Eureka Moment: An Archimedean Alternative for the Determination of \( \text{cmc} \) of Surfactants via Weight Measurements

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ABSTRACT: Critical micelle concentration (\( \text{cmc} \)) is a key parameter of generally used surfactants, and many experimental techniques like tensiometry, conductivity, spectrophotometry, fluorometry, etc. for its determination have been reported. However, these contemporary methods for \( \text{cmc} \) determination are tedious, are time-consuming, are sensitive, and require sophisticated instrumentation. Herein, we demonstrate that the \( \text{cmc} \) of the surfactants can be estimated via monitoring the variation in the apparent weight of a density bottle floating in a surfactant solution as a function of surfactant concentration. The proposed method requires the use of a simple weighing balance; a cost-affordable instrument always available in scientific laboratories. The proposed method is simple to execute and does not require any complicated data analysis procedures. As an experimental proof attached to the claim, we demonstrate the estimation of the \( \text{cmc} \) of all types of surfactants, viz., anionic, cationic, and nonionic, through the formulated method. The results obtained in terms of \( \text{cmc} \) values of the chosen surfactants closely match those reported through the use of different standardized protocols. The formulated experimental protocol is desirable in terms of the simplicity of the protocol, accuracy, and reproducibility of the results, and cost and accessibility of the required instrument. All these attributes of the presented protocol qualify it as an appropriate substitute to the modern techniques commonly used for the \( \text{cmc} \) determination.

1. INTRODUCTION

SURFace ACTive AgeNTs (surfactants) represent a unique class of amphiphilic chemical substances encompassing a hydrophobic “tail” attached to a hydrophilic “head group”.\(^1−3\) In polar solvents, for example, water, this dual character of amphiphiles leads to a spontaneous self-association or micellization of their monomers into organized molecular assemblies known as micelles. The process of micellization occurs over a narrow range of concentration recognized as the critical micelle concentration (\( \text{cmc} \)) of the surfactant.\(^1−3\) The \( \text{cmc} \) is an important physicochemical parameter used by surface scientists to reﬂect their surface activity and self-aggregation tendency. The \( \text{cmc} \) value of a surfactant reﬂects the stability of its micelles and serves as one of the important parameters to assess their suitability and efﬁciency for the desired applications. The experimental protocols of almost all of the methods proposed for the estimation of \( \text{cmc} \) require the estimation of a particular physicochemical property of surfactant solutions as a function of the concentration of the surfactant. The apparent concentration dependence of any physicochemical property chosen for the estimation of \( \text{cmc} \) is observed to be different for pre- and postmicellar concentrations. The concentration corresponding to the inﬂection point in the physicochemical property vs surfactant concentration plots recorded during these experiments is therefore taken as the \( \text{cmc} \) of the surfactant. Often, the estimation of the \( \text{cmc} \) value from the recorded experimental data requires the use of complicated data manipulation and curve-ﬁtting procedures that reduce the accuracy of the ﬁnal result. The physicochemical properties of the surfactant solutions that have been explored so far for the estimation of the \( \text{cmc} \) value include surface tension, conductivity, density, viscosity, ﬂuorescence, UV−vis absorption, electron spin resonance, X-ray diﬀraction, nuclear magnetic resonance, potential changes, osmotic pressure, spreading oil drop method, high-resolution ultrasound spectroscopy, etc.\(^2−18\) Experiments related to the onset of micellization and estimation of the \( \text{cmc} \) represents an elementary and fascinating laboratory exercise that is much needed for practical applications in surface science.\(^4−18\) In this regard, the existing experimental techniques/methods like tensiometry, electrical conductivity, ﬂuorescence spectroscopy,
UV−vis absorption spectroscopy, capillary rise, wet-angle methods, spreading oil drop method, high-resolution ultrasound spectroscopy, etc. devoted to the estimation of the cmc of the surfactant solutions have been the subject of numerous reports related to basic and applied surface science research works. Very recently, Castro et al. reported the design of an interesting experimental setup for the estimation of the surface tension and cmc of surfactant solutions via maximum bubble pressure measurements. Dominguez et al. have demonstrated the use of UV−vis absorption spectroscopy, fluorescecence spectroscopy, and electrical conductivity for the estimation of the cmc of surfactants. Bresler and Hagen have suggested a simple tensiometric protocol for the estimation of surface excess and the cmc using DeNouy ring detachment method. Very recently, Deodhar et al. formulated a new method to determine the cmc via oil drop spreading over surfactant solutions, and in another study, Perinelli et al. reported the estimation of the cmc through the use of high-resolution ultrasound spectroscopy. However, the estimation of the cmc through the use of the above-mentioned methods/properties often requires either sophisticated, costly, and sensitive equipment or sometimes an intricate mathematical manipulation like differential derivatives/deconvolutions and dynamic simulations of the recorded experimental data. The use of such sensitive instruments necessitates significant technical training, which demands enough time and labor. The above-cited facts/literature warrants the need for the design of a simple-to-execute, cost-effective experimental protocol with higher accuracy and efficiency for the estimation of the cmc of surfactant solutions irrespective of their nature, viz., cationic, anionic, and nonionic. The present study demonstrates a simple, economical, easily accessible, and reliable experimental setup/method for the estimation of the cmc of the surfactants. The devised method for the cmc estimation is based on the measurement of the apparent weight of a density bottle floating in a surfactant solution as a function of the surfactant concentration via a simple weighing balance. The working principle of the method approximates that the concentration dependence of the interfacial tension/buoyant force experienced by a floating object in a surfactant solution must be different in the pre- and postmicellar concentrations. The cmcs estimated for some model surfactants through the devised method match closely with those reported through different standard protocols. The formulated experimental setup/method is preferable in terms of handling, accuracy, cost, and accessibility, which makes it appropriate for cmc determination.

2. EXPERIMENTAL SECTION

2.1. Materials. Chemicals used in the present study: tetradecyltrimethylammonium bromide (TTAB, 99%), sodium dodecyl sulfate (SDS, 98%), and (Brij56, 98%). All of the chemicals were procured from Sigma-Aldrich with ACS reagent grade purity and used as such without any further purification. Deionized water was used throughout the study.

2.2. Method. A pictorial representation of a homemade experimental setup designed for the estimation of the cmc of surfactant solutions via the proposed method is depicted in Figure 1. The setup includes a weighing balance (Schimadzu, AUW220D), a beaker (100 mL) with a stand to hold it without touching the weighing pan, and an additional stand placed on the weighing pan for hanging a density bottle via a pulley into the surfactant solution placed in the beaker. With this kind of setup, the buoyancy and interfacial tension affected apparent weight of the density bottle floating in the surfactant solution can be estimated with an accuracy dictated by the accuracy of the weighing balance. To estimate the cmc of the surfactant solution, the beaker inside the balance was filled with 20 mL of triply distilled water and placed on the beaker stand. A density bottle was hung from the other stand (resting on the weighing pan) in such a way that it floated over the liquid content placed in the beaker. This arrangement allows the determination of the apparent weight of the density bottle from the weighing balance. A stock solution of each of the surfactants used, viz., SDS (250 mM), TTAB (150 mM), and Brij56 (15 mM), was prepared in water. Incremental additions of the stock solution of the surfactants were made to the beaker contents, and the apparent weight of the density bottle was recorded after each addition.

3. RESULTS AND DISCUSSION

Critical micelle concentration (cmc) is a fundamental characteristic of the surfactants; quite often used to reflect/evaluate their ability to adsorb across interfaces and form micellar assemblies in interfacial science and engineering applications. Experimentally, the cmc of any surfactant is determined graphically by plotting the magnitude/variations of an appropriate physical property as a function of surfactant concentration. The data corresponding to the chosen physical property obtained through the corresponding method/technique usually fits into two straight lines with different slopes for the pre- and postmicellar concentrations. The concentration corresponding to the intersection point of these two straight lines on the concentration axis represents the cmc of the surfactant solution. The physical property that is monitored as a function of surfactant concentration in the present study is the apparent weight of an object floating in a surfactant solution. The apparent weight of the density bottle is expected to be different than its actual weight because of the buoyancy and interfacial forces that it experiences while
The experimental protocol described in the present study provides a simple-to-operate, cost-effective, and easy-to-access method with good accuracy for the estimation of the cmc of surfactant solutions through the use of a simple digital weighing balance. For experimental demonstration, cms of three model surfactant solutions, viz., SDS, TTAB, and Brij56, were estimated using the devised method and the estimated cms are in unison with the cms for these surfactant solutions reported in the literature.

4. CONCLUSIONS

The variations of both these properties as a function of surfactant concentration have been employed for the estimation of the cmc. Hence, the interfacial tension and buoyancy impact on the apparent weight of the floating object is expected to be very different for the pre- and postmicellar concentrations of the surfactant. Therefore, a plot of the apparent weight of the object floating in the surfactant solution as a function of the latter’s concentration should exhibit a breakpoint at a concentration corresponding to the cmc of the surfactant in the solution. To estimate the cmc of the selected surfactant through the proposed method, the apparent weight of a properly cleaned density bottle hanging into a surfactant solution was measured as a function of the surfactant concentration using a weighing balance. As expected, and mentioned above, the addition of the surfactant solution changed the apparent weight of the density bottle due to interfacial forces/buoyancy that it experiences. The recorded apparent weights of the density bottle in the surfactant solutions of SDS, TTAB, and Brij56 were plotted as a function of increasing surfactant concentration in an aqueous medium, and the corresponding sample plots are depicted in the form of Figure 2. The data reflects a linear decrease in the apparent weight up to a reproducibly specific surfactant concentration, followed again by a linear decrease in the weight but with a different slope. The apparent weight vs surfactant concentration data recorded for the density bottle in surfactant solutions fits two straight lines with different slopes, with the concentration corresponding to their intersection point assumed as the cmc of the surfactant added (Figure 2).

The experiments corresponding to the estimation of the cmc through the presented technique were repeated five times and the reproducibly estimated cms with the calculated standard deviations, from plots like Figure 2 were found to be 7.3 ± 0.46, 3.74 ± 0.20, and 0.078 ± 0.002 mM for SDS, TTAB, and Brij56, respectively. To validate our results, the cms of the chosen surfactants were also determined through a more advanced technique, viz., fluorescence emission spectroscopy using pyrene as a probe. A comparison of the cmc values obtained through the presented method with values obtained through the fluorescence emission spectroscopy and literature values for the investigated surfactants is presented in the form of Table 1. As can be seen from the entries of Table 1, the cmc values corresponding to the investigated surfactants are in concurrence with those estimated through a more advanced technique and reported in the literature.

Except for the requirement of large volumes, the proposed method is advantageous over the reported ones in many ways: (i) it can be used for the estimation of the cmc of any type of surfactant, i.e., cationic, anionic, or nonionic; (ii) it requires the use of a simple-to-operate, easily accessible, and cost-effective weighing balance as an instrument; and (iii) estimation of the cmc from the experimental data does not require the use of complicated mathematical processing/manipulations.

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Notes
The authors declare no competing financial interest.

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**DEDICATION**

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