

A Simplified Method for the Determination of Critical Micelle Concentration

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Surfactants are versatile compounds with a wide range of applications in soaps, detergents, pharmaceuticals, motor oils, and as membrane mimics; they may also be useful in chemistry for kinetic studies, among other uses. Surfactants are amphiphilic molecules composed of a hydrophobic part and a polar "head" group. A long hydrocarbon chain usually constitutes the hydrophobic moiety, while the hydrophilic head can be either an ionic or a polar nonionic group.

In water, surfactant molecules arrange themselves into organized molecular assemblies known as micelles. The concentration above which this phenomenon occurs is called the critical micelle concentration (cmc). The value of the cmc can be determined by the change in the physicochemical properties of the surfactant solutions as the concentration of the amphiphilic molecules is increased.

Several experiments have been reported to familiarize undergraduate students with micellar solutions and with techniques to measure the cmc (1–4).

A method using fluorescein and cetyl trimethyl ammonium bromide has been reported (1, 2). The effect of charge association between cationic micelles and fluorescein dianion can be analyzed by fluorescence, but this technique requires the availability of a fluorometer for cmc determination.

The drop-weight method based on Tate's law (3) is a simple method for cmc determination. However, its simplicity is handicapped by the requirement of correction factors, not always available, for quantitative determination. Moreover, it seems difficult to achieve the very slow formation of drops that is necessary to obtain accurate results by the experimental procedure proposed.

Some of the reported methods may be considered indirect, since they require the addition to the surfactant solution of organic compounds that can affect the observed cmc value. Oil-soluble dyes readily soluble in micellar solutions (4), or changes produced by surfactants in the UV-visible spectrum of benzoylacetone (5) allow the use of accessible spectrophotometers for the determinations. A method based on the fluorescence emission of pyrene monomers in the presence of surfactants has also been reported (5).

Note that electrical conductivity can only be applied to measure the cmc of ionic surfactants (5). Among commercial tensiometers, the du Nouy apparatus and the Wilhelmy apparatus are widely known.

However, many laboratories do not have the appropriate equipment or have only one instrument. When the work is

done as a class experiment, students do not get the desired experience in working with the equipment. The need for a suitable and didactic method for surface tension measurement prompted us to design a simple device based on the maximum bubble pressure method (6).

The experiment described below does not require any additive. It is a traditional method for measuring surface tension that has been adapted to the current requirements of a laboratory of physical chemistry for undergraduate students. The Laplace equation (eq 1) is the theoretical underpinning for the design of the apparatus:

$$P_2 = P_1 + (2\gamma/r) \quad (1)$$

where P_2 is the pressure inside, P_1 is the pressure outside, γ is the surface tension, and r is the capillary radius. Equation 1 expresses the fundamental result that the pressure inside a phase that has a curved (concave) surface is greater than that outside (convex). The difference in pressure in passing across a curved surface is the physical reason for capillary rise and capillary depression. From this relation it is possible to determine the surface tension from the maximum pressure required to form a bubble at the bottom of a capillary tube immersed just below the surface.

The cmc was taken as the concentration at the point of intersection of the two linear portions of the γ vs concentration plots. The slope of the linear portions of each curve in the plot was determined by the method of least mean squares, using confidence intervals of linear regression of SigmaPlot 4.01.

Materials and Procedures

The apparatus (Fig. 1) is composed of:

A pressure generator: a funnel (500 mL) and a filtering flask (1 L). When the funnel is opened the water falls and the displaced air transmits pressure to the capillary.

A cell, which contains the sample. A capillary is placed so it just touches the liquid surface. The pressure produced by the water leads to the formation of a bubble.

A manometer made with a glass U tube is filled with a colored saturated solution of iodine in hexane ($\rho = 0.657\text{g/cm}^3$). The glass tube is fixed on a wood plate with a paper marked in millimeters on it.

Table 1. CMC Determination of SDS

SDS Concn/(mol L ⁻¹)	γ /(mN m ⁻¹)
0.2000 ± 0.0008	35.52 ± 1.82
0.1500 ± 0.0006	35.95 ± 1.82
0.1000 ± 0.0004	36.40 ± 1.83
0.0900 ± 0.0004	36.70 ± 1.84
0.0700 ± 0.0003	36.98 ± 1.84
0.0500 ± 0.0002	37.46 ± 1.85
0.0400 ± 0.0002	37.62 ± 1.85
0.0300 ± 0.0002	37.91 ± 1.86
0.0200 ± 0.0001	37.79 ± 1.86
0.0180 ± 0.0001	37.59 ± 1.86
0.0150 ± 0.0001	37.74 ± 1.86
0.0120 ± 0.0001	37.72 ± 1.86
0.0090 ± 0.0001	38.35 ± 1.86
0.0080 ± 0.0001	39.66 ± 1.89
0.0070 ± 0.0001	41.63 ± 1.91
0.0060 ± 0.0001	43.39 ± 1.94
0.0050 ± 0.0001	57.14 ± 1.99
0.0045 ± 0.0001	47.59 ± 2.00
0.0030 ± 0.0001	52.49 ± 2.07
0.0010 ± 0.0001	66.55 ± 2.27
0.0009 ± 0.0001	66.98 ± 2.27

The capillary is calibrated using liquids of known surface tension (γ), from which the capillary radius can be easily determined as the slope of the curve resulting from the graph of ΔP vs γ .

Hazards

No significant hazards are associated with this experiment.

Results and Discussion

Calibration of the Capillary Radius

The apparatus was calibrated using 20 liquid substances of known surface tension, which were selected to cover a wide range of surface tension values; ΔP was measured according to the above procedure, and the plot of ΔP vs γ allowed the calculation of radius. Using linear regression data and the Laplace equation in the form $\Delta P = 2\gamma/r$, a value of $r = 0.078 \pm 0.003$ mm was estimated. Undergraduate students should perform measures on at least 10 standard substance, as indicated by linear regression calculations.

Determination of SDS cmc

Once the capillary radius had been estimated, surface tension was determined for a series of solutions of SDS in distilled water, in concentrations ranging from 10^{-4} to 2×10^{-1} M. ΔP was measured (Table 1) as described and γ was calculated through eq 1 ($\gamma = \Delta P r/2$). SDS was selected because it is one of the most widely used surfactants. It is recommended that at least 15 points be determined. The plot of γ vs concentration allowed the determination of the cmc (Fig. 2). A value of $(8.1 \pm 0.8) \times 10^{-3}$ M was obtained, in agreement with the literature (8).

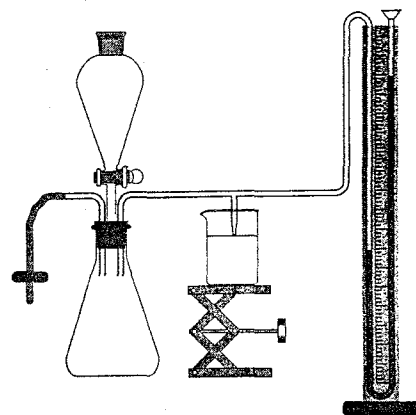


Figure 1. Drawing of the apparatus.

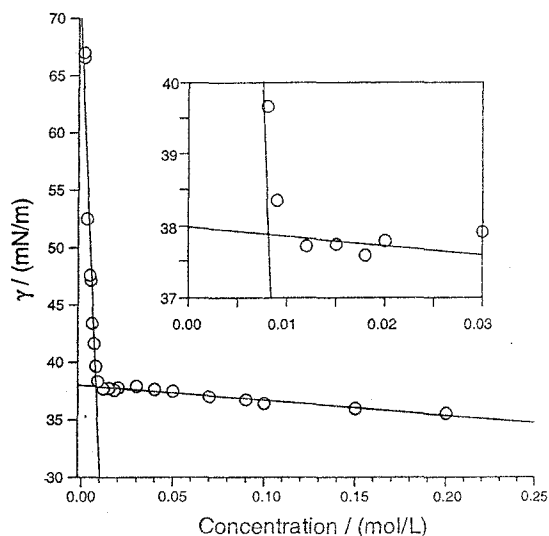


Figure 2. Plot of surface tension vs micelle concentration. The inset is an enlargement of the region of interest.

Supplemental Material

Detailed instructions for students and notes for the instructor (information on the theory behind the experiment, necessary laboratory preparations, equipment needs, and γ and ΔP values for various liquids) are available in this issue of *JCE Online*.

Literature Cited

- Rujimethabhas, M.; Wilairat, P. *J. Chem. Educ.* 1978, 55, 342.
- Roessler, N. *J. Chem. Educ.* 1979, 56, 675.
- Worley J. D. *J. Chem. Educ.* 1992, 69, 678.
- Furton, K. G.; Norelus, A. *J. Chem. Educ.* 1993, 70, 254.
- Domínguez, A.; Fernández, A.; González, N.; Iglesias, E.; Montenegro, L. *J. Chem. Educ.* 1997, 74, 1227.
- Möbius, D.; Miller, R. *Drops and Bubbles in Interfacial Research*; Elsevier: New York, 1998; pp 279–326.
- CRC Handbook of Chemistry and Physics*, 78th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1997–1998; pp 6-135–6-138.
- Elworthy, P. H.; Mysels, K. J. *J. Colloid Sci.* 1966, 21, 331.