/529.2 nm, and 556/575 nm, respectively. The excitation wavelength is 450 nm for the AO–RB mixed systems. The experiments are carried out at the room temperature. The water used in this experiment is distilled for three times.

3. Results and discussion

3.1. The excitation and emission spectra of AO and RB molecules

The fluorescence technique is very important in the study of the physico-chemical properties, such as the micropolarity, the microviscosity and the aggregation number of the aggregates formed by surfactants. AO and RB are common dye molecules (the protonated molecular structures are shown in the following scheme). The excitation and emission spectra of the AO and RB molecules in aqueous solution are shown in Fig. 1. It is known that the emission of the donor overlaps the excitation of the acceptor is necessary for the occurrence of Förster resonance energy transfer (FRET). It can be seen from the figure that the emission spectra of AO overlapped with the excitation spectra of RB molecule. So the energy can be transferred from AO molecule to RB molecule in the suitable condition.



RB

3.2. The fluorescence spectra of AO and RB in different surfactant concentrations

The fluorescence spectra of AO and RB in the AOT and NaDEHP solutions are given in Fig. 2. It can be seen that there are two fluorescence peaks centered around 498 nm and 530 nm for AO molecule, respectively. According to Ref. [23] the first peak is the fluorescence

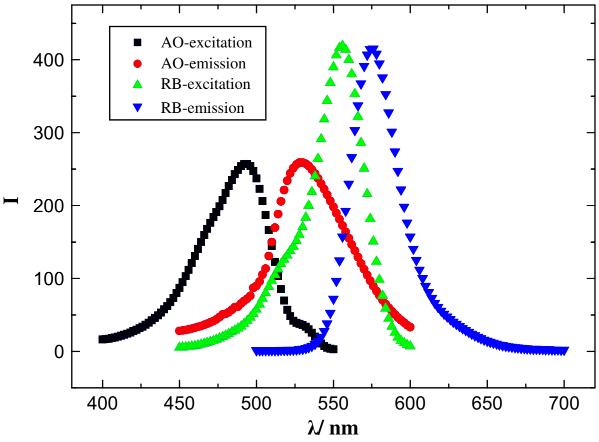
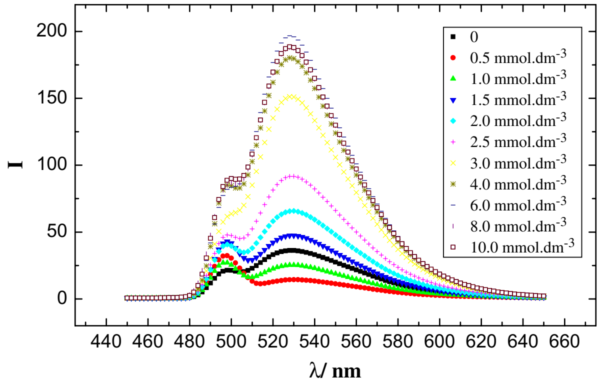


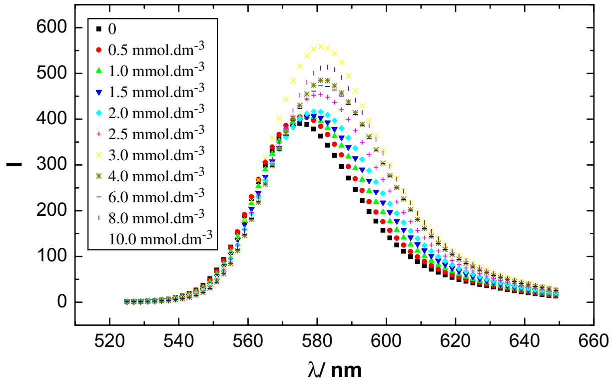
Fig. 1. The excitation and emission spectra of AO and RB molecules.

emission spectra of unprotonated AO molecule and the second is the characteristic peak of AO molecule. In AO fluorescence spectra initially the fluorescence intensity of AO with a small amount of AOT is lower than that in the absence of it. However, with AOT concentration increasing the fluorescence intensity becomes larger than that of the system without AOT. The fluorescence intensity increases with the rise of AOT concentration but it becomes smaller when AOT concentration is larger than its cmc. But no shift is observed on the maximum peak position. AO is a cationic dye molecule, while AOT is an anionic surfactant, these two molecules can bind with each other via the electrostatic attraction. So the fluorescence intensity of AO in the presence of small amount of AOT is lower than that in the absence of it due to binding with surfactant. The fluorescence intensity increases with the increase of AOT concentration, indicating the formation of the pre-micelles and AO molecules are condensed, while the fluorescence intensity is a little decreased when the AOT concentration is larger than its cmc, which may be caused by the dimer of AO which has no fluorescence, formed at the interface of micelle and the water [24]. Also it can be seen from the figure that the fluorescence intensity rapidly increases when AOT concentration reaches 3 mM. From the surface tension measurements the cmc of AOT and NaDEHP are about 3 mM and 15.6 mM, respectively [20] and at the moment the regular micelles are formed in the solution. AO molecules are solubilized into the micelles, thus the fluorescence intensity is distinctly increased. For NaDEHP system, the peak intensity changes little until the concentration reaches 5 mM. However, this concentration is far smaller than the cmc of NaDEHP. AO is a cationic dye molecule and strongly interacts with anionic surfactants AOT and NaDEHP, they form mixed micelles and reduce the cmc of AOT and NaDEHP. This phenomenon is more obvious than that in AOT system.

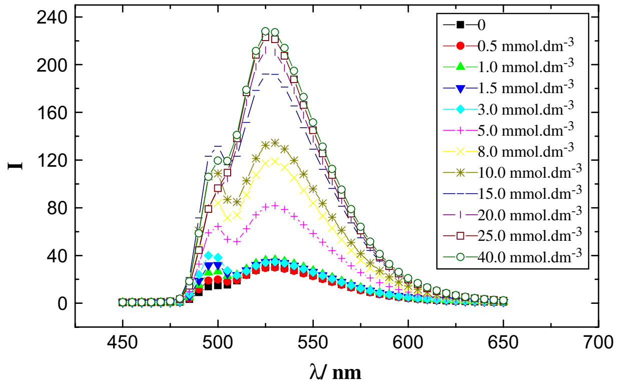
It can be seen from Fig. 2C that the fluorescence intensity of RB gradually rises with the increase of AOT concentration. The maximum peak position shows bathochromic shift with the rise of AOT concentration and the wave number of the maximum peak changes from 575 nm to 583 nm when the AOT concentration changes from 0 mM to 10 mM. This may be caused by the binding of RB with the two surfactants through the electrostatic interaction. The RB fluorescence spectra increase not obviously until the NaDEHP reaches 5 mM and after that concentration point the fluorescence intensity rapidly increases until 15 mM. The mixed micelles are formed when the concentration changes from 5 mM to 15 mM.



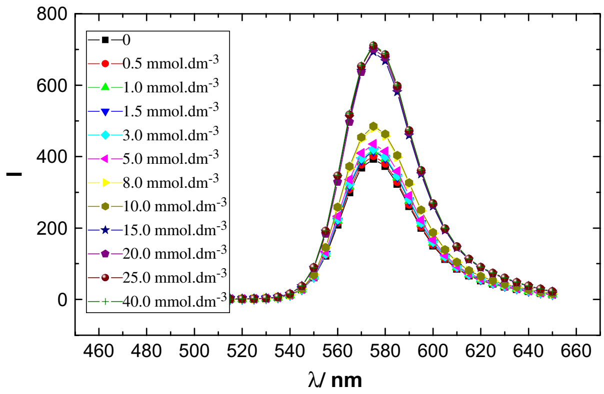
(A) AOT



(B) NaDEHP



(C) AOT



(D) NaDEHP

Fig. 2. The fluorescence spectra of AO (A and B) and RB (C and D) in different concentration of AOT and NaDEHP.

3.3. The fluorescence spectra of AO–RB mixed system in AOT and NaDEHP solutions

The self-quenching usually occurs when the concentration of the dye molecules is larger than 10^{-4} M in the fluorescence analysis [25]. So the concentration of the dye is usually lower than that. The fluorescence spectra of different concentrations of AO–RB (The molar ratio of AO to RB is 1:1.) are given in Fig. 3. It can be seen from the figure that the fluorescence intensity of the AO–RB mixed system is the simple sum of the AO and RB fluorescence spectra and it increases with the increase of the total dye concentration. Only one broad peak around 530 nm appears when the total dye concentration is smaller than 10^{-6} M. The two peaks centered around 530 nm and 574 nm are observed when their total concentration is larger than 5.0×10^{-6} M. So in our experiments the dye concentration is chosen 1.0×10^{-6} M.

The wavelength of 450 nm is chosen to excite the donor (AO) molecule and to minimize the excitation of the acceptor (RB) molecules. From Fig. 1 we know that AO has larger absorption and RB has no excitation at this excitation wavelength. Fig. 4 shows the fluorescence spectra of AO–RB in the different concentrations of AOT and NaDEHP solutions. It can be seen from Fig. 4A and B that only the fluorescence peak around 530 nm appears in the absence of the surfactants. The surfactant molecules can form aggregates in the solution and shorten the distance between the dye molecules. So the FRET may occur in the suitable microenvironment. It can also be seen from the figure that no FRET occurs in the dilute solution due to the large distance between the donor molecules and the acceptor molecules. The fluorescence spectra of the mixed system change distinctly upon addition of small amount of AOT (0.5 mM). The fluorescence spectra of AO at 530 nm is rapidly decreased, simultaneously the peak of RB at 574 nm peak is obviously increased, which clearly indicates efficient energy transfer from the excited AO molecule to RB molecule, leading to the emission from the excited RB as shown in the following equations:

$$AO + h\nu_{AO} \rightarrow AO^{*} \quad (1)$$

$$AO^{*} + RB \rightarrow AO + RB^{*} \quad (2)$$

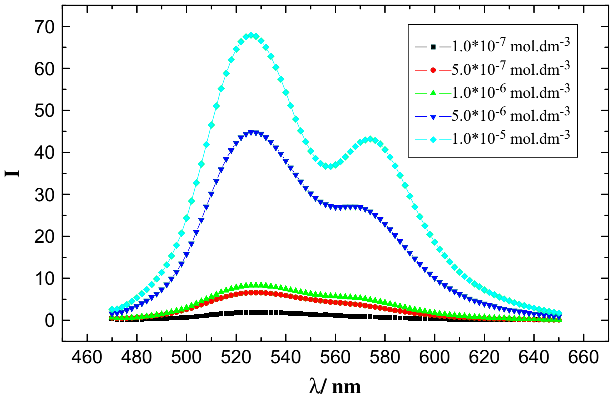


Fig. 3. The fluorescence intensity of different concentration of AO–RB mixed solution (the molar ratio of AO to RB is 1:1).

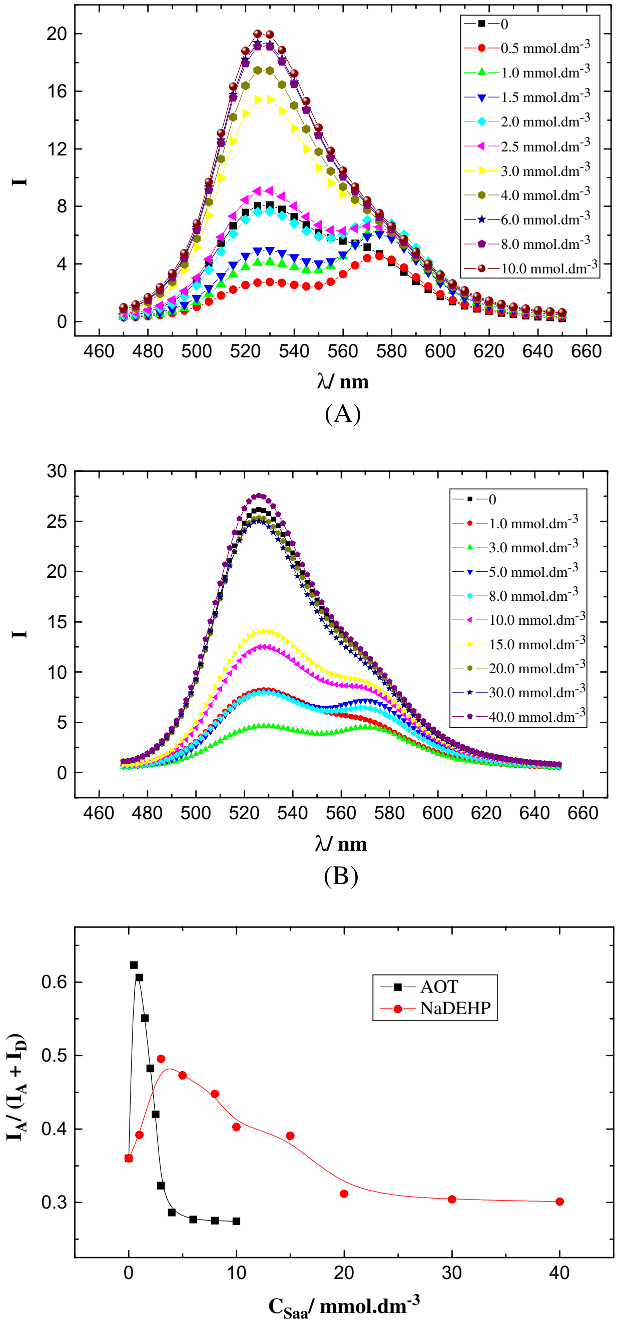


Fig. 4. The fluorescence spectra (A and B) and the ϕ_a(C) dependences of AO–RB on the concentrations of the surfactants.

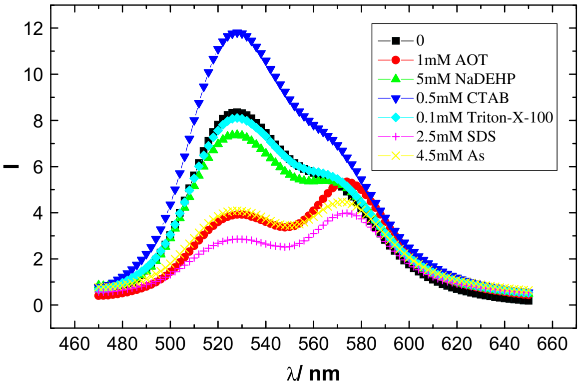


Fig. 5. The fluorescence spectra of AO–RB in different surfactant solutions.

$$\mathrm{RB}^* \rightarrow \mathrm{RB} + h\nu_{\mathrm{RB}} \tag{3}$$

where AO* and RB* stand for the excited AO and RB molecules, respectively; $h\nu$ represents the irradiation light; $h\nu_{\mathrm{AO}}$ and $h\nu_{\mathrm{RB}}$ refer to the absorption energy of AO molecule and the emission energy of RB molecules, respectively.

When the concentration of AOT is larger than 2.5 mM only AO fluorescence spectra is shown in the mixed solutions. This is because the fluorescence radiation rate of AO is expedited when AOT concentration reaches certain value. So the fluorescence peak of AO is enhanced. In this course the fluorescence intensity of RB changes little, the FRET decreases. This is caused by the competition of the energy transfer and the fluorescence radiation of the donor molecules.

According to Wu and Jiang's [3] and Chen et al.'s [26] view, the apparent energy transfer efficiency (ϕ_a) of the two dye molecules can be approximately calculated as follows:

$$\phi_a = I_A/(I_A + I_D)$$

where I_A and I_D are the fluorescence intensity of the acceptor and donor molecules, respectively. According to above equation the values of ϕ_a are calculated. The dependence of ϕ_a of AO–RB mixed system on the surfactant concentrations is shown in Fig. 4C. There are maximum ϕ_a values in the plots of $\phi_a - C_{\mathrm{Saa}}$ when the concentrations of AOT and NaDEHP are about 1.0 mM and 3.0 mM, respectively, which are smaller than their cmc. So it can be concluded that the mixed micelles enriched by the dye molecules are formed in the solution. The FRET cannot occur in the absence of the surfactant due to the comparatively far distance between the dye molecules. But it occurs when the small aggregates are formed, which shorten the distance between the dye molecules. The ϕ_a decreases after the regular micelles are formed. This is attributed to the formation of dimer of the dye that cannot fluoresce [24].

Table 1
The cmc of the surfactants

Surfactant	AOT	NaDEHP	CTAB	SDS	Triton-X-100	AS
Cmc/Mm	2.99	15.6	0.92	8.2	0.20	14.0

Note: All the cmc of the surfactants are obtained by surface tension measurements except AS. The cmc of AS is taken from Ref. [30].

3.4. The fluorescence spectra of AO–RB in different kinds of surfactant solutions

From the above study we know that the energy transfer can effectively occur in the suitable concentration of AOT and NaDEHP solutions. In order to study the effects of different kinds of surfactants on the ϕ_a of AO–RB mixed system, anionic surfactants (SDS, AS, AOT and NaDHEP), cationic surfactant (CTAB) and nonionic surfactant (Triton-X-100) are chosen in our study. The fluorescence spectra of AO–RB in these surfactant solutions are given in Fig. 5. From the literature it is known that the efficient transfer takes place only before or close to its cmc [27–29]. So the concentrations of the surfactants in this experiment are chosen about one-third or half of its cmc. The cmc of the studied surfactants are shown in Table 1. The values of ϕ_a of AO–RB in different surfactants solutions are shown in Table 2. From Fig. 5 and Table 2 it can be seen that the anionic surfactants, AS, SDS and AOT can effectively cause the energy transfer from AO to RB molecules, while the effects of the CTAB and Triton-X-100 are not so obvious. AO and RB molecules bear positive charges and more easily interact with the anionic surfactants through the electrostatic attraction. But there are repulsive interactions or no obvious interactions between cationic dye molecules and cationic surfactants or cationic dye molecules and nonionic surfactant.

4. Conclusions

The aggregation behaviours of double-chain surfactant AOT and NaDEHP are investigated via energy transfer between dye molecules AO and RB. The fluorescence intensity of the dye molecules distinctly

Table 2
The effect of surfactant structure on the ϕ_a value of AO–RB

Surfactants	0	1.0 mM AOT	5.0 mM NaDEHP	0.5 mM CTAB	0.1 mM Triton-X-100	2.5 mM SDS	4.5 mM AS
$I_A/(I_A + I_D)$	0.37	0.57	0.40	0.35	0.39	0.58	0.52

increases before the surfactant concentration reaches its cmc, indicating that the cationic dye molecules strongly interact with the anionic surfactants and form the mixed micelles. The apparent energy transfer efficiency (ϕ_a) of AO and RB in different kinds of surfactant are calculated. The energy transfer between the two dye molecules can effectively occur in the anionic surfactants, while it nearly does not occurs in the nonionic and cationic surfactants.

Acknowledgements

The authors gratefully acknowledge financial support from National Natural Science Foundation (29973023) and Natural Science Foundation (Y2001B08) of Shandong Province in China.

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