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Can optical fiber compete with profile analysis tensiometry in critical micelle concentration measurement?

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Abstract: Critical micelle concentration (CMC) is one of the important nominal characteristics of the surfactants which can be measured using various methods. In this study, to detect the CMC of two ionic surfactants, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS), two methods were utilized: (a) optical fiber and (b) drop profile analysis tensiometry (PAT) techniques. The spectrum width center and surface tension of the solutions at different concentrations of the surfactant were measured. The preliminary outcomes showed a compliance between optical fiber method and PAT technique. However, there were differences in the behavior of two surfactants in optical fiber measurement. In this method, when the solid surface of fiber is put in the system, the interactions between surfactant molecules and the fiber surface must be carefully considered.

Keywords: critical micelle concentration (CMC); optical fiber; profile analysis tensiometry; surfactants.

1 Introduction

Surfactants, or surface active agents, are comprehensively involved in food, pharmaceutical, cosmetic, cleaning, petroleum, and wastewater treatment

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industries [1–8]. These substances are potentially able to alter the interfacial or surface tension. This performance is because of the adsorption of surfactants onto the interfaces such as air–liquid, liquid–liquid and solid–liquid interfaces. In case of solid–liquid interfaces, the adsorption of the surfactant molecules depends on the structural groups of the solid surface, surfactant nature, its concentration, and the aqueous phase surrounding the surfactant and solid phase [9].

Above a certain concentration of surfactants, micellization occurs in the bulk. The concentration at which micelles are formed is called the Critical Micelle Concentration (CMC). The CMC amount for each surfactant at a defined temperature is a unique parameter. The measurement of CMC, as one of the most important properties of the surfactant solutions, is necessary because it affects both interfacial phenomena such as surface tension reduction and bulk characteristics like detergency. In addition to analytical chemistry methods such as titration [10], the electrochemical techniques like conductometry, potentiometry, voltammetry, and electromigration methods have also been applied for CMC measurement [11]. However, most of these methods are sample-consuming or take a long time to be performed.

One of the conventional methods of CMC measurement is tensiometry in which the surface tension of the surfactant solutions is measured. Although this method is well-known and one of the concise ways in this area, it also requires a long time to achieve the results [12].

Optical fiber sensors have attracted research interests mainly because of low cost, small size, possibility of in-situ measurements of chemical parameters, low amount of required sample, and rugged construction [13–15]. According to these capabilities, fiber-optic sensors can be considered as an alternative in determination of the CMC of the surfactants.

In this study, the CMC of two ionic surfactants, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS), was measured using two methods: (a) optical fiber method and (b) PAT technique. To fulfill the primary purpose of this study, the results measured by the optical fiber sensor were compared to those of PAT, as a verification procedure, to evaluate the potential of optical fiber as a promising method for CMC measurements in different industrial technologies. More analysis and interpretation of data acquired by optical fiber manifested that there are more critical details in this method which must be considered in the future, but they might have been overlooked in the previous studies. These considerations will be helpful in developing the optical fiber-based methods and devices for CMC detection.

2 Experimental

2.1 Materials

A cationic surfactant, CTAB, $[\text{CH}_3(\text{CH}_2)_{15}](\text{CH}_3)_3\text{NBr}$ with a molecular weight of 364.46 g/mol, of AnalaR brand name was supplied from BDH Chemical Ltd., UK. The anionic surfactant SDS, $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}$, with 288.38 g/mol of molecular weight was purchased from Sigma Aldrich Chemie GmbH, China. Both surfactants were purchased with a purity grade $\geq 99\%$ and used as received.

Water used in solution preparation was deionized and purified by PURELAB[®] Option-Q7 (Elga LabWater, UK) system. The resistivity of the ultrapure water used here was greater than 18 M Ω cm, with a surface tension of 71.99 mN \cdot m⁻¹, without any appreciable kinetics over several hours, measured at 25 ± 0.2 °C.

2.2 Methods

The stock solutions of each surfactant, CTAB and SDS, with a concentration of 1e-1 M were prepared by dissolving the solid form of the surfactants in deionized water. Then, samples with the concentrations of 1e-2, 5e-3, 2.5e-3, 1e-3, 5e-4, 1e-4, 5e-5, 1e-5, 5e-6, and 1e-6 M were prepared from the stock solutions by dilution method. To increase the accuracy of the measurements, due to the surfactant nature it was necessary to eliminate the bubbles formed in solutions. Therefore, each solution was put in an ultrasonic bath of Fisher brand (FB15053, Fisher Scientific, UK) for mixing and degasification.

The optical fiber sensor used in the experiment was a singlemode-no core-singlemode (SNCS) fiber structure, where a short section of silica no core with a diameter of 125 μm was fusion spliced between two traditional single mode fibers [16]. The length of the sensing region was 5 cm. The optical spectrum analyser (OSA), model AQ6370C, with a working range of 600–1700 nm (Yokogawa Test & Measurement Corporation, Japan) and a superluminescent diode (SLD) as the light source of a class 1M laser working in the range of 1450–1660 nm were used for optical fiber measurements. An aluminum cell with one facet open to air was applied as the bed and container of the surfactant solutions in direct contact with the optical fiber. The spectrum width center, λ_c , as the response of this set-up (Figure 1) was measured four times for each solution at room temperature.

The surface tensions of the solutions were measured using a Profile Analysis Tensiometer (PAT1M, SINTERFACE Technologies, Germany) using the pendant drop mode (Figure 2). In profile analysis tensiometer (PAT), the solution is pumped into a syringe and pumped out through the tubes into a steel capillary where a drop is formed at its tip. Drop profile analysis used in PAT

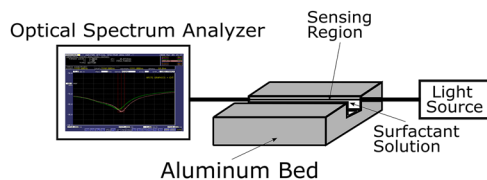


Figure 1: Measurement set-up using the optical fiber.

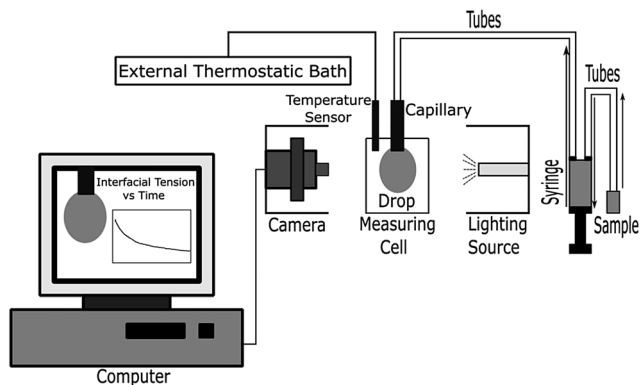


Figure 2: A schematic diagram of the profile analysis tensiometer (PAT) set-up.

utilizes the shape of a pendant drop to determine the surface tension of it. In fact, the software connected to the instrument determines the coordinates of the drop and fits the Gauss–Laplace equation to the drop profile.

In this work, the capillary radius was 1 mm and the formed drop on the tip was of a constant area of 25 mm^2 . The temperature was set stable at $25 \pm 0.2 \text{ }^\circ\text{C}$ by a water bath. The measurement of surface tension for each sample was repeated three times. Data analysis and statistical studies were performed using Minitab® 18 Statistical Software [17]. The IsoFit program was applied for fitting the Frumkin model, as one of the adsorption isotherm models, to the experimental data [18].

3 Results and discussion

3.1 Results

The spectral responses and central wavelength shift, λ_c , of the optical fiber sensor at different concentration of surfactant in aqueous solutions were plotted (Figure 3a, b). As the graphs showed, the trend in the behavior of λ_c is suddenly altered in the vicinity of a specific concentration in both, CTAB and SDS, cases. In first step, we assumed that this concentration is the CMC as it has been shown in Figure 3. At the concentrations less than CMC, there was a linear trend while it changed to logarithmic relationship at the concentrations higher than CMC. The interceptions of the trendlines resulted in achieving the CMC by this method. For CTAB and SDS, the CMC amounts attained by optical fiber method were $1.60\text{e-}3 \text{ M}$ and $6.50\text{e-}3 \text{ M}$, respectively.

In the next step, CMC of each surfactant was determined by measuring the dynamic surface tension using PAT. The surface tension was plotted versus concentration for each type of pure surfactant, CTAB and SDS. As Figure 4

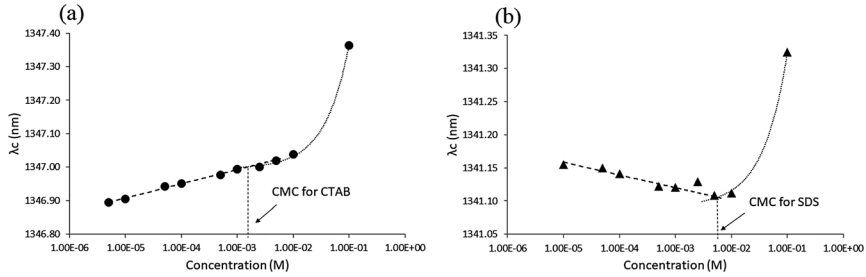


Figure 3: Spectrum width center versus surfactant concentration for (a) cetyltrimethylammonium bromide (CTAB), and (b) sodium dodecyl sulfate (SDS).

demonstrates, two main regions can be recognized for any individual surfactant. The first one is a concave-shaped curve zone. The data in this region can be fitted to an adsorption isotherm model. The second region where the graph reaches the plateau indicates that CMC has been reached. The CMCs for CTAB and SDS using PAT were 1.30×10^{-3} M and 4.23×10^{-3} M, respectively.

3.2 Discussion and conclusion

By plotting the outputs of optical fiber set-up, λ_c , against the concentration of surfactant solutions, the concentration values at which there was a sudden change in λ_c trend were attributed to the CMC of each surfactant. These amounts of CMC obtained by optical fiber method were approximately in the range of the CMC values achieved by PAT technique known as a reliable method of CMC detection.

In optical fiber sensor measurement, although there was a similarity between two surfactants in terms of the sudden change in the optical fiber output trend as

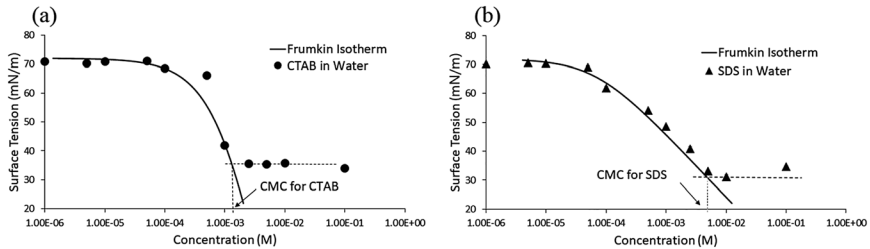


Figure 4: Surface tension against concentration of the surfactant for (a) cetyltrimethylammonium bromide (CTAB) and (b) sodium dodecyl sulfate (SDS). The method to find the CMC for each surfactant is to intercept the curve with the dashed line.

an indicator of the CMC, the behavior of λ_c at the concentrations below CMC was completely different. For CTAB, λ_c was increasing while it was decreasing for SDS. The reason of opposite wavelength shift for the two surfactants at the concentrations below CMC is not clear and further study in explaining this phenomenon is in progress.

The first hypothesis for this difference between CTAB and SDS can be attributed to the various mechanisms of adsorption of each surfactant onto the sensing region of the fiber – this mechanism affects the refractive index and effective diameter which, in turn, results in different wavelength shifts for various surfactants. The solid surface of the fiber is exposed to the surfactant molecules. Based on the material used on the outer layer of the fiber (its functionalization), as well as the hydrophobic and/or electrostatic interactions among the surfactant molecules and solid surface of the fiber determine the mechanism of the adsorption onto the solid surface.

In this experiment, the fiber was made of silica which can be either hydrophilic or hydrophobic. In the case of hydrophobic silica, it may seem that there should be no difference between cationic and anionic surfactants. However, this assumption is not correct as there are still discrepancies between CTAB and SDS in terms of the length of the hydrophobic group and size of the surfactant's head which leads to differences in the packing of surfactant molecules on the presumably hydrophobic surface of the fiber. In case of hydrophilic surface of the fiber, it can be either positively or negatively charged. This will also result in different mechanisms of adsorption due to the usage of ionic surfactants (anionic SDS and cationic CTAB) with various charges of the head groups. If there is an electrostatic attraction between the headgroup of the surfactant and the surface of the fiber, there is a possibility of the formation of the bilayers of surfactant onto the surface of the fiber which definitely affects the fiber and the output. This can happen at higher concentrations of the surfactant.

According to the mentioned points about the interactions of surfactant molecules and solid surface of the fiber, the different adsorption mechanisms and colloidal structures in the liquid for each surfactant might be the source of the different trends of what was observed in Figure 3.

Therefore, the design of the future studies will be based on the below considerations:

- The principle of optical fiber sensor method is that the attachment of surfactant molecules on the fiber surface will introduce refractive index and effective diameter changes to the fiber sensor and, thus, the measured wavelength shift [19–22]. Further studies related to these interactions of surfactant molecules and optical fiber will focus on measuring the below parameters and factors:
 - 1) The hydrophilicity/hydrophobicity of the optical fiber,

- 2) The zeta-potential of the solid surface of the optical fiber,
 - 3) The thickness of the fiber after interactions with surfactant molecules,
 - 4) The refractive index differences between CTAB and SDS, and
 - 5) The amount of the surfactant adsorbed onto the fiber sensor at different concentrations.
- In the optical fiber sensor technique, two different interfaces can be determined. The first one is the solid–liquid interface between the optical fiber and solutions, and the second one is the air–liquid interface between air and solutions. The tendency of surfactant molecules towards these interfaces and the adsorption competition between these interfaces might affect the output of the optical fiber. Therefore, further study will be designed to eliminate air–liquid interface, introducing a closed volume as the bed of optical fiber in which the fiber can be immersed and the temperature can be controlled.
 - Due to the limited wavelength shifts before CMC for both CTAB and SDS surfactants, there is a possibility that the observed opposite wavelength shifts is a measurement error. To improve the sensitivity of the fiber, a tapered SNCS fiber sensor, that has 10 times higher sensitivity than that of the normal SNCS fiber sensor, will be used to study the CMC of the surfactant solutions. This will significantly improve the measurement accuracy and minimize measurement error.

The above-mentioned points can be categorized in three sections that have been shown in Figure 5.

In summary, in the experimental set-up the optical fiber sensor measurements were used to introduce a feasible and convenient method to detect the CMC of bare surfactant solutions. Two ionic surfactants, CTAB and SDS, were utilized as

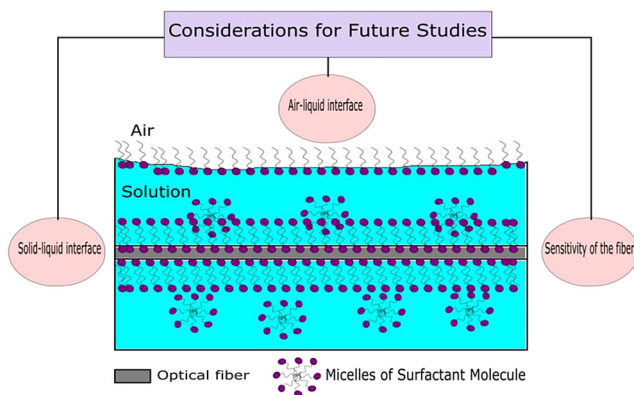


Figure 5: The main considerations for the future studies.

aqueous solutions with various concentrations. An SNCS fiber structure was used as an optical fiber sensor to monitor the behavior of the investigated solutions.

Then, the results of this method were compared to surface tension measurements obtained using a well-known drop Profile Analysis Tensiometry, PAT. The CMC of both surfactants at 25 ± 0.2 °C were experimentally determined by means of PAT. The values of the CMC obtained by both methods were approximately identical. This indicates that due to their sensitivity, optical fiber sensors are very promising in detection of the changes in the surfactant solution, which means they could be applied as an alternative method for CMC detection, in the future. However, there are critical considerations about the interactions between surfactant molecules and the fiber which should not be overlooked in the design of experiments.

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