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A novel surfactant-like fluorophore and its probing ability to the aggregation of amphiphilic compounds

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ABSTRACT

A novel surfactant-like non-ionic fluorophore, 3-(bis(2-hydroxyethyl)amino)-*N*-(4-(pyrene-1-sulfonamido)butyl) propanamide (PSDA-DEA), was designed and prepared. Fluorescence and surface tension studies revealed that the fluorophore aggregates in aqueous medium, and its critical aggregation concentration (CAC) is $\sim 3.3 \times 10^{-5}$ M. Cryogenic transmission electron microscopy (cryo-TEM), dynamic light scattering (DLS) and atomic force microscopy (AFM) measurements demonstrated that the diameter of the aggregates as formed is of a few hundred nano-meters. It was also shown that the profile of the emission spectrum of the compound is well dependent upon the polarity of its medium, as indicated by a change up to 53% of its intensity ratio at 399 nm and 380 nm (I_{399}/I_{380}) when the solvent changed from water to ethanol. It is of the polarity sensitive property that the fluorophore can be used for monitoring micelle formation of several anionic, cationic and non-ionic surfactants. Furthermore, PSDA-DEA is also a valuable probe for sensing transition of different aggregates such as micelles to vesicles. Comparative studies demonstrated that the present probe is more versatile than pyrene when it is used as a fluorescence probe.

1. Introduction

Abundant information relevant to intra-/inter-molecular interactions and supramolecular aggregation and dis-aggregation of organic molecules can be obtained by utilization of fluorescence techniques [1–4]. This is because compared to other techniques, fluorescence techniques possess a number of superiors including but not limited to multiples in parameters, which can be selected for meeting different purposes, abundance in fluorophores, which are the bases for the techniques to find a wide variety of applications, and easiness in use, etc. In addition, the techniques are sensitive to small changes in the micro-environment of the relevant fluorophores. However, selection of a suitable fluorophore is a priority for the successful utilization of the techniques. Practically, these fluorophores can be introduced into the systems to be studied either as probes or as labels [1,5–8]. For a fluorophore to be used as a label, it must be chemically attached at a specific position of a system to be studied, but for the one to be used as a probe, it is, as a general practice, simply introduced in a physical way.

In the studies of various aggregates, such as micelles, vesicles and lamellar phases, traditional methods including electron microscopy and light scattering can only provide limited information about the structures of the aggregates at a molecular level. Different from the methods as mentioned, fluorescence probes are highly sensitive to the changes of the properties of their micro-environment, such as micro-polarity and micro-viscosity, and thereby they can provide more detailed information of the systems under study [1,5,6,9–13].

In the studies of amphiphilic aggregation, positioning of the fluorescence probe in the aggregates is a key issue. However, for most commercially available probes, they are not ideal for this kind of studies because the fluorescence parameters recorded are combinations of the contributions from the molecules of the probes directly sensing the process and those far away from the process. As an example, pyrene and 1,6-diphenyl-1,3,5-hexatriene (DPH) have been widely used to determine the critical micelle concentration (CMC) of various surfactants since they are typical polarity or mobility probes [4,14–16]. These probes, however, are only effective for monitoring formation of micelles of surfactants, and display poor ability to probe transformation of different aggregates of them. To improve the performances of pyrene-like known fluorescence probes in monitoring formation of complex aggregates of surfactants, various efforts have been made [14,17,18]. One of the strategies to solve this problem is to use fluorescence probes which behave as surfactants in aqueous medium. It is believed that this kind of fluorescence probe may take part in the formation of the aggregates, and thereby provides reliable

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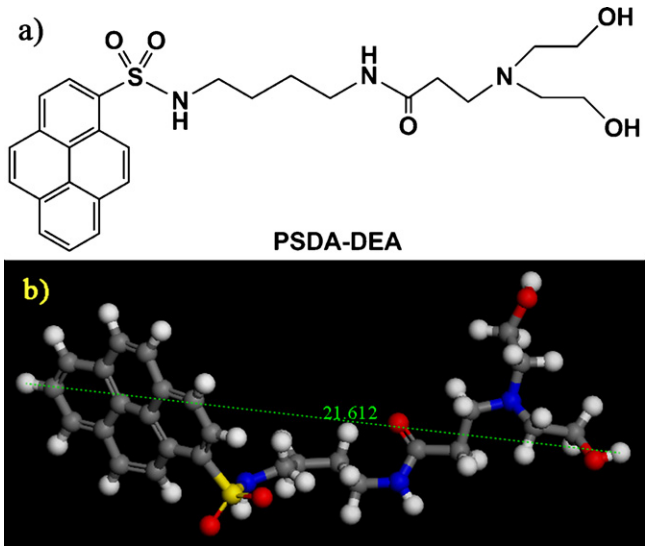

Scheme 1. (a) Structure of the PSDA-DEA and (b) molecular dynamics modeling of the PSDA-DEA.

information which is directly relevant to the formation and structures of the aggregates. For example, Huang and co-workers [19] designed an anionic surfactant-like fluorescence probe, sodium 12-(*N*-dansyl)aminododecanate (12-DAN-ADA), which well remains the polarity and viscosity sensitive properties of dansyl, a key structure of the probe, in aqueous medium. It was shown that the emission maximum and fluorescence anisotropy of the probe changes greatly along with transformation of the aggregates from micelles to vesicles, a change hardly observed by employing pyrene or DPH as a probe [14,16]. However, the probe reported by them cannot be used for monitoring aggregation of cationic surfactants in aqueous medium due to electrostatic attraction between the probe and the surfactants. Even so, Huang's probe is still distinctive. This is because in the design Huang and co-workers put intentionally the dansyl group at the far end of the surfactant tail. It is believed that this design may report changes occurring in the most interior of the aggregates under study.

It is well known that the aggregation behavior of surfactants in aqueous medium is usually complex and depends strongly on their structure and solution conditions. Therefore, interrogation of the processes and the details of the structures of the assemblies need various approaches. For fluorescence techniques, there must be no universal probes, and thereby a probe library needs to be built. Based upon these considerations, a novel non-ionic surfactant-like fluorophore, PSDA-DEA (Scheme 1a), was designed and synthesized in the present work. Its aggregation behavior has been investigated, and its application in probing formation of micelles and their transformation to vesicles of some surfactant systems was also studied. As expected, this probe is more adaptive and displays superior probing abilities to the aggregation of various surfactants and to the transformation of different aggregates of some surfactant systems. It is believed that this finding is of values for exploring details of aggregation and aggregate structures. This paper reports the details.

2. Materials and methods

2.1. Materials

Acryloyl chloride (AC, Sinopharm Chemical Reagent Co., 98%) was distilled at reduced pressure before use. Pyrenesulfonyl chloride (PSC) was synthesized by adopting a literature method [20]. 1,4-Diaminobutane (Acros, 99%) and diethanolamine (DEA, 99%) were used as received without further purification. Triethylamine (TEA) was vacuum distilled over CaH_2. Sodium dodecyl sulfate (SDS, 99%) and polyoxyethylene (10) isooctylphenyl ether (Triton X-100, 99%) were purchased from Acros, and were used as received without further purification. Dodecyltrimethylammonium bromide (DTAB, 99%) and dodecyltriethylammonium bromide (DEAB, 99%) were synthesized from *n*-alkyl bromide and corresponding trialkylamine. These two products were re-crystallized from acetone–ethanol for five times. The purity of all the synthesized cationic surfactants was examined and no surface tension minimum was found in the surface tension curve. Other starting materials were purchased commercially and used as received. Solvents were of analytical grade, unless otherwise noted. Water used throughout was de-ionized and then double distilled.

2.2. General instruments

^{1}H NMR and ^{13}C NMR spectra were recorded by a Fourier Digital NMR spectrometer (AVANCE 300 MHz, 300 MHz) in $CDCl_3$, and chemical shifts are reported in parts per million relative to TMS in proton spectra. All ^{13}C spectra were determined with complete proton decoupling. Dynamic light scattering (DLS) measurements for aggregate diameters were determined by BI – 90Plus laser particle size analyzer (Brukerhaven Instrument, USA) equipped with a 15 mW solid-state laser (659 nm). AFM measurements were conducted on a SOLVER P47 PRO system. The sample was prepared by drop casting the dilute aqueous solution of PSDA-DEA (5×10^{-5} M) onto a freshly cleaved, mica surface. For cryogenic transmission electron microscopy (cryo-TEM) characterization, samples were prepared in a controlled environment vitrification system (CEVS) at preset temperature. Typically, a 5 μL sample solution was loaded onto a carbon-supported lacey TEM grid, which was held by tweezers. The excess solution was blotted with a piece of filter paper, resulting in the formation of thin films suspended on the mesh holes, and the samples were quickly plunged into a reservoir of liquid ethane (cooled by liquid nitrogen) at its melting temperature. The vitrified samples were then stored in liquid nitrogen until they were transferred to a cryogenic sample holder (Gatan 626) and examined using a JEM 2200FS TEM (200 keV) at about −174 °C. The phase contrast was enhanced by under focus. The images were recorded on a Gatan multiscan CCD and processed with Digital Micrograph.

All of the fluorescence measurements were conducted with a time-correlated single photon counting Edinburgh FLS 920 fluorescence spectrometer at room temperature (25 °C). The path length of the quartz cell is 1 cm. The samples containing PSDA-DEA and pyrene were both excited at 345 nm and determined at 380 nm. Fluorescence lifetimes were calculated from time-resolved fluorescence intensity decays using an FLS 920 fluorescence spectrometer in the time-correlated single-photon-counting mode. FLS 920 is equipped with a thyratron-gated nanosecond flash lamp filled with hydrogen as the plasma gas (0.38–0.40 bar) and is operated at 40 kHz. For each measurement, at least 5000 photon counts were collected in the peak channel to ensure the decay quality. The value of χ^2, which is an indicator of the goodness of fit to a decay curve, is close to 1, and generally it is less than 1.2.

2.3. Experimental method

Stock solutions (1.0×10^{-3} M) of the fluorophores, PSDA-DEA and pyrene, were prepared in water and ethanol, respectively. A certain amount of pyrene stock solution was added to a volumetric flask and heated slightly to remove the solvent. Then the final concentration of pyrene solution was adjusted by adding an