

# On the Measurement of Critical Micelle Concentrations of Pure and Technical-Grade Nonionic Surfactants

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**ABSTRACT:** The critical micelle concentrations (CMC) of nine commercial nonionic surfactants (Tween 20, 22, 40, 60, and 80; Triton X-100; Brij 35, 58, and 78) and two pure nonionics [ $C_{12}(EO)_5$  and  $C_{12}(EO)_8$ ] were determined by surface tension and dye micellization methods. Commercially available nonionic surfactants (technical grade) usually contain impurities and have a broad molecular weight distribution owing to the degree of ethoxylation. It was shown that the surface tension method (Wilhelmy plate) is very sensitive to the presence of impurities. Much lower CMC values were obtained with the surface tension method than with the dye micellization method (up to 6.5 times for Tween 22). In the presence of highly surface-active impurities, the air/liquid interface is already saturated at concentrations well below the true CMC, leading to a wrong interpretation of the break in the curve of surface tension ( $\gamma$ ) vs. concentration of nonionic surfactant ( $\log C$ ). The actual onset of micellization happens at higher concentrations, as measured by the dye micellization method. Furthermore, it was shown that when a commercial surfactant sample (Tween 20) is subjected to foam fractionation, thereby removing species with higher surface activity, the sample yields almost the same CMC values as measured by surface tension and dye micellization methods. It was found that for monodisperse pure nonionic surfactants, both CMC determination methods yield the same results. Therefore, this study indicates that precaution should be taken when determining the CMC of commercial nonionic surfactants by the surface tension method, as it indicates the surface concentration of all surface-active species at the surface only, whereas the dye method indicates the presence of micelles in the bulk solution.

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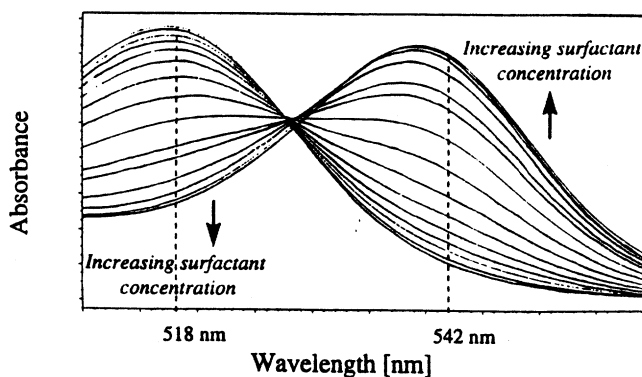
**KEY WORDS:** Critical micelle concentration; differences in CMC; dye micellization method; foam fractionation; minimum surface tension; pure nonionic surfactants; surface tension method; technical-grade nonionic surfactants.

Ionic surfactants such as sodium dodecyl sulfate (SDS) or alkyl trimethylammonium bromides are usually easier to obtain in pure form than the ethoxylated nonionic surfac-

tants. Commercially available (technical grade) ethoxylated surfactants have a distribution not only in the hydrophobe but also in the degree of ethoxylation. The distribution pattern of ethoxylation has been a subject of study for some time (1). However, the importance of this aspect to the measurement of critical micelle concentration (CMC) has not been satisfactorily brought out in the literature. A large difference between CMC values of nonionic surfactants determined by different methods is often observed. Furthermore, for nonionic surfactants, a clear break in the surface tension ( $\gamma$ ) vs. concentration ( $\log C$ ) curve is not usually obtained. This is attributed to a broad molecular weight distribution and the presence of impurities (2,3).

A number of methods have been employed for CMC determination of surface-active agents (4,5). In this paper the effect of the distribution pattern of ethoxylation on two commonly used methods for CMC determination will be discussed, namely dye micellization and surface tension methods.

**CMC determination by the dye micellization method.** Dyes can be used in many ways for measuring CMC. Dyes such as merocyanine, eosin, rhodamine and Sudan are known to show a shift in the wavelength maximum ( $\lambda_{\max}$ ) due to the presence of micelles (4,5). This shift for eosin Y is shown in Figure 1. Eosin Y in water shows a wavelength maximum at 518 nm. Increasing the surfactant concentra-



**FIG. 1.** Ultraviolet-visible absorbance spectrum of eosin Y in aqueous surfactant solution. The wavelength maximum ( $\lambda_{\max}$ ) shifts from 518 nm in the absence of surfactant to 538 nm as the surfactant concentration increases. The rise is most significant at 542 nm.

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tion, however, results in an increase of the absorbance at 542 nm. This shift is followed as either a change in  $\lambda_{\text{max}}$  or a change in absorbance of the micellized dye at a fixed wavelength (542 nm in Fig. 1) as a function of surfactant concentration. It has been suggested that the inflection point in  $\lambda_{\text{max}}$  should be treated as the CMC (4). However, not all dyes show a distinct shift in  $\lambda_{\text{max}}$  (e.g., merocyanine 540). Therefore, if the  $\lambda_{\text{max}}$  of the micellized dye is sufficiently different from the aqueous dye, the absorbance at this wavelength (for eosin Y, at 542 nm) can be followed as a function of surfactant concentration to measure the extent of dye uptake (Fig. 2). Below the CMC, the rise in absorbance is small, whereas above the CMC, the rise is sharp. At the point where roughly half the dye is in the continuous phase, the absorbance maximum shows a sharp shift (in Fig. 1 from 518 to 538 nm). Since the micellization process is known to be less sharp for nonionic surfactants than for ionic surfactants, the rise in absorbance varies strongly over a range of surfactant concentration. At high enough surfactant concentrations, the absorbance vs. concentration curve will flatten again as most of the dye shifts to the micelles, depleting the continuous-phase dye. The linear portion near the inflection point is extrapolated to the point where the absorbance matches that of the dye in the absence of any surfactant (represented by the horizontal dashed line in Fig. 2), and this concentration is defined as the CMC.

A second method involves solubilization of a water-insoluble (hydrophobic) dye in micellar solutions. This solubilized dye can then be measured by its ultraviolet-visible absorbance. This method yields satisfactory results for some surfactants. However, sometimes the solubilization of such a dye is so high that the micellar structure is affected by the dye. If the solubilization is weaker, the dye taken up by the micelles is often insufficient to produce a

reasonable absorbance signal. Especially when the CMC is very low, the pseudo-phase volume fraction of the micellar phase at concentrations just above the CMC is far too low to solubilize a significant amount of dye. Therefore, it is difficult to define a clear CMC for nonionic surfactants using this method and hence this approach was not pursued in this paper.

**CMC determination by the surface tension method.** The surface tension of aqueous solutions of surface-active agents decreases rapidly with addition of surfactant until the CMC is reached and then stays constant above the CMC. Regardless of the instrument employed for measuring CMC, the following point must be recognized regarding the surface tension method: This method is based upon the fact that the free surfactant concentration remains almost unchanged after the onset of micellization even if the total surfactant concentration is increased. However, because of surface-active impurities, the surface may become saturated with highly surface-active molecules, although the actual onset of micellization may take place at a higher surfactant concentration. The surface tension may thus become invariant with surfactant concentration even below the CMC. Therefore, saturation of the surface, as identified as the CMC using the surface tension method, does not always imply the presence of micelles in the bulk solution. In this study a comparison is made of the CMC of some commercial surfactants (Tween 20, 22, 40, 60, and 80; Triton X-100; Brij 35, 58, and 78) as measured by the surface tension method (Wilhelmy plate) and the dye micellization method. When impurities are preferentially removed from a commercial surfactant sample, the CMC value as measured by surface tension is expected to be closer to the value measured by the dye micellization method. This work compares the surface tension and dye micellization behavior of pure (monodisperse) and commercial (technical-grade) nonionic surfactants.

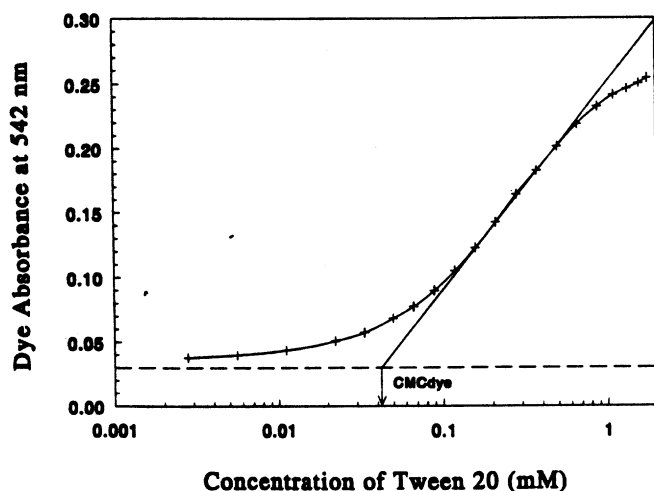


FIG. 2. Critical micelle concentration (CMC) determination of Tween 20 (CMC = 0.042 mM) using the dye micellization method (absorbance at 542 nm). Eosin Y concentration: 0.019 mM. Horizontal dashed line represents dye absorbance in water in the absence of surfactant.

## MATERIALS AND METHODS

Tween 20, 22, 40, 60, and 80; and Brij 35, 58, and 78 were supplied by ICI Americas, Inc. (Wilmington, DE). Triton X-100 was obtained from Aldrich Chemical Company (Milwaukee, WI). The pure nonionics pentaethyleneglycol mono *n*-dodecyl ether [ $C_{12}(EO)_5$ , where EO is ethylene oxide] and octaethyleneglycol mono *n*-dodecyl ether [ $C_{12}(EO)_8$ ] were purchased from Nikko Chemicals Co. (Tokyo, Japan). Eosin Y and merocyanine 540 dye (high-purity grades) were supplied by Acros Organics (Fair Lawn, NJ). Deionized, distilled water was used in all experiments. Surfactant concentrations were calculated using their molecular weights disregarding the presence of any probable impurities.

Surface tensions were measured by the Wilhelmy plate method in freshly prepared solutions at 22°C. The platinum plate was always cleaned and heated to a red/orange color with a Bunsen burner before use.

Eosin Y was used for CMC determination of the nine commercial surfactants using the dye micellization method. Merocyanine 540 was used for the two ultra-pure nonionic surfactants. Absorbance spectra were taken using a Hewlett-Packard UV-VIS spectrophotometer (Palo Alto, CA) with temperature control. All spectra were taken at 22°C.

Foam fractionation was done for a sample of Tween 20 and C<sub>12</sub>(EO)<sub>5</sub> by shaking 25 mL of the surfactant solution vigorously such that the volume of the foam and the liquid together was four times the volume (100 mL) of the initial liquid. One-half of the initial liquid was then separated from the foam as a foam-fractionated sample and used for surface tension and dye micellization studies. The sample is now expected to contain a relatively lower proportion of highly surface-active impurities.

The surfactant loss due to foam fractionation was determined by a Tekmar-Dohrmann Phoenix 8000 Total Organic Carbon (TOC) Analyzer (Cincinnati, OH).

## RESULTS AND DISCUSSION

Table 1 shows CMC values from the surface tension and dye micellization methods as well as ratios of the two values. The CMC values from the dye micellization method are approximately 1.6 to 6.5 times higher than those obtained by surface tension. Figure 3 shows different CMC values obtained for Tween 20. Breaks in the  $\gamma$  vs.  $\log C$  curve are thus not an indication of the CMC. The small difference between CMC values measured for Tween 80 (Table 1) indicates that this sample does not contain a large amount of surface-active impurities or a wide distribution in the ethoxylation. The largest difference was observed for Tween 22. This is probably due to the large ethoxylation number (80), which makes a wide distribution of ethoxylation more likely.

It is expected that if the impurities are removed, the two methods will yield results that are closer to each other. It

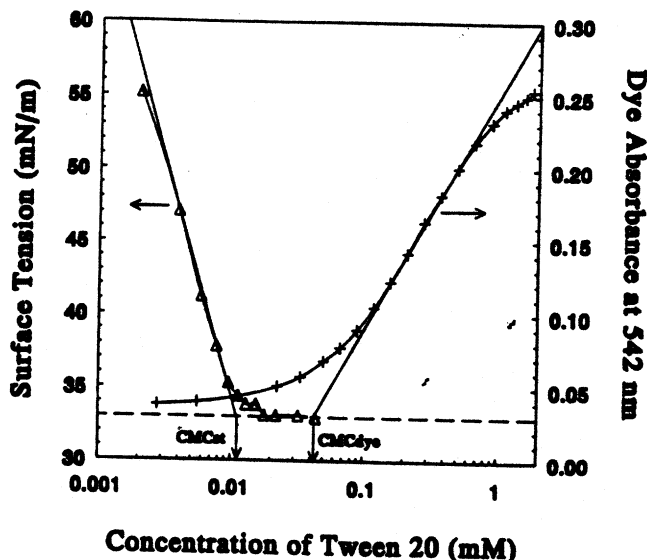


FIG. 3. CMC of Tween 20 determined by surface tension ( $\Delta$ , CMC = 0.011 mM) and dye micellization methods (+, CMC = 0.042 mM). Eosin Y concentration: 0.019 mM. The horizontal dashed line represents dye absorbance in water in the absence of surfactant as well as the equilibrium surface tension. For abbreviation see Figure 2.

has been suggested (6–8) that foaming and consequently skimming the foam away can purify a surfactant solution. This process, called foam fractionation, is a process in which solute species are adsorbed at a gas-liquid interface between a dispersed phase (gas bubble) and a continuous phase (bulk liquid). Foam fractionation processes have been used to remove surface-active agents from aqueous solutions (9). To confirm this, solutions of Tween 20 and C<sub>12</sub>(EO)<sub>5</sub> were subjected to foam fractionation, and the remaining solution was used for CMC determination. Total organic carbon analysis showed that less than 5% of the total surfactant concentration was removed and therefore the concentration was taken to be the same as before foam fractionation.

TABLE 1  
CMC as Determined by Surface Tension and Dye (eosin Y) Micellization Method and the Ratio of the Two Values

Surfactant	Structure	CMC by surface tension (mM)	CMC by dye micellization (mM)	$\left( \frac{\text{CMC}_{\text{Dye}}}{\text{CMC}_{\text{S.T.}}} \right)$
Tween 20	Sorbitan laurate ester (EO <sub>20</sub> )	0.011	0.042	3.8
Tween 22	Sorbitan laurate ester (EO <sub>80</sub> )	0.013	0.084	6.5
Tween 40	Sorbitan palmitate ester (EO <sub>20</sub> )	0.0067	0.024	3.6
Tween 60	Sorbitan stearate ester (EO <sub>20</sub> )	0.0055	0.022	4.0
Tween 80	Sorbitan oleate ester (EO <sub>20</sub> )	0.018	0.028	1.6
Triton X-100	Octyl phenol ether (EO <sub>10</sub> )	0.080	0.20	2.5
Brij 35	Lauryl alcohol ether (EO <sub>23</sub> )	0.030	0.068	2.3
Brij 58	Cetyl alcohol ether (EO <sub>20</sub> )	0.0028	0.01	3.6
Brij 78	Stearyl alcohol ether (EO <sub>20</sub> )	0.0018	0.0071	3.9
C <sub>12</sub> (EO) <sub>5</sub> <sup>a</sup>	Lauryl alcohol ether (EO <sub>5</sub> )	0.060	0.058	0.98
C <sub>12</sub> (EO) <sub>8</sub> <sup>a</sup>	Lauryl alcohol ether (EO <sub>8</sub> )	0.072	0.070	0.97

<sup>a</sup>Pure nonionic surfactant. Merocyanine 540 dye was used for the CMC determination. Abbreviations: CMC, critical micelle concentration; EO, ethylene oxide; S.T., surface tension.

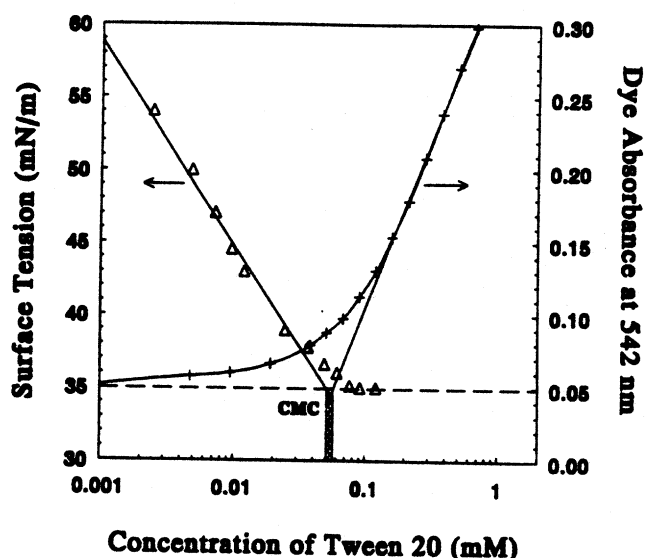


FIG. 4. CMC of Tween 20 determined after foam fractionation by surface tension ( $\Delta$ , CMC = 0.051 mM) and dye (eosin Y, 0.019 mM) micellization method (+, CMC = 0.057 mM). The horizontal dashed line represents dye absorbance in water in the absence of surfactant as well as the equilibrium surface tension. For abbreviation see Figure 2.

Figure 4 shows a graph of the CMC determined by the dye micellization and surface tension methods for the foam-fractionated Tween 20 sample. Both methods clearly show values much closer to each other (0.051 vs. 0.057 mM), indicating that the surface-active impurities as well as the lower ethoxylated molecules were removed from the original solution. Figure 5 shows the CMC curves for the pure (monodisperse) nonionic surfactant  $C_{12}(EO)_5$ . In this case, a

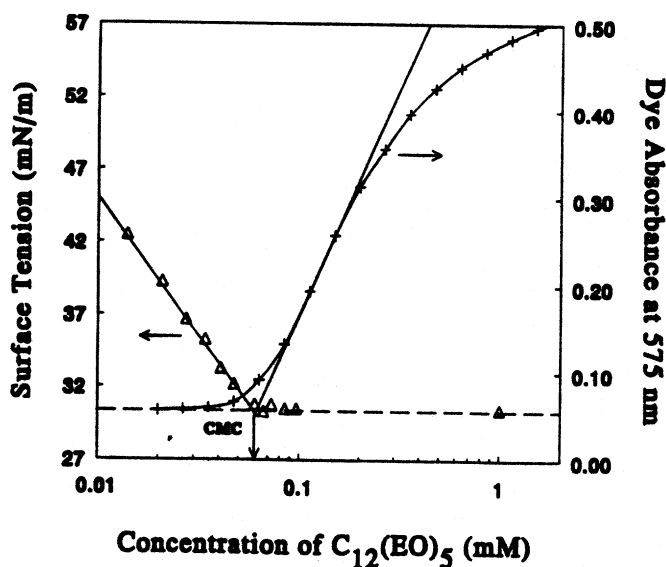


FIG. 5. CMC of pure  $C_{12}(EO)_5$  determined by surface tension ( $\Delta$ , CMC = 0.058 mM) and dye micellization methods (+, CMC = 0.06 mM). Dye used was merocyanine 540 (0.019 mM). The horizontal dashed line represents dye absorbance in water in the absence of surfactant as well as the equilibrium surface tension. For abbreviation see Figure 2.

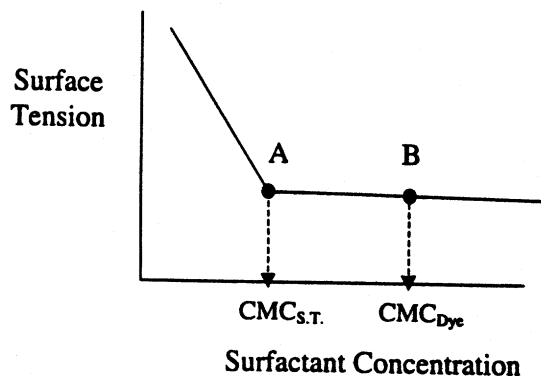
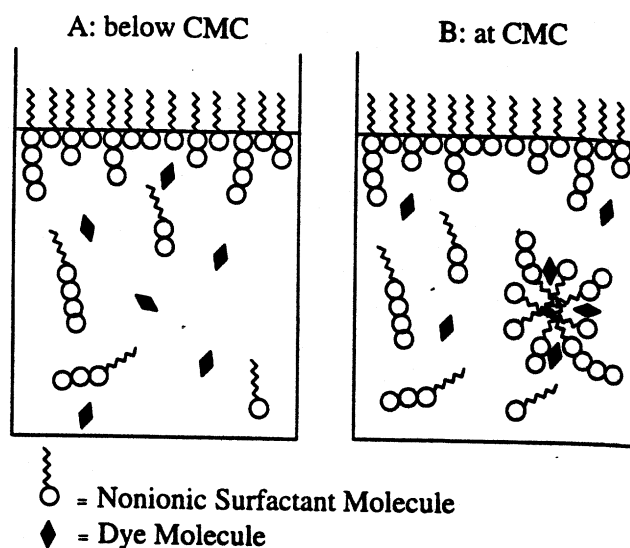


FIG. 6. Schematic diagram showing how the surface tension method would suggest a lower CMC for technical-grade nonionic surfactants than the dye micellization method because of early saturation of the air/liquid interface (solution A). Micelles start to form at a higher surfactant concentration as determined by the dye micellization method (solution B). Open circles represents a fixed number of ethylene oxide groups. For abbreviation see Figure 2.

different dye was used, merocyanine 540, which shows a micellized dye peak at 575 nm. In the absence of impurities, both surface tension and dye micellization methods yield the same result (see also Table 1). Furthermore, the CMC values of monodisperse  $C_{12}(EO)_5$  were the same before and after foam fractionation, indicating the absence of highly surface-active impurities and the reliability of both methods for CMC determination of pure surfactants.

This study shows that the surface tension method can be erroneous for commercial (technical grade) surfactants under common conditions. The onset of micellization in the case of a pure surfactant causes the free (nonmicellized) surfactant concentration (monomers) to remain constant when the total surfactant concentration is increased. This is correctly interpreted as the CMC of the pure surfactant. In case of impure surfactants or surfactant mixtures, however, the situation is different. An impure sample of SDS, for example, invariably contains lauryl alcohol, which is

more hydrophobic than SDS and thus has a higher adsorption coefficient (10,11). Thus, lauryl alcohol can saturate the surface and exhibit constant surface tension without any micelle formation in the bulk solution. Recently, Goebel and Lunkenheimer (12) reported the importance of purity in the measurement of interfacial tension. As was shown in their study, using water/*n*-alkane interfaces, trace impurities significantly influence the interfacial tension. For nonionic surfactants, the lower ethoxylated species, which are always present in a commercial (technical grade) ethoxylated nonionic surfactant, have a higher affinity for adsorption than the higher ethoxylated species. At concentrations well below the true CMC value, the air-liquid interface is already saturated with the more surface-active species (visualized in Fig. 6A). An increase in the bulk surfactant concentration from this point on will ultimately result in the formation of micelles at a specific surfactant concentration, which is the true CMC of the surfactant solution. (Fig. 6B). Although the CMC is indeed lowered by the presence of more surface-active species, the lowering is not as significant as suggested by the results from the surface tension method. The dye micellization method in such a situation would certainly yield a higher CMC than the surface tension method as it detects the presence of micelles in the bulk solution. In contrast, the surface tension method only measures the surface concentration of all surface-active species and does not detect the presence of micelles in the bulk solution. The stability of micelles and its effect on interfacial processes, such as foaming, wetting, emulsification, solubilization, detergency and wetting, have been described by Shah and coworkers (13,14).

## ACKNOWLEDGMENTS

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