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# Fluorophotometric determination of critical micelle concentration (CMC) of ionic and non-ionic surfactants with carbon dots via Stokes shift

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## ABSTRACT

A new and facile method for the determination of critical micelle concentration (CMC) of ionic and non-ionic surfactants is proposed in this article. Carbon dots exhibited substantial fluorescence and therefore enhanced the sensitivity of this evaluation. Understanding the formation of surfactant micelles is vital for the applications of biomedicine such as drug fabrication and smart molecular vehicles in delivering therapeutic dosage to various molecular sites. The fluorescence property of carbon dots was utilized for the first time to estimate the critical micelle concentration of surfactants. The central concept of the approach is based on the Stokes shift determination of a system composed of constant amount of carbon dots with varying concentrations of ionic and non-ionic surfactants. The synthesized carbon dots were characterized by FTIR, TEM, XRD, Raman, UV, and fluorescence spectroscopy. The carbon dots were excited at 280 nm so as to obtain maximum emission for the Stokes shift measurement. The CMC value of cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS), Triton X-100, dodecylmethyl(3-sulfopropyl)ammonium hydroxide (SB-12) evaluated by this approach was found to be 0.98, 7.3, 0.19, and 3.5 mM, respectively. The signals of spectra were assigned and explained in terms of both electron transitions between specific molecular orbital and the interaction with solvent.

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## 1. Introduction

Surfactant is a unique group of compounds containing both a hydrophobic long-chain (tail) and a hydrophilic polar group (head) in their structures [1,2]. When the concentration reaches a specific narrow range, called critical micelle concentration [3], the molecules tend to self-associate with tails aggregating inward into an assembled micellar structure which is favored thermodynamically in polar solvents [4]. The formed micelles have a center of hydrophobic (tail) moiety and an outward head (hydrophilic) moiety took place in a continuous phase generally observed in aqueous phase. In contrast, when the outer portion of micelles is comprised of tail (hydrophobic) moiety and the head moiety

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assembled in center of the micelles it is called as the reverse micelle which is formed in oil phase. In this study all the experiments were specifically conducted in aqueous phase. The formed micelle has been described as structure of aggregate; it has characteristically various interactions such as hydrophobic, electrostatic interaction and hydrogen bonding. These micelles comprise unique characteristics such as uniform nanosize, core-shell structure, and being stable thermodynamically in physiological conditions due to their low critical micelle concentration [5,6]. With this amphiphilic structure, surfactants have been extensively employed in applications including the fields of chemistry [7], biotechnology, and pharmacy [8]. A variety of surfactants have been utilized with their capability to enhance the permeability of drugs across biological membranes [9]. In complex systems, surfactants were widely used in membrane protein separation, crystallization, purification and stabilization. Since the physicochemical properties of solutions below and above CMC demonstrate drastic changes, such as surface tension, electrical conductivity,

turbidity, osmotic pressure, density, viscosity, and light scattering [10]. Many methods have been proposed to determine the CMC of plethora of surfactants, e.g. spectrophotometry [11], colorimetric [12], potentiometry, refractometry, conductometry, capillary electrophoresis, light scattering [13], pyrene 1:3 ratio method [14], and so forth. Among these methods, spectrophotometry is a simple and reliable tool for determination of CMC. Due to the outstanding fluorescence exhibited by carbon dots (C-dots) [15], the nanodots were introduced in an attempt to enhance the sensitivity for the fluorophotometric determination of CMC.

Most of the methods reported for the determination of critical micelle concentration have several disadvantages such as low sensitivity, the necessity of dye or probe, large volume of sample, tedious experimental techniques as well as the interpretation tools required. Additionally, some methods are particularly applicable to the CMC determination of a specific surfactant which is one of the major drawbacks of those methods [16]. In the present work, in order to solve these problems, we have developed a modified technique based on the fluorescence and the Stokes shift of C-dots, which is one category of highly fluorescent materials based on carbon materials [17] to investigate the CMC of CTAB, SDS, Triton X-100, and SB-12.

C-dots are growing popular among the families of quantum dots because of the excellent optical and biomedical properties [18]. The advantages of being able to emit intense and tunable photoluminescence (PL) have made C-dots to be a favorable ingredient for the applications in the fields of catalysis and energy [19]. Additionally, carbon quantum dots demonstrated special characteristics, e.g. non-blinking, high aqueous solubility, and non-toxicity [20]. There are many established protocols for the synthesis of amorphous as well as crystalline C-dots using facile routes such as thermal cracking of organic compounds [21], microwave mediated synthesis [22], laser ablation of graphite [23], electro-oxidation of graphite, and oxidation of candle soot [24].

The central concept of this work is based on the Stokes shift, the difference of peak maxima in excitation and emission spectra [25], of C-dots in the presence of varying concentration of surfactants. The C-dots decorated with both positive as well as negative charged moieties were found to be efficiently interacting with charged or non-charged head group surfactants. This phenomenon leads to the exhibition of sharp Stokes shift in the presence of the surfactants. Herein, cationic cetyltrimethyl ammonium bromide (CTAB), anionic sodium dodecyl sulfate (SDS), non-ionic Triton X-100, as well as zwitterionic dodecyltrimethyl (3-sulfopropyl)ammonium hydroxide (SB-12) surfactants were investigated and the CMC were evaluated. Note that this zwitterionic surfactant has seldom been studied [26]. Since the zwitterionic surfactant is electrically neutral in nature, it is easily to be distinguished from others. For the determination of CMC values, the intersection of the extrapolation of curves in a graph of Stokes shift versus concentration was perceived as a point of change and was typically denoted as the CMC. All of the experiments were performed at room temperature.

## 2. Materials and methods

Sucrose was purchased from J.T. Baker (USA). Cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS), Triton X-100, sulfuric acid and sodium hydroxide were purchased from Sigma-Aldrich (USA). Quinine sulfate was supplied by Alfa Aesar (Great Britain). Dodecyltrimethyl(3-sulfopropyl)ammonium hydroxide (SB-12) was supplied by Tokyo Chemical Industry Co., Ltd. (Japan). Ultrapure water from a Milli-Q Plus water purification system (18.2 M $\Omega$ , Millipore, and Bedford, MA, USA) was used for all experiments.

### 2.1. Preparation and purification of fluorescent carbon dots (C-dots)

C-dots were prepared by controlled carbonization of sucrose modified method proposed by Minghong Wu group [27]. 2.5 g of sucrose was weighed and dissolved by adding 2 mL of deionized water. Add 3 mL concentrated sulfuric acid dropwise into the solution with continuous vigorous stirring. The yellowish brown colored reaction mixture was neutralized with sufficient amount of NaOH. The dark brown color reaction mixture was isolated by a centrifuge operated at 18,000 rpm for 10 min. It was further purified by dialysis (MW cutoff 12–14 kD) against Milli-Q water for 24 h under constant stirring condition. In order to concentrate the amount of C-dots the solution was dried in a rotary vacuum evaporator (Büchi, Germany) and frozen dried for the quantification of C-dots.

#### 2.1.1. Quantum yield measurement

The quantum yield ( $Q$ ) of the C-dots has been calculated using the following equation, Eq. (1). Quinine sulfate ( $Q$  is 0.54) was chosen as a reference to determine  $Q$ , where  $Q$  denotes for quantum yield,  $I$  represents measured integrated emission intensity,  $n$  denotes the refractive index, and  $E$  is the optical density.  $R$  represents the fluorophore of known quantum yield for reference [28,29].

$$Q = Q_R \frac{I E_R n^2}{I_R E n_R^2} \quad (1)$$

### 2.2. Determination of critical micelle concentration of surfactants

2 mg of dried C-dots was mixed with varying concentrations of CTAB, SDS and Triton X-100 and make up to 5 mL as the total volume. The stock solutions of all surfactants were prepared and used for further experiments. The concentrations of stock solutions for CTAB, SDS, Triton X-100, and SB-12 were 10 mM, 50 mM, 5 mM, and 25 mM. In case of CTAB, aqueous dilutions were prepared from 0.2 to 2 mM at the interval of 0.2 mM from a stock solution. As for SDS, 2–20 mM diluted solutions were prepared with increment of 2 mM from stock solution. In the case of Triton X-100, various dilutions prepared from 50 to 500  $\mu$ M with increment of 50  $\mu$ M from the stock solution. For SB-12, solutions were prepared from 0.5 mM to 6.0 mM with increment of 0.5 mM from the stock solution. 2 mg of highly purified C-dots was added in all the dilutions and make up the volume up to 5 mL. These solutions were sonicated for 5 min in order to equilibrate the solution. Similar procedure was followed for SDS except the dilutions were varied from 2 to 20 mM from a stock of 50 mM. 10 mM Triton X-100 stock solution was prepared and 50 to 500  $\mu$ M dilutions were prepared from the stock solution. After equilibrating the C-dots-surfactants solution, the excitations as well as the emission spectra were recorded using the fluorescence spectroscopy (Hitachi F 2700, Japan). The excitation maxima relative to emission maxima were recorded for each concentration of dilution sample.

The Stokes shift was calculated using the following equation:

$$\Delta\nu(\text{Stokes shift}) = \nu_{\text{ex}} - \nu_{\text{em}} \quad (2)$$

where  $\nu_{\text{ex}}$  and  $\nu_{\text{em}}$  refer to the excitation and the emission maximum, respectively.

From the graphical representation of the Stokes shift versus concentration, CMC values of the surfactants were evaluated.

### 2.3. Characterization of carbon dots (C-dots)

The morphology and uniformity of C-dots were measured by a high resolution transmission electron microscope (JEOL, Japan). Spectral properties of C-dots were studied by a UV–vis spectroscopy

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