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Detection of the critical micelle concentration of cationic and anionic surfactants based on aggregation-induced emission property of hexaphenylsilole derivatives

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We report a fluorescence "turn-on" method to detect the critical micelle concentration (CMC) of surfactants. This method works well for both cationic and anionic surfactants. It employs an unprecedented mechanism (aggregation-induced emission, or AIE) to determine the CMC values, and the results are consistent with the data obtained by the classical techniques. In addition, this method renders the convenient detection of the CMC values. Any large and professional instruments are unnecessary, instead, a portable UV lamp and an ultrasonic generator are enough to carry out the detection in an ordinary laboratory. Considering that micelles are interesting entities and have found applications in many important fields such as emulsion polymerization, template of nanosized materials synthesis, controllable drug delivery and macromolecular self-assembling. Our experimental results may offer a facile, sensitive and promising method to detect the formation of micelles constructed by the new amphiphilic molecules and macromolecules.

aggregation-induced emission, critical micelle concentration, fluorescence, probe

1 Introduction

Micelles are ubiquitous in nature. They have attracted considerable research attention due to their multiple functions as entities of emulsion polymerization[1−3], templates for nanostructure synthesis[4−7], and controllable drug delivery[8−12]. Varieties of natural and synthetic amphiphilic molecules and macromolecules have been derived to build micelles for specific applications. Therefore, the determination of the critical micelle concentration (CMC) becomes a fundamental task. A few methods, e.g. osmotic pressure, equivalent conductivity, excitation spectroscopy, surface and interfacial tension, have been introduced to measure CMC values. But all these methods depend on professional instruments and thereby are time-consuming and expensive. Herein, we report a novel, facile and efficient method for CMC measurement.

The basic principle of this method is aggregation-induced emission (AIE) of organic fluorescence (FL) chromophores. Molecules showing AIE property usually display very weak FL in good solvents, but emit efficiently when they are in a certain aggregation state[13−26]. Systematic studies have shown that the AIE phenomenon of molecules origins from the restriction of intramolecular

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rotation of the peripheral phenyl groups attached to the conjugated cores in solid state or in solid matrices[16−28]. Given a lipophilic AIE compound, poorly soluble in water but highly soluble in organic solvents, the dilute solution of such a compound will exhibit faint FL. Upon introducing surfactant into the solution, a faint FL is expected to be observed for the systems when the surfactant concentration is lower than the CMC. Once the concentration reaches or becomes higher than the CMC, the surfactant molecules must self-assemble into micelles. Driven by hydrophilic-hydrophobic interactions, the lipophilic AIE molecules will enter and aggregate in the hydrophobic cores of the micelles. As a result, amplified FL will be recorded. Fortunately, the above-mentioned assumption has been confirmed by our recent experiments. Herein, we report the experiment results.

2 Experimental

2.1 Materials and instrumentation

The AIE-active compounds used as fluorescence probes are 1,1-bis[*p*-(diethylamino-methyl)phenyl]-2,3,4,5-tetraphenylsilole (**M1**) and 1,1,2,3,4,5-hexaphenylsilole (**M2**), whose chemical structures are shown in Figures 2(b) and 5(b). Their synthesis and AIE behavior were described elsewhere[14,28]. The cationic and anionic surfactants are cetyltrimethyl-ammonium bromide (CTAB) and 1-dodecane-sulfonic acid sodium salt (AS), respectively. UV-vis spectra were recorded on a Milton Roy Spectronic 3000. Fluorescence (FL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. The transmission electron microscope (TEM) images were recorded with a JEOL/JEM-200 CX TEM at an accelerating voltage of 160 kV. The TEM instrument was equipped with an EX 500 W CCD camera.

2.2 Detection of the CMC value with AIE-active molecules as fluorescent probes

Owing to the diethylamine groups, **M1** is an organic base, thus it can be protonated by reaction with acids and thereby can be endowed with water solubility in acidic aqueous solution. **M1** displays some solubility in water at pH 5.5 and shows higher solubility at lower pH values[28]. Such a property allows us to introduce **M1** molecules into the acidic aqueous solution as fluorescent probes.

Acidic aqueous solution with pH 4 was prepared by addition of H_2SO_4 into the deionized water. **M1** has desirable solubility in this acidic medium and 10^{-3} mol·L^{-1} solution can be obtained. Meanwhile, a series of CTAB aqueous solutions with different surfactant concentrations (mg·mL^{-1}) were prepared. Into a clean vial, 9 mL of CTAB aqueous solution was added; then, 1 mL of **M1** acidic aqueous solution (10^{-3} mol·L^{-1}) was dropwise introduced into the same vial. A series of mixed solutions were obtained and all the solutions underwent ultrasonic treatment for 10 min and then stood still for 1 h. Finally, the mixtures were transferred to the fluorescence measurement.

The anionic surfactant used in our experiment was AS. To avoid the latent interactions between the anionic AS and cationic **M1** molecules, a neutral AIE compound **M2** was used as a FL probe. A series of aqueous solutions of AS were prepared by mixing different amounts of AS in 10 mL water. Meanwhile, an **M2** hexane solution at a concentration of 10^{-3} mol·L^{-1} was prepared. Into a sample vial containing 10 mL AS solution, 0.3 mL **M2** hexane solution was introduced and it formed a cover layer. Dealing with the solutions with ultrasonicating for about 10 min and waiting for the thorough evaporation of hexane, the **M2** molecules aggregated and the aggregates were driven into the micellar cores by hydrophobic force when micelles formed in the solution. Removing the uncapped **M2** solid by filtration, solutions of AS micelles containing **M2** aggregates were obtained. Then the FL spectra of these filtrates were measured and recorded.

3 Results and discussion

3.1 AIE property of M1

M1 is highly soluble in acetonitrile. In dilute acetonitrile solution (10^{-5} mol·L^{-1}), **M1** exhibits an absorption peak at 364 nm (Figure 1(a)), and the solution shows very weak fluorescence when excited at 370 nm at room temperature (Figure 1(b)). However, the solubility of **M1** in water is very low. When enough water was introduced into the **M1** acetonitrile solution, **M1** molecules would aggregate in the acetonitrile/water mixture in high water content, thereby the mixture becomes emissive.

The solution was macroscopically homogenous and no precipitate was formed for days, suggesting that nano-scaled aggregates had been formed in the mixture solution. This was confirmed by TEM measurement results (Inset of Figure 1(b)). The fluorescence quantum

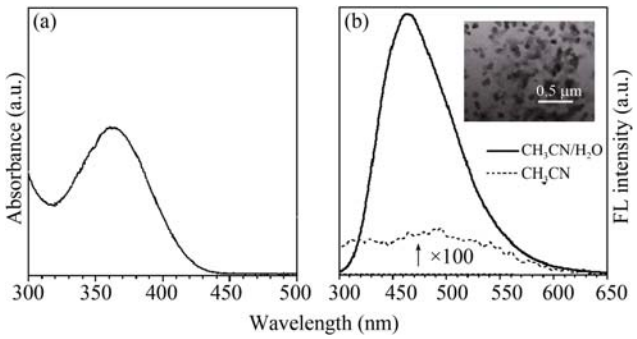

Figure 1 (a) UV-vis spectrum of **M1** solution (10 μmol·L^{-1}) in acetonitrile; (b) fluorescence spectra of **M1** in acetonitrile solution (10 μmol·L^{-1}) and acetonitrile/water mixtures (1∶9, *V*∶*V*).The excitation wavelength is 370 nm. Inset of (b) shows a typical TEM image of **M1** nanoparticles formed in acetonitrile/water mixture.

yield is boosted from 2.0×10^{-3} in pure acetonitrile to 28% and 39% in the acetonitrile/water mixtures with water fractions of 90% and 99%, respectively[28]. Thus, **M1** is an AIE-active compound.

3.2 Detection of the CMC value of CTAB with M1 as fluorescent probes

The fluorescence spectra of the solutions recorded at different CTAB concentrations are shown in Figure 2. It is noted that when CTAB concentration ([CTAB]) is lower than CMC, the solutions also display the emission from **M1**, though the emission is weak, and the relative intensity is higher than that observed in dilute acetonitrile solutions. These results can be tentatively ascribed to the ultrasonic treatment, which offers energy to induce the micelle formation and the aggregation of **M1** molecules. Fortunately, the ultrasonic treatment had led to only weak interferences to the CMC detection. It speeded up the micelle formation. A sharp increase of the FL intensity has been derived as shown in Figure 2(a). Quantitatively, when CTAB concentration is lower than 0.1 mg·mL^{-1}, the FL intensity changes very little. At [CTAB] = 0.3 mg·mL^{-1}, the FL intensity is enhanced abruptly. By further increasing [CTAB] from 0.3 to 5.0 mg·mL^{-1}, the FL intensity becomes higher.

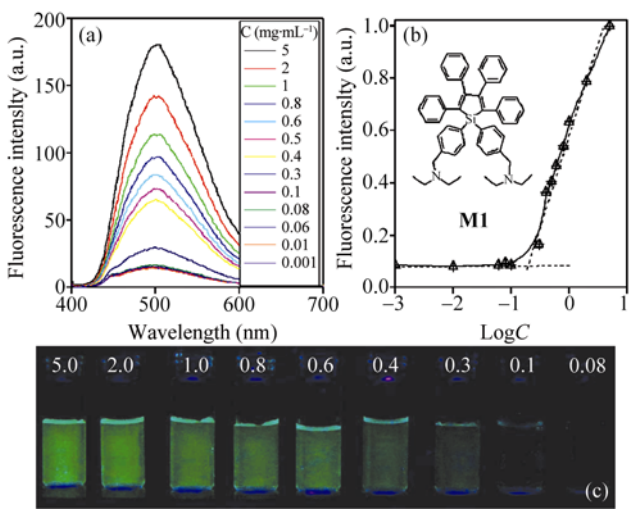

Figure 2 (a) FL spectra of aqueous solution of **M1** with different [CTAB] (mg·mL^{-1}); (b) plot of FL peak intensity vs. lg[CTAB]; (c) photographs of **M1** in aqueous solution with different [CTAB] taken at room temperature (r.t.) and under illumination of a portable UV lamp. [**M1**] = 10^{-4} mol·L^{-1}, pH 4, λ_{ex} = 365 nm.

The plot of the maximum on FL curves vs. [CTAB] is given in Figure 2(b), and an inflexion at around 0.23 mg·mL^{-1} can be derived. Before the inflexion, the fluorescence intensity keeps unchanged with the changing of [CTAB]. On the contrary, after the inflexion, the intensity elevates monotonously with the increase of [CTAB] in the concentration scope of our experiment. We rationally assign the inflexion to the CMC of CTAB in water. According to the literature, the CMC for CTAB is 0.3 mg·mL^{-1}. The experiment result reported here is well consistent with the accredited date[29].

More importantly, taking the advantage of AIE phenomenon, the CMC of a surfactant can be determined not only by plotting the peak intensity of the FL spectrum vs [CTAB], but also by direct observation of the FL emission of the solutions under the illumination of a portable UV lamp, which is available in an ordinary chemistry laboratory. Figure 2(c) presents the evolution of FL emission of **M1** aqueous solutions with different [CTAB]. Clearly, when [CTAB] is higher than 0.3 mg·mL^{-1}, green light can be clearly seen with naked eyes. The results indicate that one can practically determine the CMC of a surfactant by simply using a portable UV light and AIE compound as fluorescent probe.

3.3 Mechanism of the detection of CMC with AIE molecules as fluorescence probes

The basic principle of using AIE phenomenon for CMC detection is schematically demonstrated in Figure 3. Figure 3(a) presents a dilute aqueous solution of AIE compound (e.g. **M1**) and surfactant molecules. In this case, very faint fluorescence or even no fluorescence can be recorded. Once the concentration of the surfactant reaches to or becomes higher than the CMC, the lipophilic AIE molecules will be encapsulated into the hydrophobic cores of the micelles and aggregate there (Figure 3(b)). Upon UV illumination, emission from the aggregates of AIE molecules can be observed, as shown in Figure 3(c).

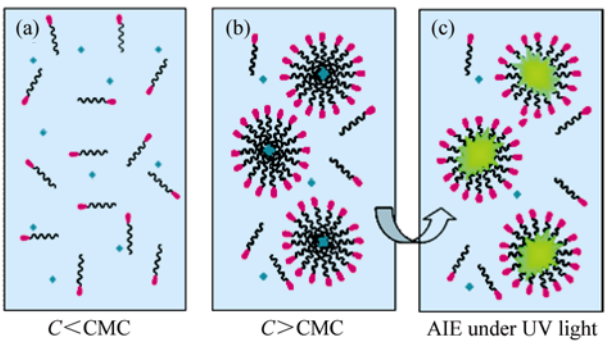

Figure 3 A schematic illustration of the detection of CMC based on the mechanism of aggregation-induced emission (AIE). The pink spindle and black ripple line stand for the hydrophilic head and hydrophobic tail of a surfactant molecule, and the blue diamonds and green burst-stars the AIE molecules and light emission, respectively.

The formation of micelles encapsulating **M1** aggregates was further proved by TEM images. The characteristic morphology of the entities derived from the solution containing 10^{-4} mol·L^{-1} **M1** and 0.6 mg·mL^{-1} CTAB is dominated by nanoparticles, which are embedded with smaller particles (Figure 4(a)). While at higher [CTAB], e.g. 1 mg·mL^{-1}, the morphology is characterized by pupa-like entities with smaller aggregated particles in the core (Figure 4(b)). It is well known that micelles transform from a spherical to a cylindrical shape when the concentration of surfactant is much higher than CMC. Therefore, we can assign the spherical and cylindrical entities with lower contrast and the smaller particles with higher contrast to micelles and **M1** aggregates, respectively.

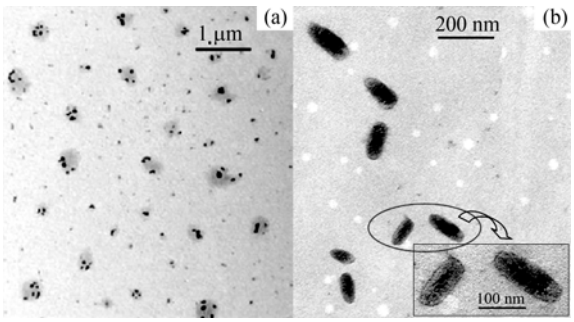

Figure 4 TEM images of the entities obtained in 10^{-4} mol·L^{-1} **M1** aqueous solution containing 0.6 (a) and 1.0 mg·mL^{-1} (b) CTAB, respectively.

3.4 Detection of the CMC value of AS with M2 as fluorescent probes

Aggregation-induced emission property of **M2** was reported in our previous paper. The fluorescence spectra of the solutions recorded at different AS concentrations ([AS]) are shown in Figure 5(a). Similar to the observation found in Figure 2(a), there is a sharp increase in fluorescence intensity when [AS] approaches to about 0.1 mg·mL^{-1}. As shown in Figure 5(b), the inflexion on the plot of the maximum on FL curves vs. the concentration of ([AS]) indicates that the CMC of AS is 0.1 mg·mL^{-1}, which is a little lower than the data reported in literature[29]. It is a common phenomenon that different methods give rise to different CMC values for the same surfactant (e.g. sodium dodecyl sulfate)[30,31]. In our case, it is noted that the CMC can also be directly determined under UV light (Figure 5(c)), and characteristic blue emission from **M2** aggregates was observed when micelles were formed in the solution.

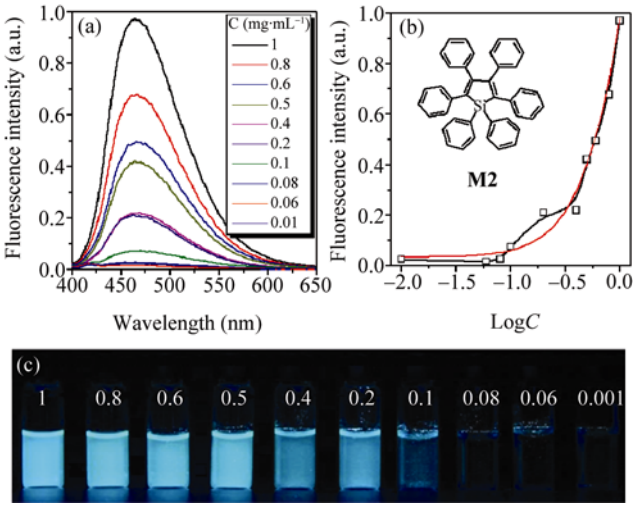

Figure 5 (a) FL spectra of the solutions with different [AS] (in mg·mL^{-1}), removing the uncapped **M2** solid by filtration; (b) plot of FL peak intensity vs lg[AS]; (c) pictures showing the emission of the solutions were taken under illumination of a portable UV lamp at room temperature.

4 Conclusions

In summary, we have demonstrated a novel method to detect the CMCs of surfactants. Experimental results have shown the following remarkable characteristics of this method. Firstly, it is a general technique working well for detecting the CMCs of both cationic and anionic surfactants. Secondly, this method has high efficiency and high sensitivity, because it relies on a fluorescence turn-on mechanism[32]. In addition, it employs an unprecedented mechanism to determine the CMC, and the results are consistent with the data obtained with other classical techniques. Finally, it is convenient for the tentative detection of the CMCs of new surfactants in laboratory. Large and professional instruments are not necessary, instead, a portable UV lamp and an ultrasonic

generator are enough to conduct the measurement. Now, we are trying to extend this method to the CMC detection of other systems with intentionally designed AIE active molecules.

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