

Experimental Study of CMC Evaluation in Single and Mixed Surfactant Systems, Using the UV–Vis Spectroscopic Method

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Abstract In this study, the critical micellar concentration (CMC) of anionic, cationic and nonionic surfactants was determined using the UV–Vis spectroscopic method. Sodium lauryl sulfate (SDS) as anionic, hexadecyl-trimethyl-ammonium bromide as cationic, *tert*-octylphenol ethoxylates TOPEON (with $N = 9.5, 7.5$ and 35) and lauryl alcohol ethoxylate (23EO) as nonionic surfactants have been used. Concentration of surfactants varies both from below and above the CMC value in the pyrene solution. In addition, the amount of the CMC was determined using the values from the data obtained from the graph of absorbance versus concentration of surfactants. A comparative study was conducted between the results of the present study and the literature which shows a good agreement, in particular for TOPEO9.5 and LAEO23. Furthermore, the CMC value of SDS (as an ionic surfactant) in the presence of nonionic surfactants was also examined. The result reveals that with addition of small amount of nonionic surfactant to the anionic SDS surfactant, a decline in the CMC value of the anionic–nonionic system relative to the CMC of pure anionic surfactant was

observed. In addition and for the first time, the effect of UV irradiation on the size of the micelle formations was studied. It was found that UV irradiation causes the formation of smaller micelles which is of prime concern in membrane technology.

Keywords Critical micellar concentration (CMC) · UV–Vis spectroscopic method · Surfactant · Anionic–nonionic system · UV irradiation

Introduction

The critical micellar concentration (CMC) is the first identifiable physical change in a solution containing surfactants, as its concentration increases. Surfactants in solution below their CMC are monomeric and dispersed while above their CMC they are self-associated, in spheroidal micelles or micelles of other morphologies, to lower their free energy. Thus, the critical micelle concentration, for a surfactant in a given solvent, is a primary means of surfactant characterization [1].

Various techniques are routinely used to determine the CMC in aqueous solution. The most commonly applied methods are conductivity [2, 3], capillary electrophoresis [4, 5], voltammetry [6], calorimetry, scattering techniques [7, 8], surface tension, UV–Vis and fluorescence spectroscopy [7, 9, 10], which all are based on an abrupt change in the related physical properties upon micelle formation. Particularly, luminescence probing techniques have advanced rapidly over the past three decades, as a result of the development of a large number of dyes and specific probe molecules [11]. Scientists have applied various probes for determination of CMC using UV–Vis and fluorescence spectroscopy methods, such as Near-Infrared

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(NIR) Hydrophobicity Probe [12], Platinum 2,2': 6',2'-terpyridine complexes [13], 5-methoxy tryptamine molecular [14] and pyrene [15]. The commonly used dye in the study of micellization is pyrene, which shows a significantly fine structured emission spectrum (vibronic bands) [16]. Pyrene has several interesting photophysical properties which make it suitable for use as an effective probe [17]. Pyrene exhibits characteristic absorption spectra with strong and weak peaks in the UV-region [15].

Now, mixed surfactants (nonionic and cationic or anionic surfactant mixtures) are of great interest in scientific and industrial application [18–20]. Surfactants used in practical applications almost always consist of mixtures of them and the solution properties of mixed surfactant systems are often superior in application to that of the individual ones [21].

Several studies have been published on the determination of the CMC of surfactants using various methods [22–28]. But, there are a few reports on the determination of CMC for surfactants (anionic, cationic and non ionic) by UV spectroscopy [29]. Therefore, it was the aim of this study to determine the CMC of different types of surfactant (anionic, cationic and nonionic) in an aqueous medium using UV spectroscopy. Furthermore, the effect of the presence of nonionic surfactants on the CMC of SDS as an anionic surfactant was investigated using this method. Interestingly, it was found that UV irradiation has an effect on the size of the formed micelles. Finally, this effect on the size of micelles was studied.

Experimental Procedures

Materials

In this study, ionic and nonionic surfactants were employed to investigate their CMC at the contact temperature (about 25 °C) and pH (about 7). They were the sodium docyl sulfate (SDS) and the cetyl trimethyl ammonium bromide (CTAB), three *tert*-octyl phenol ethoxylates Triton X-100, X-114, X-405 from Sigma, with a degree of ethoxylation “*N*” of 9.5, 7.5 and 35 respectively, and abbreviated TOPEON, and a lauryl alcohol with a degree of ethoxylation of 23, Brij35 from Sigma abbreviated LAEO23. These surfactants were selected because their literature CMC data were reliable [11, 21, 26, 30]. The concentration of the surfactants in 2 μ M pyrene solution varies both from below and above the CMC amount. The spectrophotometric tests on aqueous solutions of this surfactant were also carried out.

In this study, all the chemicals were desiccated before use and in the process of preparation deionized water was employed.

Instrumentation

Absorbance measurements were taken using an Avantes Avaspec-3648 single beam spectrophotometer using 10-mm path length quartz cuvettes. The spectra were recorded in the 200–400 nm wavelength range. Also, the synthesized SDS micelles were characterized by their particle size distribution using a Zetasizer Nano ZS apparatus (Malvern Instruments Ltd.) as a laser particle sizer.

Preparation of the Pyrene Solution

A stock solution of pyrene was prepared by adding a specific amount of the compound in 20 wt% ethanol in water. Then, this mixture was sonicated to produce a clear solution. For this work, a 2 μ M solution of pyrene was prepared and the ethanol concentration was diluted to about 0.5 % where a small concentration of the ethanol would not affect the spectral and self-aggregation behavior of amphiphiles.

Method of CMC Determination by UV–Vis Spectroscopy

The CMC determination of the surfactants was carried out using pyrene as a probe by the UV–Vis spectroscopy method. Fig. 1 shows a simple UV-spectrum of pyrene in water. The four peaks of pyrene are due to multiple rings and are clearly visible in the spectrum. Strong peaks are observed at 240, 272, 320 and 335 nm, as shown in Fig. 1.

The absorbance of the pyrene peaks increases by increasing the surfactants concentration. Therefore, the CMC was obtained from the combined spectra by monitoring the absorbance values at different peaks for different concentrations of surfactant. The concentration of the surfactant solution was varied both from below to above the CMC of the surfactants and curves of absorbance value

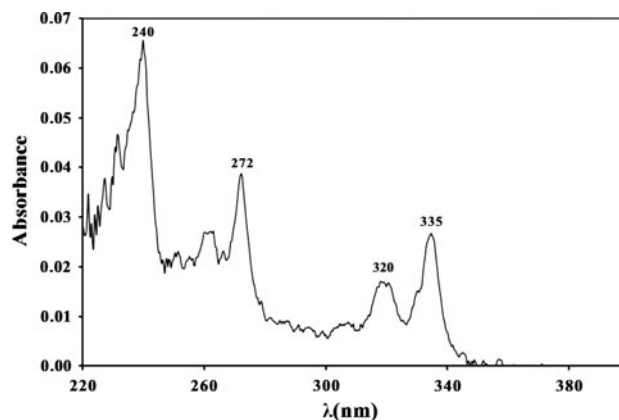


Fig. 1 Simple UV-spectrum of pyrene in water

verses concentration of surfactants were used for the determination of the CMC. The inflection point of the absorbance versus concentration of the surfactant plot was taken as the CMC of the surfactant in the corresponding pyrene solutions.

Investigation of the UV Irradiation Effect

In a typical experiment, an SDS surfactant solution was placed in a spectrophotometer cell and irradiated by UV light (125 W high pressure mercury vapor lamp) under continuous stirring. The experiment was conducted at a constant room temperature, as water circulated around the cell for 5 h. Furthermore, UV irradiation effect on size of SDS micelle was also examined.

Result and Discussion

Determination of the CMC for a Single Surfactant

Simple absorbance spectra with varying concentration of surfactants give some useful information about the formation of micelles in solution. The intensities of peaks were changed with the variation of the surfactants concentration in aqueous solutions. The absorbance spectra in different concentrations of surfactants (varies both from below and above the CMC amount) are shown in Figs. A1a–A6a (Supplementary material). In this study, determination of the CMC was obtained from the plot of the concentration of surfactant (mM) versus absorbance (Figs. A1b–A6b in Supplementary material). As exhibited in these Figures, there is a very big shift in the CMC point except for the TOPEO9.5 surfactant. Plot of the TOPEO9.5 surfactant follows Beers law. As shown in Fig. A6b (Supplementary material) and for TOPEO9.5, a sharp increase is observed below the CMC amount with the rise in concentration of the surfactant. However, for values above this concentration it does not change appreciably.

Figures A1b–A5b (Supplementary material) show that for the CMC (speckled line) concentrations of 3.46, 0.035, 0.2, 0.65 and 1.67 there is a big shift where the absorbance values rise sharply. This domain occurs where the formation of micelles takes place. The Beer's law plot demonstrates that the plot is linear at first with a positive slope, then a short discontinuity is observed and finally the slope is constant (Fig. A6b in Supplementary material), where the point of discontinuity represents the CMC amount. It is worth mentioning that the linearity of a Beer's law plot is not necessarily evidence of the absence of association, as shown experimentally. Other researchers have demonstrated that it could occur with greatly associated solutes, provided that the particle size distribution

remains constant with the increase in concentration [31]. The intersection of the two linear portions of the plot for TOPEO9.5 occurs at a concentration of 0.2 mM. The sigmoidal shape of the absorbance/mM of surfactants (except TOPEO9.5) indicates that below the CMC, the absorbance spectrum of pyrene corresponds to a “water-like” environment (as shown in Figs. A1b–A5b in Supplementary material). An increase in the surfactant concentration indicates a decline in polarity and, thus, a more hydrophobic environment. Well above the CMC, the intensity of the peaks remains almost constant and independent of the surfactant concentration. This indicates a complete integration of the pyrene molecules into the hydrophobic region of the micelles.

Figures A4–A6 (Supplementary material) show that for the TOPEON ($N = 9.5, 7.5$ and 35) surfactant series, the absorbance spectrum at 272 nm increases with the surfactant concentration in a more gradual way than that found for the other surfactants. This behavior is particularly known for technical grade surfactants and is generally associated with the polydispersity.

In this work, we determined the CMC values of surfactants with the UV–Vis spectroscopic method and the results were compared with values presented in literatures [11, 21, 26, 30], as shown in Table 1.

As shown in Table 1, the CMC values determined using the spectrophotometric method are near to the CMC values obtained by other methods, except the CMC values of TOPEO35 and CTAB surfactants. The values of the CMC obtained in the present study for TOPEO35 and CTAB are different to those in the literature. This discrepancy is associated with their polydispersity, notwithstanding that for some nonionic surfactants; the observed phenomena could also be elucidated in terms of a premicellar effect or by the formation of small aggregates between the pyrene molecule and the surfactant.

Shift of λ_{\max} by the Formation of Micelles

There was only a small shift in λ_{\max} of pyrene (about 1–2 nm) that took place by the formation of micelles. For

Table 1 CMC surfactants adopted in this work

Surfactant	CMC ^a (mM)	CMC ^b (mM)
SDS	3.46	4.84 (21)
LAEO23	0.035	0.038 (26)
TOPEO9.5	0.20	0.21 (21)
TOPEO35	1.67	0.904 (21)
TOPEO7.5	0.21	0.27 (30)
CTAB	0.65	0.90 (11)

^a This study

^b Values presented in the literature

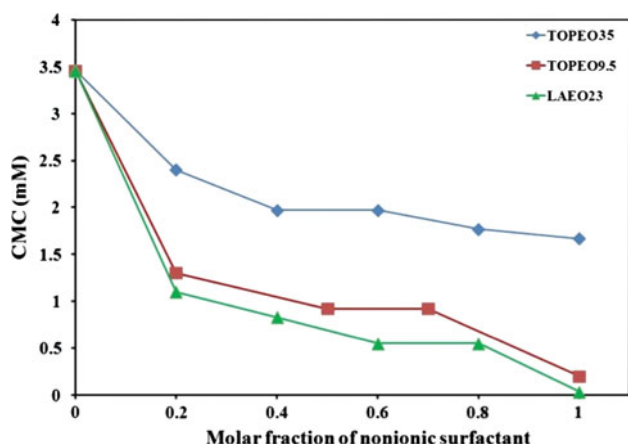


Fig. 2 Variation of the CMC of SDS with molar fraction of nonionic surfactants in a SDS-nonionic surfactants mixed system

example, as shown in Fig. A7 (Supplementary material) for CTAB surfactants, this shift is just next to the CMC value of the surfactant. For concentrations above the CMC, the solution enters a micellar domain where micelle formation takes place. The sudden jump in absorbance (Fig. A7 in the Supplementary material) is due to the tendency of hydrophobic pyrene to be in a nonpolar environment which is provided by the formation of CTAB micelles. The micelle interior is a nonpolar media where the aqueous bulk is polar. Pyrene is naturally tends to reside in the nonpolar interior of the micelle which reduces the hydrophobic forces of repulsion between water and pyrene. Secondly, there is no hydrophilic functionality of pyrene which may possibly cause pyrene to reside on the interface. After micellization, there exists a small rise in the absorbance due to the increased concentration of surfactant because more micelle formation takes place and hence more pyrene monomers are incorporated inside the newly formed micelles. Above this point, there exists a small drop in absorbance at one point. With this exception, the absorbance is almost constant [32].

Determination of the CMC for Mixed Surfactants

The effect of adding small amount of nonionic surfactants on the CMC of the SDS surfactant as an ionic surfactant was investigated by the UV spectroscopy method. A plot of the variation of the CMC with the mole fraction of nonionic surfactants (LAEO23, TOPEO9.5 and TOPEO35) is displayed in Fig. 2. The findings of this study reveals that the more nonionic surfactants was added to SDS (ionic surfactant) the more the CMC value was depressed and the more surfactant becomes available in the micellar form and the lower the amount of monomeric surfactants is. Previous studies [19–21, 25, 28] have shown that addition of small amount of nonionic surfactant to the SDS (as an ionic

surfactant) results in a decrease in the CMC value of the anionic–nonionic system, relative to the CMC amount of the pure ionic system. In the case of pyrene which is most likely solubilized in the micellar core, the presence of synergism was attributed to the presence of an interaction between the hydrophobic chains of the surfactants. As confirmed by the more restricted motional freedom of SDS molecules in mixed micelles as compared to that in SDS self-aggregated micelles [20], reflects a more rigid pyrene microenvironment in SDS-nonionic surfactants mixed micelles. The CMC value of SDS in the presence of non-ionic surfactants is significantly lower as compared to that of a single surfactant system. The CMCs of the SDS-nonionic system exhibit the expected behavior as a function of the mole fraction. However, the behaviors of the CMC values with the molar fractions for LAEO23, TOPEO9.5 and TOPEO35 are characterized by a very small decrease in the CMC in the range of low mole fractions, followed by an abrupt decrease in the CMC value at higher mole fractions.

Effect of UV Irradiation on the Size of Micelles

Interestingly, it was found that UV irradiation could affect the size of the micelles formed. To scrutinize this phenomena, two solutions of SDS (concentration of SDS was above of the CMC) in deionized water was prepared. One was placed on a stirrer under UV irradiation and other on a stirrer in a dark chamber under the same operating condition (i.e., 25 °C). As shown in Fig. 3, UV irradiation reduces the size of micelles. For the indirect interaction, there are two possible domains in the chemical structure of SDS that could be sensitive to these irradiation attacks: the hydrocarbon chain (12-carbon tail) and the sulfate group. This could be caused by the reduction in the size of the micelles under UV or the action of hydroxyl (OH) radicals in an aqueous system of a SDS surfactant under UV irradiation. In this case, the size of the micelles under UV and in the dark was about 40 and 100 nm, respectively.

Conclusion

In this paper, it has been shown that UV absorption of pyrene in surfactant solution or mixed surfactants solutions is a convenient method for the determination of their CMC value. We also examined the sizes of CMC values for two ionic (i.e., SDS and CTAB) and four nonionic surfactants (i.e., TOPEON ($N = 9.5, 7.5$ and 35) and LAEO23). The results reveal that CMC values were in the same range as those measured by a previous researcher, except for TOPEO9.5 and LAEO23. Furthermore, the CMC value of the ionic SDS surfactant in the presence of nonionic

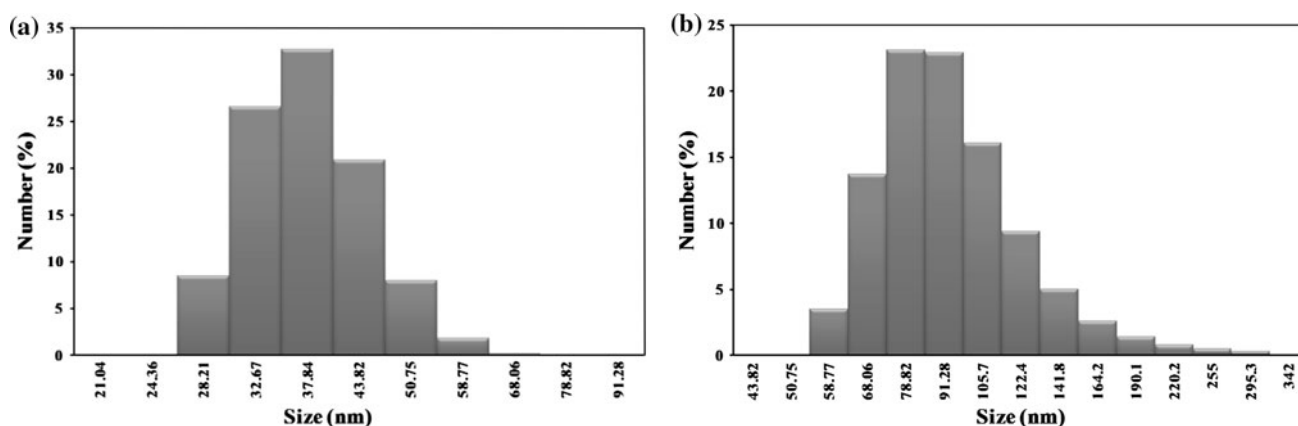


Fig. 3 Particle size (a) under UV irradiation and (b) in a dark environment

surfactants was also examined. The CMC value of SDS in a mixed system was significantly lower in comparison with those of the single SDS surfactant system. However, the behaviors of the CMCs with the mole fraction for LAEO23, TOPEO9.5 and TOPEO35 are characterized by a small decrease in the CMC in the range of low mole fractions, followed by an abrupt decrease in the CMC at higher mole fractions.

For the first time, a novel method was presented to assess the effect of UV irradiation on the size of micelles. It was demonstrated that UV irradiation causes the formation of smaller micelles. The findings of this result reveal that the understanding of the dependency of UV irradiation on the size of micelles could be useful in membrane technology, i.e., in micellar enhanced ultrafiltration (MEUF) applications.

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