

Determination of Surface Tension of Surfactant Solutions through Capillary Rise Measurements: An Image-Processing Undergraduate Laboratory Experiment

Cristián Huck-Iriart,^{†,‡} Ariel De-Candia,[‡] Javier Rodríguez,^{‡,§} and Carlos Rinaldi^{*,‡,‡,‡}

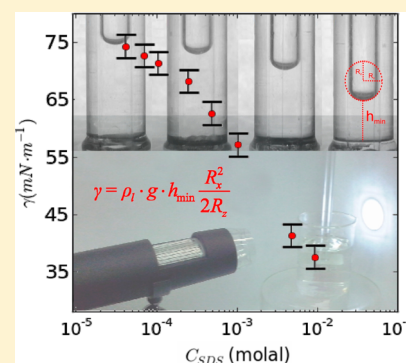
[†]Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata 1900, Argentina

[‡]Escuela de Ciencia y Tecnología, Universidad del General San Martín, San Martín, Buenos Aires 1650, Argentina

[§]Departamento de Física de la Materia Condensada and [‡]Instituto de Nanociencia y Nanotecnología, Comisión Nacional de Energía Atómica, San Martín, Buenos Aires 1650, Argentina

Supporting Information

ABSTRACT: In this work, we described an image processing procedure for the measurement of surface tension of the air–liquid interface using isothermal capillary action. The experiment, designed for an undergraduate course, is based on the analysis of a series of solutions with diverse surfactant concentrations at different ionic strengths. The objective of the work is to illustrate some concepts such as Gibbs isotherm and surface excess for the case of ionic surfactants. To perform the experiment, it is necessary to use glassware commonly found in a chemistry lab along with an USB microscope and digital image processing program (available in the public domain). The experiment can be completed in a 4 h laboratory session.



KEYWORDS: Upper-Division Undergraduate, Physical Chemistry, Computer-Based Learning, Surface Science, Thermodynamics

INTRODUCTION

The capillary effect is the result of the subtle interplay between the gravity and attractive and repulsive forces that occurs at the air–liquid interface of a system. For the case of a system in which liquid, gaseous, and solid phases coexist, the mechanical equilibrium is reached when the contact area between the phases is minimized constrained to a given set of boundary conditions that include the characteristics of the phase components (van der Waals forces, density, and surface tension), the geometrical properties of the confining environment, and other thermodynamic variables such as temperature and pressure.¹

MECHANICS OF CAPILLARY RAISE

The surface tension is a defined intensive property related to the Gibbs free energy (G) according to

$$\left(\frac{\partial G}{\partial A}\right)_{T,P} = \gamma \quad (1)$$

The surface tension (γ) can be interpreted as the free energy per unit of area (A) for a pure system. Additionally, from a mechanical perspective, this parameter could be associated with a restorative force constant, which tends to minimize the area of a given interface.²

Several phenomena, such as the spreading of a liquid over a solid surface, the nucleation process, and the solubility of the small particles, are related to the surface tension. Particularly, it is observed that when a water solution is placed within a cylindrical-like glass container, a concave quasi-ellipsoidal meniscus appears. The curvature of the surface at each point of the interface is the result of the difference between the pressures of the gas and liquid phases in contact, balanced by the capillary pressure. According to the Young–Laplace law, for a system with two main radii of curvature,³ this pressure difference corresponds to

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

If, because of the geometrical characteristics of the container, a circular cross-section is assumed, this equation yields a simple relation between the curvature at the center of meniscus (R_o) and the height of the liquid column within the capillary probe:

$$\gamma = \rho_l g h_{\min} \frac{R_o}{2} \quad (3)$$

Received: February 15, 2016

Revised: May 27, 2016

Moreover, if the meniscus surface could be represented by an elliptical surface with axial and equatorial radii equal to R_z and R_x respectively, eq 3 becomes

$$\gamma = \rho_l g h_{\min} \frac{R_x^2}{2R_z} \quad (4)$$

where ρ_l is the solution density, g is the acceleration due to gravity, and h_{\min} corresponds to the solution column height at the lower extreme of the meniscus (see Supporting Information for more details).

■ THERMODYNAMICS OF THE INTERFACE: THE GIBBS ISOTHERM

The surface tension of a solution could be strongly affected by the presence of amphiphilic molecules known as surfactants (or surface active compounds). These molecules are widely distributed in natural liquid systems and also can be found in several commercial products (detergent, shampoo, food products, etc.). The chemical structure of this tensioactive material is characterized by the presence of a polar or even ionic “head” and hydrophobic “tail”. In aqueous solution, these compounds are mainly located at the air/water interface due to their particular moieties. The presence of a surfactant lowers the surface tension of a solution when the surfactant concentration is lower than the critical micellar concentration.⁴

The affinity of a substance for the interface can be quantified through the Gibbs isotherm. This equation establishes the relation between the variations of the surface tension of the systems with the chemical potentials (μ_i) of their components at a given temperature:

$$(d\gamma)_T = - \sum_i \Gamma_{i(j)} d\mu_i \quad (5)$$

Gibbs names the variable $\Gamma_{i(j)}$ as the surface excess of the i th component in a j solvent. $\Gamma_{i(j)}$ can be understood as a surface concentration of the i th component for a surface conventionally located at an arbitrary plane where $\Gamma_{i(j)}$ is equal to zero. $\Gamma_{i(j)}$ could take positive or negative values depending on how the surface tension is affected by the addition of the solute i . For surface active molecules, this magnitude yields positive values.

In this work, we employed an ionic surfactant: sodium dodecyl sulfate (SDS), whereas in certain experiments, the ionic strength was mainly determined by the addition of a neutral halide salt like the NaCl. Under these circumstances, the variation of the chemical potential of SDS can be written as⁵

$$d\mu_{\text{SDS}} = RT \left[d \ln(f_{\pm}^2) + d \ln(C_{\text{SDS}}) + d \ln(C_{\text{SDS}} + C_{\text{NaCl}}) \right] \quad (6)$$

where R is the gas constant, C_{SDS} is the molal concentration of SDS, C_{NaCl} is the molal concentration of NaCl, and f is the Debye–Hückel activity factor.

The activity factor of the ionic species in aqueous solutions at 298 K can be modeled by the Debye–Hückel equation:⁶

$$\ln(f_{\pm}) = \frac{-1.17 \sqrt{C_{\text{SDS}} + C_{\text{NaCl}}}}{1 + 1.25 \sqrt{C_{\text{SDS}} + C_{\text{NaCl}}}} \quad (7)$$

Consequently, the differential expression for the activity factor is expressed by

$$d \ln(f_{\pm}^2) = C_{\text{SDS}} \left[\frac{-1.17}{(\sqrt{C_{\text{SDS}} + C_{\text{NaCl}}})} \frac{1}{(1 + 1.25 \sqrt{C_{\text{SDS}} + C_{\text{NaCl}}})^2} \right]_{\text{SDS}} \quad (8)$$

By combining eqs 5, 6, and 8, the following expression for the SDS surface excess is obtained:

$$\Gamma_{\text{SDS}} = \frac{-1}{RT \left(\frac{2C_{\text{SDS}} + C_{\text{NaCl}}}{C_{\text{SDS}} + C_{\text{NaCl}}} - \frac{1.17}{\sqrt{C_{\text{SDS}} + C_{\text{NaCl}}}} \frac{C_{\text{SDS}}}{(1 + 1.25 \sqrt{C_{\text{SDS}} + C_{\text{NaCl}}})^2} \right)} \frac{\partial \gamma}{\partial \ln(C_{\text{SDS}})} \quad (9)$$

where the surface excess results proportional to the first derivative of the surface tension versus the logarithmic form of the CSD concentration. The large denominator has two terms: the first one corresponds to the ideal contribution, while the second one take into account deviations typically associated with the presence of electrolytes solutions.

■ MATERIALS AND METHODS

Solutions were prepared using deionized water (less than 18 M Ω /cm). Electrophoresis-grade sodium dodecyl sulfate (SDS) and sodium chloride (NaCl) were obtained from Sigma-Aldrich. A total of 16 solutions were prepared. Eight of them corresponded to SDS concentrations equal to 4.0×10^{-5} , 7×10^{-5} , 1×10^{-4} , 2.5×10^{-4} , 5.0×10^{-4} , 1.0×10^{-3} , 5.0×10^{-3} , and 9.5×10^{-3} molal, respectively. The remaining ones had different SDS concentration and also included a convenient amount of NaCl to get a final concentration of 0.1 molal in NaCl. The corresponding SDS concentrations for these samples were equal to 5×10^{-5} , 7.5×10^{-5} , 1.0×10^{-4} , 2.5×10^{-4} , 5×10^{-4} , 1.0×10^{-3} , 1.0×10^{-2} , and 5.0×10^{-2} molal, respectively.

Each of these samples was placed in a flat glass. A clean glass pipet of 2.9 mm internal diameter was then immersed in the solution (Figure 1). To get a proper alignment, the pipet was

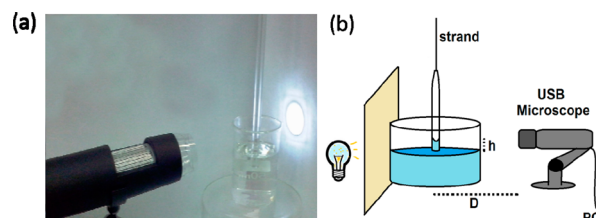


Figure 1. (a) Snapshot and (b) scheme of the experimental setup.

vertically held with a flexible strand. A white paper with a strong back illumination was placed behind the pipet and provided an enhanced contrast to the meniscus profile. USB microscope was used to capture the images of the meniscus. Under the experimental conditions described above, the solutions yield capillary rises ranging from 4–12 mm (h). Higher solvent columns can be achieved if a smaller capillary tube is employed. Image resolution of the order of 0.02 mm/pixel could be obtained for the experimental setup previously described. The distance between the sample and the optical lens (D) was set to approximately 60–100 mm. The microscope was vertically aligned employing the pure water meniscus height as a reference. Since the distance D is much greater than h , the corresponding parallax error is negligible. Special attention must be paid to the fact that this error results proportional to

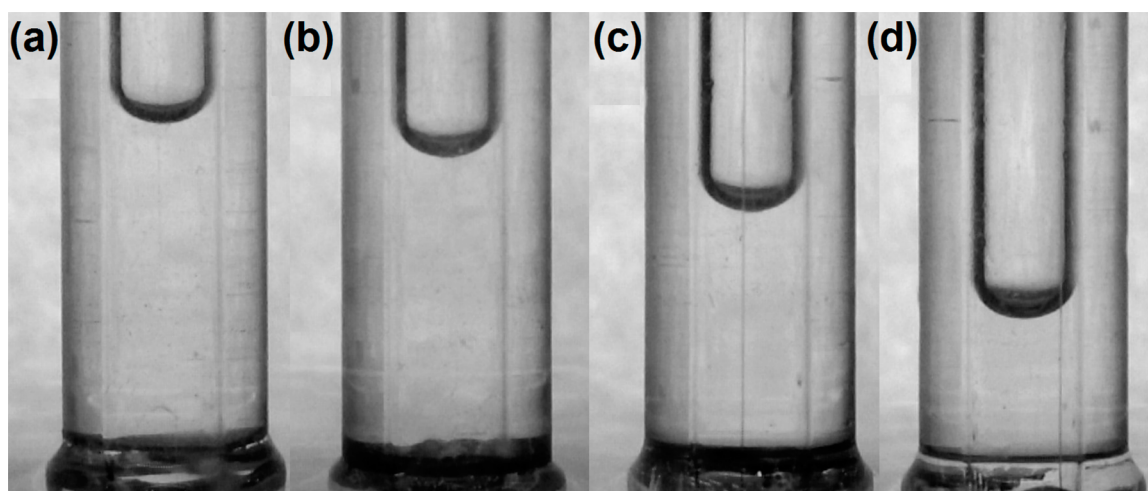


Figure 2. Capillarity action for four increasing SDS solution concentrations (molal): (a) 4×10^{-5} ; (b) 1×10^{-4} ; (c) 5×10^{-4} ; (d) 1×10^{-3} . The experiment was performed in a 2.9 mm glass pipet at room temperature, $T = 295$ K.

h/D . On the other hand, any point can be employed as reference for the position of the water surface plane.

Image processing was made using ImageJ public domain software.⁷ The pictures were transformed into monochromatic 32-bit images, and the edge contrasts were enhanced by a vertical derivative operation (north oriented shadow). A length benchmark (like a ruler) should be used to set the pixel/length scale. The height of the liquid column was determined measuring the height of a rectangle that spans between the minimum of the meniscus and the plane of water surface (this procedure yields more accurate results to those obtained using a single vertical line). The radius of the meniscus in each tube was obtained by an ellipsoidal fitting of its profile. To that end, an eye-guided matching of the meniscus must be done by employing the draw ellipse tool provided by the image processing software.

HAZARDS

Special care must be taken in the preparation of solutions of SDS from the solid reagent. This chemical can cause allergic reactions in the respiratory tract and skin. No other significant hazards are associated with this experiment.

RESULTS

Figure 2 shows results corresponding to four different SDS solutions, all of them without NaCl added. The decrease in the capillary rise with the increment of the SDS concentration is clearly perceived. Note that, from Figure 2, panels a–d, the SDS concentration varies two orders of magnitude, still below the critical micellar concentration (1–5 mm).⁴

The three measured parameters, capillary height at the minimum of the meniscus and equatorial and axial radii (h_{min} , R_x , R_z), obtained by the image processing methodology are shown in the Figure 3. It is important to stress that the measurement of the capillary height (h_{min} , Figure 3a) represents the main source of error in this methodology. Depending on the composition of the solution, the wetting of the external surface of the glass pipet may interfere the determination of a reliable reference height for the surface of the liquid. It is important to note that the meniscus usually shows a nonspherical shape ($R_x \neq R_z$) (see for instance Figure 3b). For these cases, the curvature radii are not equal to the capillary

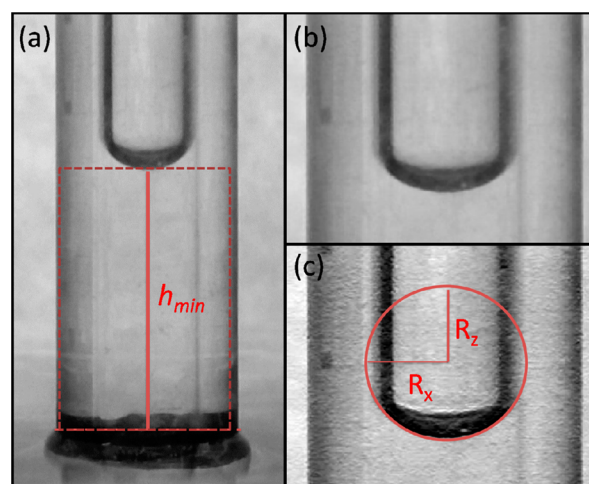


Figure 3. Image analysis to obtain the Young–Laplace ellipsoid curvature radius and capillary height. (a) The capillary height is obtained from the measurement of the distance between the bottom of the meniscus and the solution surface. (b) Capillary meniscus after zooming. (c) The intensity contrast of meniscus edges can be enhanced by a vertical differentiation using a north direction shadow in ImageJ. By using the same software, it is possible to match the edges of the meniscus with an ellipsoid.

radius; therefore, the elliptical fitting of the meniscus profile will provide both radii R_x and R_z . To improve the results of the fitting procedure, a previous image enhancement operation is recommended. In Figure 3, panel c, the contrast enhancement of the meniscus edges obtained after applying a north shadow improvement operation is clearly observed. Under the given experimental conditions, the fitting of the meniscus profile employing an ellipsoid geometrical shape results in a more accurate determination of the surface tension than the classical measurement of the contact angle between the liquid and the glass wall.

The experimental value of the surface tension for pure water at 295 K obtained from our measurements corresponds to 76 ± 2 mN/m, a result that is in good agreement with other reported values.⁶ The thickness of the edges of the liquid that preclude us from a precise identification of the meniscus surface limit, along with errors associated with the image handling, are

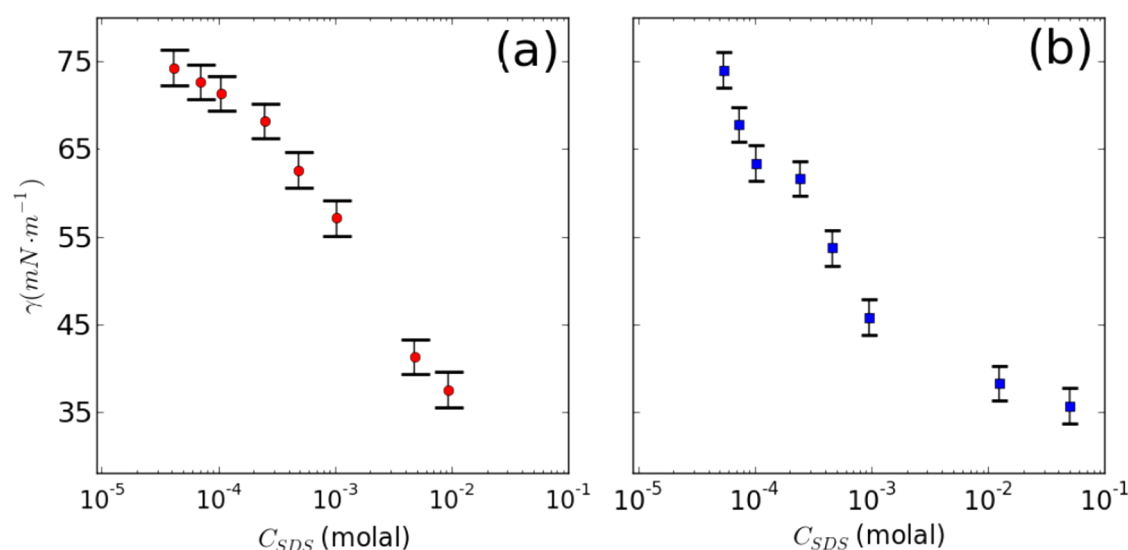


Figure 4. Surface tension as a function of the SDS concentration in semilogarithmic scale (a) without NaCl added and (b) with 0.1 m of NaCl added.

mainly responsible for the uncertainty of our measurements, which roughly corresponds to a value of 2 mN/m. It is interesting to notice that the meniscus radius does not significantly vary with the addition of SDS. Meanwhile, R_x was approximately 1.65×10^{-3} m for all solutions, and R_z values of 1.45×10^{-3} m and 1.7×10^{-3} m were obtained for SDS solutions with and without NaCl addition, respectively.

The values for the liquid/air surface tension calculated through eq 4 as a function of SDS concentration are shown in Figure 4.

The surface excess was calculated using eq 9, where the individual slope was calculated by splines interpolation. As can be seen in Figure 5, significant differences between the two curves can be observed. From these experiments, student should notice the effect of salt addition in an ionic surfactant like the SDS.

Surfactant activity of SDS is a direct consequence of the hydrophobic effect. The charged heads of the surfactant are well solvated with the water molecules, and hydrocarbon chains are expelled from the polar phase. Like in other known adsorption processes, as more SDS molecules are incorporated into the bulk phase, the (adsorbing) surface of the liquid becomes more populated with surfactant molecules. As the surface excess increases, effects associated with lateral interaction between chains and Coulombic repulsion between charged heads become more intense. Beyond this point, surface excess reaches a plateau value, which denotes the saturation of the surface. The presence of NaCl in the system screens out Coulombic repulsion between ionic moieties, which allows for the appearance of a more packed structure for the adsorbed phase. Consequently, for similar bulk concentrations of SDS, greater values of surface excess are obtained in the presence of salt. Since high occupancies of the surface are achieved at low bulk surfactant concentrations, the saturation of the surface occurs at a lower SDS concentration. As a consequence, surface excess shows minimal differences between the majorities of the SDS concentrations analyzed.

Instructors will discuss this issue with students. As a complementary activity, differences and similarities between these particular systems and the commonly employed adsorption isotherms models could also be debated in class.

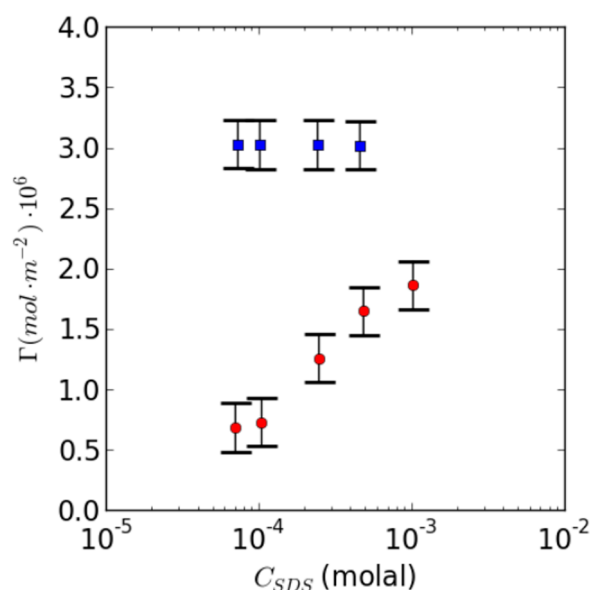


Figure 5. Surface excess as a function of the SDS concentration: in circles, the surface tension is plotted without NaCl added and in squares for solutions with 0.1 m NaCl.

Despite the small accuracy of the methodology, when it is compared to other advanced image processing such as entropic edge detection,⁹ the dependence of the surface tension with concentration is consistent with bibliography sources.^{5,8,10} This method proved to be a reliable method to measure and understand properties in aqueous/air interfaces.

CONCLUSIONS

In this work, we present a simple and inexpensive methodology for the determination of surface tension of aqueous solutions for an undergraduate physical chemistry lab. Compared with the experiments that rely on the use of other techniques, the present one has two important advantages: (i) the simplicity of the required instrumentation, a fact that allows easy implementation of this experiment; and (ii) the simplification of the operational work that has to be done by the students,

which makes it possible to carry out the experiment in the course of a typical laboratory class (~4 h)

The results obtained with this technique do not show significant differences when our results are compared to those obtained with more refined methodologies.

The practice illustrates the thermodynamical principles of surface tension, capillary action, and detergency.^{11,12} Some concepts as surface excess, along with details pertaining the surface structure of ionic solutions, are also explored within the framework of this experiment.

In addition, the activity allows students to become familiar with image processing and data analysis techniques.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00128.

Theoretical approach for instructors and students; notes, directions for students; tables of experimental data (PDF, DOC)

Determination of surface tension and surface excess; splines and derivatives (XLS)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rinaldi@cnea.gov.ar.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the ECyT UNSAM for providing material means required for the development and implementation of this laboratory experiment.

■ REFERENCES

- (1) Hiemenz, P. C.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*, 3rd ed.; Marcel Dekker: New York, 1997; pp 248–261.
- (2) Ip, S. W.; Toguri, J. M. The equivalency of surface tension, surface energy and surface free energy. *J. Mater. Sci.* **1994**, *29*, 688–692.
- (3) Adamson, A. R.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; John Wiley and Son, Inc: New York, 1997; pp 24–67.
- (4) Marcolongo, J. P.; Mirenda, M. Thermodynamics of Sodium Dodecyl Sulfate (SDS) Micellization: An Undergraduate Laboratory Experiment. *J. Chem. Educ.* **2011**, *88*, 629–633.
- (5) Persson, C. M.; Jonsson, A. P.; Bergström, M.; Eriksson, J. C. Testing the Gouy–Chapman theory by means of surface tension measurements for SDS–NaCl–H₂O mixtures. *J. Colloid Interface Sci.* **2003**, *267*, 151–154.
- (6) Slavchov, R. I.; Karakashev, S. I.; Ivanov, I. B. Chapter 2: Ionic surfactants an ion specific effects. *Surfactant Science and Technology: Retrospects and Prospects*. Romsted, L., Ed.; CRC Press: Boca Raton, FL, 2014; pp 64–65.
- (7) Abramoff, M. D.; Magalhaes, P. J.; Ram, S. J. Image processing with ImageJ. *Biophotonics International* **2004**, *11* (7), 36–42.
- (8) Moreno-Dorado, F. J.; Bethencourt-Nuñez, M.; Moreno, C.; Pinto-Ganformina, J. J.; Poce-Fatou, J. A. A lab experience to illustrate the physicochemical principles of detergency. *J. Chem. Educ.* **2008**, *85* (2), 266–268.
- (9) Atae-Allah, C.; Cabrerizo-Vílchez, M.; Gómez-Lopera, J. F.; Holgado-Terriza, J. A.; Román-Roldán, R.; Luque-Escamilla, P. L. Measurement of surface tension and contact angle using entropic edge detection. *Meas. Sci. Technol.* **2001**, *12*, 288–298.

(10) Prosser, A. J.; Franses, E. I. Adsorption and surface tension of ionic surfactants at the air-water interface: review and evaluation of equilibrium models. *Colloids Surf, A* **2001**, *178*, 1–40.

(11) Poce-Fatou, J. A. A Superficial Overview of Detergency. *J. Chem. Educ.* **2006**, *83* (8), 1147–1151.

(12) Loglio, G.; Pandolfini, P.; Miller, R.; Makievski, A. V.; Ravera, F.; Ferrari, M.; Liggieri, L. Drop and Bubble Shape Analysis as a Tool for Dilatational Rheological Studies of Interfacial Layers. *Novel Methods To Study Interfacial Layers*; Möbius, D., Miller, R., Eds.; Elsevier Science: Amsterdam, The Netherlands, 2001; pp 439–483.