

Research Article

A Study on the Fluorescence Properties of New Laser Material- $n\text{-B}_{18}\text{H}_{22}$ in SDS Aqueous Solution

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The effect of anionic surfactant sodium dodecyl sulfate (SDS) on the fluorescence of $n\text{-B}_{18}\text{H}_{22}$ was studied. The experimental result revealed that the fluorescence of $n\text{-B}_{18}\text{H}_{22}$ was obviously enhanced with the increase of the concentration of SDS, mainly due to the hydrophobic protection of $n\text{-B}_{18}\text{H}_{22}$ by SDS. Under the optimum conditions, the fluorescence intensity was proportional to the concentration of $n\text{-B}_{18}\text{H}_{22}$ in the range of $0\text{-}8.0\times 10^{-3}\text{ mol}\cdot\text{L}^{-1}$ and $8.0\times 10^{-3}\text{ mol}\cdot\text{L}^{-1}\text{-}3.3\times 10^{-2}\text{ mol}\cdot\text{L}^{-1}$, respectively. It was observed that a break appeared in the curve of fluorescence intensity with surfactant concentration. The critical micelle concentration (CMC, $7.9\times 10^{-3}\text{ mol}\cdot\text{L}^{-1}$) of SDS was obtained from this break point in a good agreement with the reported value. The fluorescence intensity increased initially with time and gradually stabilized. The results form the basis for further study of the properties and application of $n\text{-B}_{18}\text{H}_{22}$ in SDS solutions.

1. Introduction

Micelles are observed when the concentration of the surfactant is above the critical micelle concentration (CMC). The fluorescence probe which is sensitive to the solubilizing medium will exhibit different fluorescence behavior in micellar and nonmicellar solutions [1–5]. Since Ishibashi first introduced the surfactant into fluorescence analysis, its action mechanism between fluorescence materials and surfactant has been attracting widespread attention because of versatile practical applications of such systems [6–9]. In recent years, such reports about the fluorescence behaviors of fluorescent materials in surfactant aqueous solution have been increasing. Wu [10] reported the influence of SDS on the fluorescence properties of kinetin; in the presence of SDS, the fluorescence intensity is 9.5 times greater than that in its absence. Muthusubramanian [11] explored the twisted intramolecular charge transfer fluorescence properties of trans-2-[4-(dimethylamino)styryl]benzothiazole in SDS and bovine serum albumin (BSA) mixed solution. Laurenti [12] presented the influence of surfactant chain length and surfactant concentration on the photoluminescence (PL) of water-soluble π -conjugated poly (thienyl ethylene oxide butyl

sulfonate) (PTE-BS). Shannigrahi [13] studied the steady-state fluorescence and photophysical properties of a ketocyanine dye in binary surfactant and polymer-surfactant mixture. In 2013, Lin [14] studied the interactions between carboxymethyl chitosan and alkyltrimethylammonium bromides using fluorescence spectroscopy method.

In February 2015, in a stimulation of $n\text{-B}_{18}\text{H}_{22}$ cyclohexane solution with a nitrogen laser under $\lambda = 337.1\text{ nm}$ carried out by scientists from Czech Republic and Spain, an efficient and anti-laser light source was discovered to radiate under $\lambda = 406\text{ nm}$ [15]. This led to the development of the first borane laser based on $n\text{-B}_{18}\text{H}_{22}$, which laid the foundation for this new material that evolved into a more environmentally friendly and economical modern laser. This invention set a key milestone in the field of lasers. Since then, $n\text{-B}_{18}\text{H}_{22}$ has aroused deep interest of relevant scientists and witnessed increasingly relevant reports [16–18].

In view of the huge potential of $n\text{-B}_{18}\text{H}_{22}$ in the aspects of photoelectric materials, medicine, and material processing, it is particularly necessary to conduct a detailed study of $n\text{-B}_{18}\text{H}_{22}$ in terms of its basic properties. On the basis of the above considerations and the synthesis of $n\text{-B}_{18}\text{H}_{22}$, the investigators expect to discover appropriate surfactant

systems that could enhance the stability of $n\text{-B}_{18}\text{H}_{22}$ in water solutions and realize the fluorescence enhancement effect. The experimental results show that the addition of SDS obviously increases its fluorescence intensity and stability in SDS aqueous solutions. At the same time, the critical micelle concentration of SDS can also be determined accurately by this technique.

2. Experimental Part

2.1. Materials and Reagents. $n\text{-B}_{18}\text{H}_{22}$ was synthesized in our laboratory according to [19, 20], and SDS was obtained from Guangdong Chemical Engineering Technology Research and Development Center. All other reagents used were of guaranteed analytical grade. Ultrapure water was employed in the preparation of solutions. All working solutions of $n\text{-B}_{18}\text{H}_{22}$ and SDS were prepared by standard procedures and appropriate dilution.

2.2. Photoluminescence Instrument. Photoluminescence (PL): PL scans were obtained with Hitachi F-4600 fluorescence spectrometer. The sample molecules were excited at 360 nm, and the emission spectra were recorded with 10 nm excitation and emission slits. The scan voltage was 700 V at scanning interval of 0.5 nm and scanning speed of 1500 nm/min.

2.3. Experimental Methods

2.3.1. Synthesis of $n\text{-B}_{18}\text{H}_{22}$. The $n\text{-B}_{18}\text{H}_{22}$ adopted for the present experiment was synthesized from $\text{B}_{10}\text{H}_{14}$, according to literature [19, 20].

2.3.2. Fluorescence Measurement. A series of SDS solutions were respectively configured, and equal amounts of $n\text{-B}_{18}\text{H}_{22}$ were added in eight kinds of SDS solutions to reach a concentration of $8.96 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$. Then, the above solutions were placed in an ultrasonic tank for one hour. After standing for 30 minutes, the corresponding fluorescence spectrum was tested under indoor temperature. The stability test was performed to measure the consecutive changes of the solution's fluorescence spectrum in one week under indoor temperature.

3. Results and Discussion

3.1. Effect of SDS on Emission Spectrum of $n\text{-B}_{18}\text{H}_{22}$. The excitation wavelength selected for the present experiment was 360 nm. Figure 1 shows the fluorescence-emission spectra of $n\text{-B}_{18}\text{H}_{22}$ in aqueous solutions with different concentration of surfactants.

As shown in Figure 1, compared with the spectrum of pure water solution, the addition of SDS did not affect the characteristic emission of the spectrum with fluorescence-emission wavelengths of approximately 440 nm. However, the fluorescence intensity underwent changes to different degrees before and after the generation of micelles. Overall, the fluorescence intensity of $n\text{-B}_{18}\text{H}_{22}$ increased as the SDS

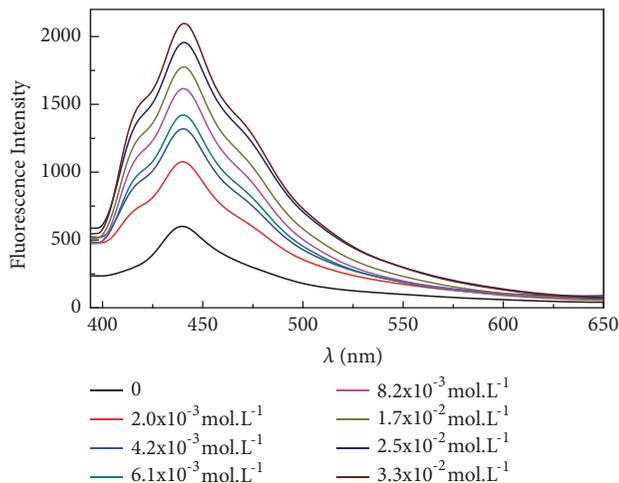


FIGURE 1: Fluorescence behaviors of $n\text{-B}_{18}\text{H}_{22}$ during the micellization of surfactant SDS in aqueous medium.

concentration increased. However, the increased ratio before and after CMC was different. When the concentration of SDS was less than the CMC, the fluorescence intensity of $n\text{-B}_{18}\text{H}_{22}$ rose rapidly with the increase of surfactant concentration. However, when the concentration of SDS exceeded its CMC, SDS formed into micelles in the solution, and $n\text{-B}_{18}\text{H}_{22}$ combined with the generated micelles, which reduced the increasing speed of its fluorescence intensity as the concentration of the surfactant increased. Changes in the fluorescence characteristics of $n\text{-B}_{18}\text{H}_{22}$ were attributed to changes of its environment. The development of the micelle enhanced photometric analysis greatly improved the photometric analysis method. Many sensitivity-enhancement mechanisms, which have been proposed in terms of the impact of surfactants on the fluorescent molecule, are related to the formation of micelles. The possible fluorescence enhancement mechanism advocated by the present study is as follows: before the formation of micelles, alkyl chains in surfactant molecules flex in the water solution to generate a hydrophobic minienvironment, providing a "solubilizing" site and a certain degree of protection for $n\text{-B}_{18}\text{H}_{22}$ and reducing its freedom of motion. The impact of the hydrophilic group coming from the water molecule and surfactant on the polarity of the surrounding environment of $n\text{-B}_{18}\text{H}_{22}$ is alleviated to protect the excited electronic state. The collisional quenching probability of fluorescent molecules under the excited state is reduced, while the fluorescence quantum efficiency increases and its intensity is enhanced, thereby realizing the dual effects of solubility enhancement and sensitivity enhancement. The formation of micelles is only the extension and strength of these effects. After the SDS concentration exceeds CMC, the increase in $n\text{-B}_{18}\text{H}_{22}$ fluorescence intensity slows down, which might result from the low intermiscibility of the trans-dual-loop structure of $n\text{-B}_{18}\text{H}_{22}$ with the internal environment of SDS micelles, making it hard for $n\text{-B}_{18}\text{H}_{22}$ molecules to effectively enter into the colloidal nucleus after the SDS forms into micelles.

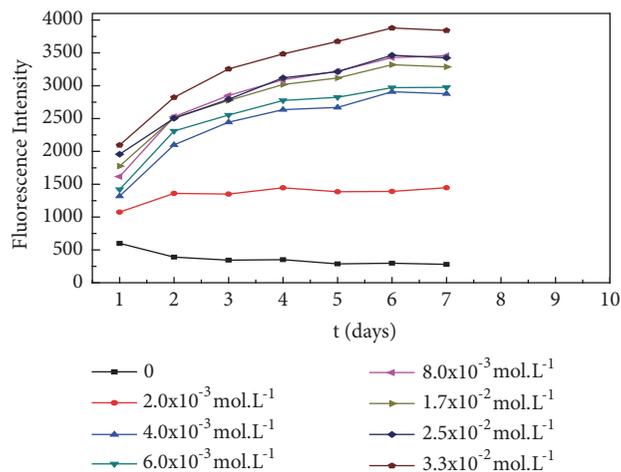


FIGURE 2: Variations of the fluorescence intensity of the SDS n - $B_{18}H_{22}$ water solution system with standing time.

Thus, the variation of the fluorescence intensity of n - $B_{18}H_{22}$ with SDS concentrations takes on a typical polyline. The inflection point of the fluorescence enhancement of n - $B_{18}H_{22}$ should correspond with the formation of micelles by SDS in the solution.

3.2. Impact of SDS on n - $B_{18}H_{22}$ Stability. Under consecutive measurement for one week, the fluorescence intensity of the surface active agent n - $B_{18}H_{22}$ water solution changes, as presented in Figure 2. As can be observed, the fluorescence intensity of the n - $B_{18}H_{22}$ pure water solution decreased slowly as the standing time increased. Furthermore, the falling trend of the curve slowed down as the time increased, which results from the slow hydrolysis of n - $B_{18}H_{22}$ in water. Compared with pure water solution, the fluorescence intensity of the surfactant- n - $B_{18}H_{22}$ water solution system was enhanced as the standing time increased, and this tended to be stable after six days. It was also observed that the fluorescence intensity of the seven different solutions (with different surfactant concentrations and the same n - $B_{18}H_{22}$ concentrations) increased by two times after standing for six days. In this paper, we think the inference mechanism of the present study is that it takes a certain time for the interaction of SDS and n - $B_{18}H_{22}$ to reach a balance. As the time increases, the interaction between surfactant and n - $B_{18}H_{22}$ becomes more complete, and the collective aggregation of n - $B_{18}H_{22}$ molecules in micelles molecular becomes more ordered and rigid, while the transfer of the nonradiation energy of the fluorescent molecule is restrained, quantum efficiency is enhanced, and fluorescence intensity is increased.

3.3. CMC Determination. Figure 3 presents the changing curve of the fluorescence intensity of n - $B_{18}H_{22}$ with the surfactant concentrations. It can be observed that, with the increase in SDS concentrations, the fluorescence intensity of n - $B_{18}H_{22}$ steeply rose up, and when the SDS concentration reached certain concentration, this increasing trend slowed down and a catastrophe point occurred on the curve. The

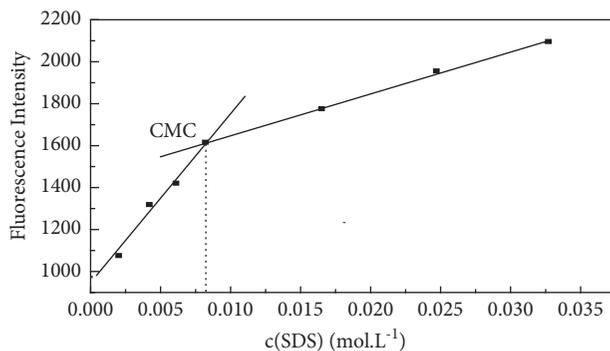


FIGURE 3: Plot of fluorescence intensity versus SDS concentration at 298 K.

concentration at which the break occurs should correspond to the critical micelle concentration (CMC). The intersection of the best fit lines drawn through the data points corresponds to $7.9 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ and is the CMC value of SDS. The CMC obtained by the technique is consistent with previously reported CMCs (8.3 mM reported in literature [21]). It is a comparatively mature method to represent CMC with the catastrophe point in the variation of the fluorescence intensity of the probe molecule along with the surfactant concentration [22–25]. The CMC obtained by our method adopted in the present study is consistent with those obtained by other methods, which testifies the reliability of this method.

4. Conclusion

The present study investigated the interaction of n - $B_{18}H_{22}$ with surfactant SDS micelles; there is a highly sensitive correlation between the fluorescence intensity of n - $B_{18}H_{22}$ in water and the formation of surfactant micelles. This can be utilized to represent the CMC of surface active agent SDS. In addition, the addition of surfactant SDS significantly enhances the stability of n - $B_{18}H_{22}$ in water. The n - $B_{18}H_{22}$ and SDS system possess potential application values in the aspects of fluorescence probe and molecular fluorescence sensors. The related research has laid the foundation for extending the application of octadecaboranes in aqueous solution.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

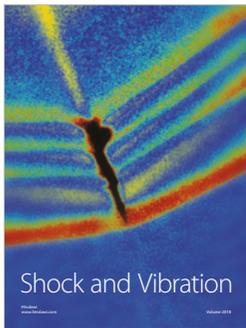
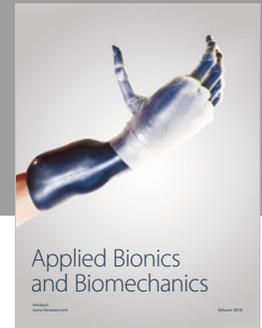
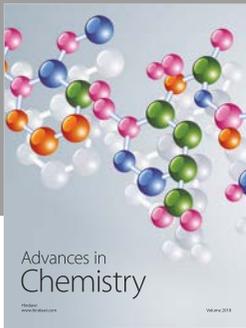
The authors declare that they have no conflicts of interest.

Acknowledgments

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