

A Surface Chemistry Experiment Using an Inexpensive Contact Angle Goniometer

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Surface phenomena such as wettability and adhesion are becoming increasingly important for many areas of applied science and technology. Data from this type of phenomena permit the improvement and optimization of many properties such as water repellency on paints and textiles, the detergency of surfactants, and the compatibility of biomaterials. The development of surface science in parallel with surface topology studies and ultra high vacuum techniques was enhanced by the evolution of techniques such as microscopy and spectroscopy. As these methods become increasingly sophisticated, the contact angle technique remains a relatively simple tool to establish fundamental surface properties such as surface tension, and it can be used, among its many applications, to monitor surface cleanliness and surface treatments. Moreover, the equipment employed in other methods is costly and requires more highly trained personnel, whereas a contact angle apparatus is more economical and easier to manipulate. Thus, the contact angle method is a suitable technique for undergraduate students.

The goals of this work are to present the construction of a goniometer and to propose a new surface chemistry experiment. The instrument described provides results very similar to those from an expensive commercial apparatus, and it is simple for students to handle.

The purpose of a large number of surface science experiments found in laboratory manuals is the measurement of surface tension. This *Journal* has published the description of an inexpensive Du Nüoy tensiometer (1) and several laboratory experiments for the determination of surface tension by both capillary rise (2, 3) and drop weight (3–5) methods. It is not so common to find laboratory experiments involving contact angle measurements, although we can point to the work of Kabza and Cochran (6), who have described the conversion of a polarimeter to a contact angle goniometer. The laboratory experiment proposed herein is the determination of a critical micelle concentration for two different surfactants.

Surfactants, or *surface-active agents* are amphiphilic compounds containing a polar or ionic head group connected to a long hydrocarbon chain. When a surfactant is dissolved in a polar solvent, usually water, above a certain concentration it self-assembles into molecular aggregates called *micelles*, and the solution becomes colloidal. The hydrophobic part of the molecules remains in the interior of the aggregate, the micelle core, while the polar head groups are located at the micelle–water interface. The concentration above which micelles form is called the *critical micelle concentration* (cmc). The value of the cmc can be determined by the change of several physico-

chemical properties of the surfactant solution as the surfactant concentration increases. Physical properties like detergency, viscosity, density, conductivity, osmotic pressure, interfacial tension, refractive index, light scattering, and surface tension can be used to determine the cmc. By adding an oil-soluble dye to the surfactant solution, UV absorption or fluorescence spectroscopy can be used to estimate the cmc (7, 8). Experimentally, the cmc value is found by plotting a physical property as a function of the surfactant concentration, which shows an abrupt change of slope at the critical micelle concentration.

The cmc was determined in water for two common surfactants, one nonionic and one anionic. The nonionic one was Triton X-100 ([polyoxyethyleneglycol]_{9–10} *p-tert*-octyl phenol, (CH₃)₃C(CH₂)₂C₆H₄(OCH₂CH₂)_{9–10}OH); the anionic one was SDS (sodium dodecylsulfate, CH₃(CH₂)₁₁OSO₃Na). The cmc values were found by measuring the surface tension and the contact angle on Teflon (polytetrafluorethylene, PTFE) of several aqueous solutions of both surfactants for a wide range of concentrations. The apparatus for the surface tension measurements is a simplified Du Nüoy–type tensiometer, built according to the design of M. Sánchez-Rubio et al. (1).

Theory

A drop of a liquid at rest upon a solid surface assumes a lens shape controlled by three forces (see Fig. 1): the surface tension of the solid–vapor interface, γ_{SV} , the surface tension of the liquid–vapor interface, γ_{LV} , and the surface tension of the solid–liquid interface, γ_{SL} .

The contact angle is defined as the angle between the solid surface and the tangent to the surface of the drop at the point of contact of the two, and its magnitude is given by the Young equation (9):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (1)$$

The liquid–vapor interfacial tension of an aqueous solution is modified by adding a salt, which increases γ_{LV} , or a surfactant, which decreases γ_{LV} . The surfactant molecules accumulate preferentially at the liquid–vapor interface with the polar head groups oriented toward the aqueous phase (Fig. 2 i). This positive adsorption of surfactant molecules decreases the liquid–vapor interfacial energy, and, consequently, the surface tension decreases (the opposite effect is verified in aqueous salt solutions, where the salt ions are hydrated in the bulk of the solution). The surface tension continues to decrease as the surfactant concentration is increased until the

critical micelle concentration is attained. At this stage the adsorbed molecules are packed close together, forming an oriented monomolecular layer (*monolayer*) (Fig. 2 ii). Above this concentration, additional surfactant molecules aggregate to form micelles in the bulk. This cooperative association process continues in the bulk with the further increase of surfactant concentration, while at the surface the molecules remain in a highly condensed state. The concentration of free surfactant is essentially constant while the

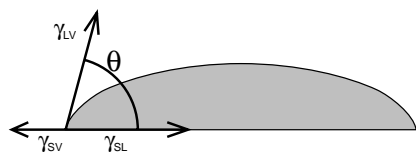


Figure 1. Three forces that control the shape of a droplet on a solid surface, where θ is the contact angle.

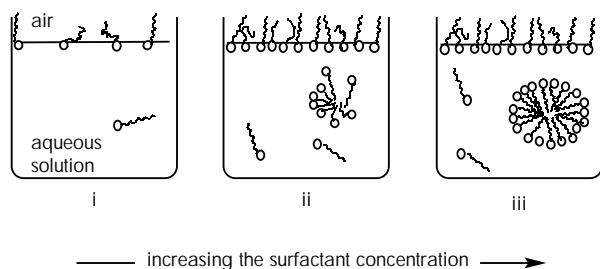


Figure 2. Schematic arrangement of surfactant molecules in aqueous solutions:¹ (i) at low concentrations (the surfactant molecules adsorb preferentially at the interface air-water) (adapted from ref 12); (ii) at the cmc (a monolayer is formed at the interface air-solution; the molecules of surfactant begin to aggregate); (iii) above cmc (the concentration of free surfactant is essentially constant; additional surfactant molecules aggregate as micelles) (adapted from ref 12).

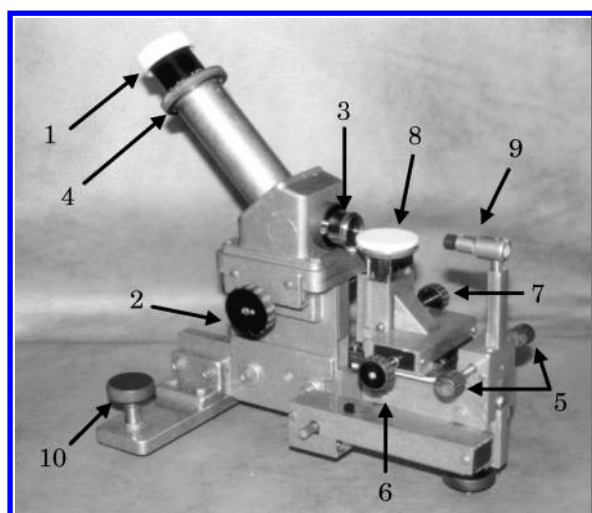


Figure 3. General configuration of the new built goniometer. (1) Eyepiece; (2) focus; (3) objective; (4) adjustment ring of the cross hair reticle; (5) fine focus or longitudinal displacement; (6) lateral displacement; (7) vertical displacement; (8) sample holder; (9) illumination device; (10) knob for horizontal positioning.

micelles concentration is increasing (Fig. 2 iii); free surfactant and micelles exist in dynamic equilibrium.

The surface tension becomes approximately constant for the studied systems because it depends only on the liquid-vapor interfacial structure. The same type of behavior is found for the contact angle magnitude; that is, as the surfactant concentration increases, the contact angle decreases until the cmc is attained. For higher concentrations the contact angle remains approximately constant.

Apparatus

The goniometer (Fig. 3) was constructed from a microscope and has a movable structure for support, a platform that holds up the sample holder, and a light source for the illumination of the sample holder.

The microscope is equipped with a 4 \times objective lens (40 mm) and a 12.5 \times eyepiece (20 mm). This optical combination produces an overall magnification of 50 \times with an approximate working distance of 37 mm. These components are combined in such a way that an image of the drop of a liquid can be observed as a real non-inverted drop image having an upper convex surface. The microscope is mounted on a movable structure, so the image is focused by adjusting the distance between the objective and the platform. Located within the microscope optical tube, at the focal plane of the eyepiece, are two glass reticles: a movable cross hair and a fixed circular protractor calibrated in degrees, which also contains cross-hair lines. The horizontal line of the protractor reticle is aligned with the top surface of the sample holder placed on the platform, while the vertical line is aligned with the edge of the drop of the liquid poured on the top of the sample holder. The cross-hair line of the movable reticle is aligned tangent to the drop profile at its edge. The contact angle is measured on the protractor scale at the contact point between the sample holder and the tangent to the drop (see Fig. 1). The platform is a circular tube that can support different solid surfaces, which are the top part of the sample holders. The illumination of the sample holder surface is assured by a high-intensity LED connected to a 1.5-V battery.

The instrument is 18 cm wide, 23 cm long, and 28 cm high and weighs less than 2 kg, which makes it more compact and lighter than similar commercial instruments. Furthermore, this apparatus does not require an external power supply, its accuracy is excellent, and it is easy to use because the drop image the user sees is not inverted.

The accuracy of this instrument was tested by comparing the values of the contact angle of several liquids (water, diiodomethane, glycerol, *n*-octane) on different surfaces with the contact angles measured by a commercial instrument (NRL Contact Angle Goniometer, catalog no. 100-00 from Ramé-Hart). The values measured with our instrument were within $\pm 2^\circ$ of values measured with the commercial instrument and in agreement with those reported in the literature.

The Experiment

The goniometer was used to measure the contact angles of aqueous solutions having various concentrations of SDS and Triton X-100 on polytetrafluoroethylene, PTFE (Teflon). The surface tensions of the same solutions were measured

Table 1. Experimental and Literature Values of CMC for SDS and TX-100

Surfactant	CMC/mol L ⁻¹			
	Experimental, by		Literature	
	Surface Tension	Contact Angle	Value	Ref
SDS	5.3 × 10 ⁻³	7.6 × 10 ⁻³	7.4 × 10 ⁻³	8
			7.8 × 10 ⁻³	8
Triton X-100	2.2 × 10 ⁻⁴	2.5 × 10 ⁻⁴	8.0 × 10 ⁻³	8,13
			2.4 × 10 ⁻⁴	14

with a Du Nüoy type tensiometer (see ref 1 for the details of construction). Analytical grades of SDS and Triton X-100 were used as received from Fluka and Merck, respectively.

CAUTION: These surfactants are harmful if ingested or if they contact the skin.

The range of concentration was from 2 × 10⁻⁴ to 2 × 10⁻¹ M for SDS and from 5 × 10⁻⁶ to 1 × 10⁻¹ M for Triton X-100. Figures 4 and 5 show the variation of both the surface tension and the contact angle with the concentration of SDS and Triton X-100. The cmc was determined as the crossing point of the two straight lines that fit the experimental values before and after the abrupt change of slope.

In Table 1, the results are summarized and compared with those reported in the literature.

Summary and Conclusions

The contact angle goniometer described herein is an inexpensive and easy-to-handle instrument that provides experimental results in good agreement with published values.

The goniometer method proposed here to measure the cmc of a surfactant is accurate and simple, suitable for an undergraduate student experiment in surface chemistry. The results are consistent with those reported in literature and also with those obtained by surface tension measurements using a simplified Du Nüoy type tensiometer, with the advantage that only very small samples of surfactant solutions are used. The experiment does not require expert operator skills for good results, and it can be done in one lab period.

Acknowledgment

We are indebted to the late Joaquim Garcia, the builder of the goniometer here described, and wrote this article in his memory.

^WSupplemental Material

Supplemental material for this article is available in this issue of *JCE Online*.

Note

1. The micelle picture in Figure 2 is an oversimplification. Detailed consideration of micelle geometry indicates that the chains are randomly arranged throughout the interior and the aggregation number (the number of monomers in the micelle) is greater. Typical micellar aggregation numbers lie in the range 30–100; different authors have determined the aggregation number for SDS as 64 (10) and 80 (11).

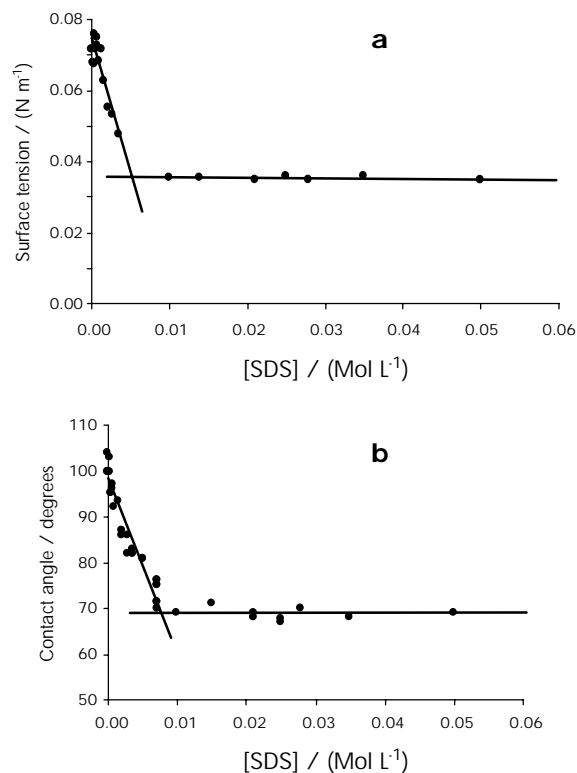


Figure 4. (a) Variation of the surface tension with the concentration of SDS in aqueous solutions at 25 °C. (b) Variation of the contact angle on Teflon with the concentration of SDS in aqueous solutions at 25 °C.

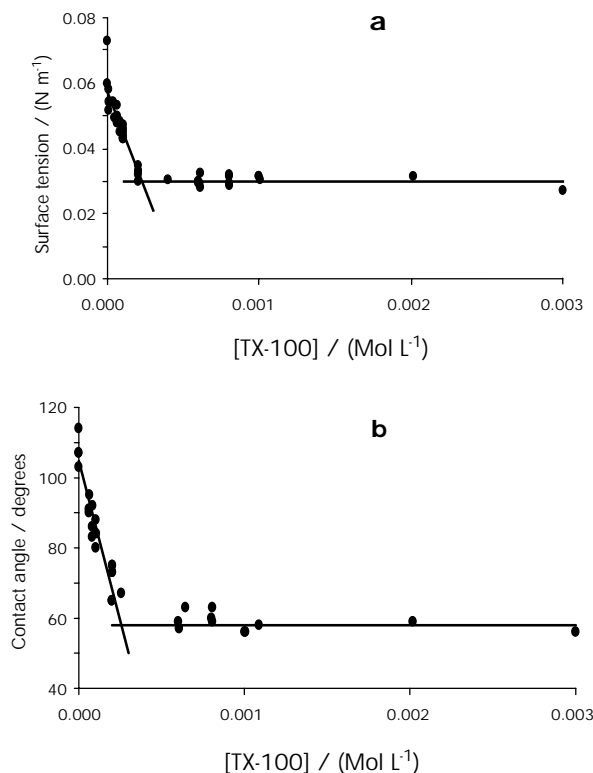


Figure 5. (a) Variation of the surface tension with the concentration of TX-100 in aqueous solutions at 25 °C. (b) Variation of the contact angle on Teflon with the concentration of TX-100 in aqueous solutions at 25 °C.

Literature Cited

1. Sanchez-Rubio, M.; Gordillo, B.; Rushforth, D. S.; *J. Chem. Educ.* **1983**, *60*, 70–71.
2. Meyer, E. F.; Wyshel, G. M. *J. Chem. Educ.* **1986**, *63*, 996–997.
3. Shoemaker, P. D. *Experiments in Physical Chemistry*, 5th ed.; McGraw-Hill: New York, 1989; pp 345–350.
4. Ewart, H. A.; Hyde, K. E. *J. Chem. Educ.* **1992**, *69*, 814–815.
5. Worley, J. D. *J. Chem. Educ.* **1992**, *69*, 678–680.
6. Kabza, K. G.; Cochran, K. *J. Chem. Educ.* **1997**, *74*, 322–323.
7. Furton, K. G.; Norelus, A. *J. Chem. Educ.* **1993**, *70*, 254–257.
8. Dominguez, A.; Fernández, A.; González, N.; Iglesias, E.; Montenegro, L. *J. Chem. Educ.* **1997**, *74*, 1227–1231.
9. Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; Wiley: New York, 1990; Chapter 10.
10. Evans, D. F.; Wennerstrom, H. *The Colloidal Domain: Where Physics, Chemistry, Biology and Technology Meet*; VCH: New York, 1994; p 139.
11. Hiemenz, P. C.; Rajagopalam, R. *Principles of Colloid and Surface Chemistry*, 3rd ed.; Marcel: New York, 1997; p 360.
12. Hunter, R. J. *Foundations of Colloid Science*, 6th ed.; Oxford University Press: New York, 1995; Vol. 1, pp 19–20.
13. Williams, R. J.; Philips, J. N.; Mysels, K. J. *Trans. Faraday Soc.* **1955**, *51*, 728–737.
14. Helenius, A.; Simons, K. *Biochim. Biophys. Acta* **1975**, *415*, 29–79.