MEASUREMENT OF PENDANT DROP TENSIOMETRY TO DETERMINE THE OPTIMUM VOLUME TO MEASURE INTERFACIAL TENSION

Beatriz Almeida Carneiro Palmeira[1], Lílian Lefol Nani Guarieiro[a], Gabriel de Veiga Cabral Malgaresi[a], Claudio Dariva [b], Josefa Manuela Santos Gonçalves [b], Iago Filipe Silva de Oliveira[b]

[a], Centro Universitário Senai Cimatec,
[b] Universidade Tirandentes

Abstract: The Pendant drop tensiometry offers a simple solution to determining surface and interfacial tension. The droplet pendant method is based on determining the profile of a droplet of a liquid with higher density than the other of lower density in mechanical equilibrium. However, to ensure the reliability of the data it is necessary to realize a preliminary study of the volume and interfacial area of the droplet formed. In this work, the influence of the droplet volume, in a system with petroleum and sodium sulfate in deionized water, was studied. It was shown that the variation of the droplet volume is independent of the droplet volume, but in order that the droplet does not stand out during the interfacial film ageing time, it was necessary to use a volume of 80%.

Keywords: Pendant drop; interfacial tension; drop volume analysis.

MEDIÇÃO DA TENSIOMETRIA DE GOTA PENDENTE PARA DETERMINAÇÃO DO VOLUME ÓTIMO PARA MENSURAR A TENSÃO INTERFACIAL

Resumo: The Pendant drop tensiometry offers a simple solution to determining surface and interfacial tension. The droplet pendant method is based on determining the profile of a droplet of a liquid with higher density than the other of lower density in mechanical equilibrium. However, to ensure the reliability of the data it is necessary to realize a preliminary study of the volume and interfacial area of the droplet formed. In this work, the influence of the droplet volume, in a system with petroleum and sodium sulfate in deionized water, was studied. It was shown that the variation of the droplet volume is independent of the droplet volume, but in order that the droplet does not stand out during the interfacial film ageing time, it was necessary to use a volume of 80%.

Palavras-chave: Gota pendante, tensão interfacial, análise do volume da gota.

1. INTRODUCTION

Molecular interactions for fluids in the interface result in a measurable tension, if constant, equal to surface-free energy required to form an interface area unit. It is equally correctly described as a measure of how much energy is required to make a unit area of interface between two immiscible liquids [1, 2]. Interfacial tension is dimensionally expressed in terms of energy per area (J/m2), which is equivalent to displacement force (N/m), and these units are the most used [1].

Interfacial tension is a concept of fundamental importance in colloidal science, describing phenomena as diverse as the formation, shape and stability of liquid drops and the cost of surface energy in the formation of an emulsion [3, 4]. Therefore, accurately, and effectively measuring interfacial tension is of critical importance for both science and industry.

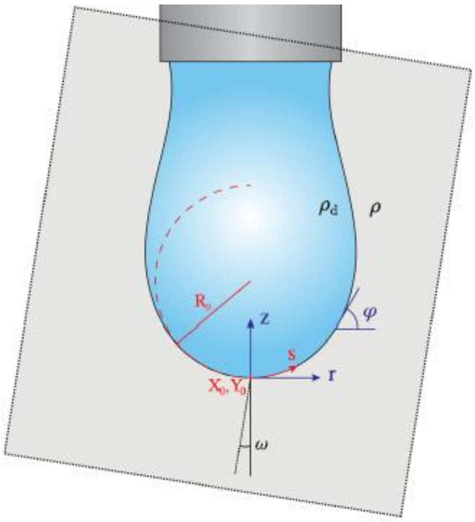
Many techniques have been proposed to measure interfacial tension, such as: Wilhelmy Plate; Maximum Bubble Pressure; Spinning Drop; Du Noüy Ring, Capillary Rise and Pendant Drop, its characteristics and qualities are described in detail by Drelich et al., (2002) [5]. The simple, robust and versatile method is pendant drop tensiometry, where the technique consists of profiling a drop of fluid, immersed in a continuous phase, and determining the interfacial tension as a function of the aging time of film formed [6].

Therefore, it is convenient to relate interfacial tension with the variation of energy to the geometric characteristics of a sphere. The Equation of Young-Laplace (1), recognized as the first fundamental principle of surface thermodynamics, correlates that relates Laplace pressure across an interface with interface with the curvature of the interface and the interfacial tension ϒ [1].

$$\Upsilon\left(\frac{1}{R_1}+\frac{1}{R_2}\right) = \Delta P \equiv \Delta P_O - \Delta\rho g z \qquad (1)$$

Where, R_1 and R_2 are the principal radii of curvature; ϒ is the interfacial tension ($mN.m^{-1}$), ΔP is the Laplace pressure across the interface ($mN.m^{-2}$), Δρ is the difference of densities between the fluids of the continuous phase and the drop phase ($kg.m^{-3}$), g is the local gravitational constant ($m.s^{-2}$), ΔP_0 is the pressure difference in the reference plane in Z = 0 ($mN.m^{-2}$), and Z is the vertical measure measured from a reference plane, as illustrated in Figure 1.

Figure 1: schematic of a pendant drop below a needle. Adapted from [7].



The factors that may alter the interfacial tension are related to diverse conditions, such as: the different shapes, size, and/or chemical nature of the solute in relation to the solvent. Commonly, organic solutes – which have limited solubility in water – are used as surface active agents, or surfactants which through physical phenomena are able to adsorb in the interfacial region [8].

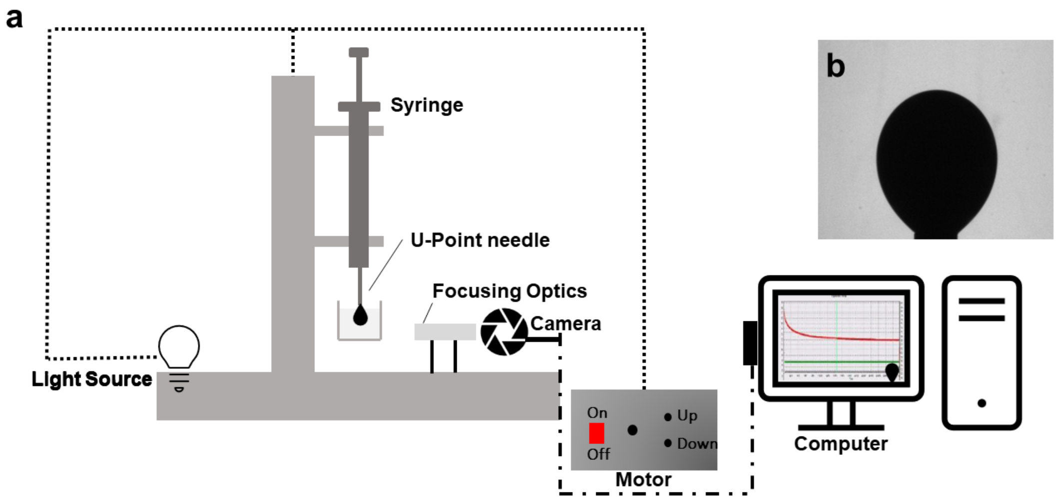
Therefore, the objective of this work is to adjust the drop profile through its volume and area to obtain the interfacial tension between an oil sample in contact with a system containing sodium octyl sulfate in deionized water, through the pending drop method.

1.1. Description of the pedant drop tensiometry technique equipment

The experimental apparatus needed for droplet tensiometry is basically: a camera, a light source, a needle and the software for drop visualization and interfacial tension calculation. A basic experimental setup is shown in Fig. 2a.

Though the experimental setup is relatively simple, some factors must be considered to ensure that image is of sufficient quality for precise determination of interfacial tension. Crucially, that needle must be keeps the drop suspended during the entire time of the test. The main factor in the drop fall down from the needle is a high drop volume. As the volume of the drop directly influences the precision of the measurements, it is necessary to carry out a prior study of the optimum volume of the drop for carrying out the tests. A typical image that is well suited to fitting is shown in Fig. 2b

Figure 2: (a) A basic experimental setup for pendant drop tensiometry; (b) a typical drop image acquired by Teclis equipment.



2. METHODOLOGY (ARIAL 12)

The study of interfacial tension was performed by means of a drop pendant tensiometer (IT concept, TECLIS) available at Núcleo de Estudos de Sistemas Coloidais. In this technique the oily phase is inserted into a syringe containing a U-shaped needle which is injected into a cuvette containing the aqueous phase composed of sodium octyl sulfate in deionized water. The camera of the equipment performs the interfacial tension calculations by solving the Young-Laplace equation.

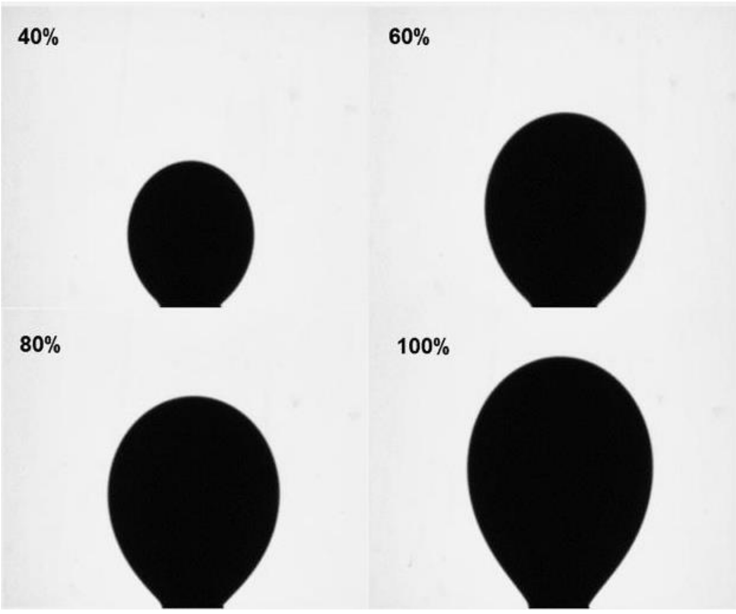
First a study was conducted to obtain the optimum value of the droplet volume, where it was selected the largest possible value of the droplet where the camera can fully visualize. From this selected droplet volume, interfacial tension measurements were performed for 30 minutes at 25ºC for this value and its fractions (100%, 80%, 60%, 40%). The interfacial tension tests were performed with duplicates and volume values used in this study.

3. RESULTS AND DISCUSSION (ARIAL 12)

The initial parameters for the study, the tests were carried out with a sample of national petroleum and aqueous solution containing sodium octyl sulfate at 3.000 ppm in deionized water at 25 °C. The optimal values of volume and interfacial area of the drop for interfacial tension tests were investigated.

Droplet volume directly interfaces with interfacial tension measurements. Thus, the calculations are performed by sketching the droplet shape, the droplet volume directly affects the noise of the interfacial tension values. Therefore, interfacial tension tests were carried out with aging time of 30 minutes for four different droplet volume values, as illustrated in Figure 3.

Figure 3: Drop volume for 40, 60, 80 and 100%. Image acquired by Teclis equipment.



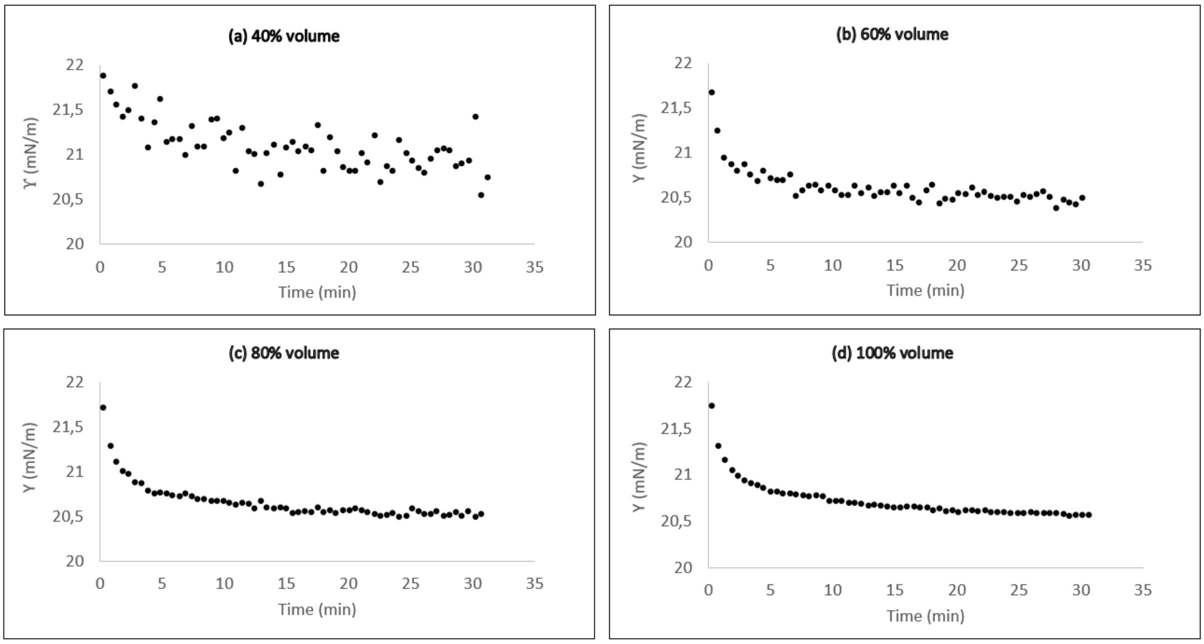
From table 1, it can be observed that although the volumes had different values, the values of the interfacial tension in the time of 30 minutes were not influenced by drop volume variation within the investigated experimental range. The values of the volumes and the corresponding interfacial area and the interfacial tension measurements are presented in Table 1.

Table 1: Values of interfacial tension during 30 minutes for given volumes and droplet interfacial area.

Drop volume percentage (%)	Drop volume (mm^3)	Interfacial area (mm^2)	Interfacial tension at 30 min (mN/m)
40	9,34	19,59	20,54
60	16,43	29,38	20,50
80	24,60	39,24	20,49
100	33,48	49,00	20,57

Although the non-significant influence of drop on interfacial tension in the oil and sodium octyl sulfate with water, also investigated the influence of drop volume on noise of interfacial tension measurements. Figure 4 related the interfacial tension curves as a function of time for all volume fractions investigated.

Figure 4: Dynamics of interfacial tension for the investigated drop volumes: a) 40%, b) 60%, c)80%, d) 100%.



Based on Figure 3, the influence of the drop volume on the noise of the interfacial tension measurements can be observed. Although all curves have similar tendence dynamics for this system, the decrease in drop volume represents a greater dispersion in interfacial tension measurements. From the graphs, it is observed that volumes less than 60% present a high noise level that would make it inadvisable to use these values for subsequent tests.

Another aspect to be considered are the experimental errors in long tests due to the detachment of the drop on the needle due to the difference in densities between the drop (oily phase) and the aqueous phase. Thus, drops with high volume values have a greater tendency to detachment, causing the cancellation of the assay. With this, it is also not advisable to use the volume of 100%.

Therefore, the optimum value of the interfacial volume and area consists of the value of 80%. From the optimal droplet volume and interfacial area, subsequent tests will be carried out to investigate the influence of sodium sulfate concentration on the interfacial tension.

4. CONCLUSION

The pendant drop method is a powerful technique that can be used to accurately determine the interfacial tension. For data reliability, it is extremely important to estimate the volume and interfacial area as premises for subsequent interfacial tension testing.

Therefore, for the oil/sodium octyl sulfate system in deionized water it was determined that the optimum droplet volume for interfacial tension tests was equivalent to 80%, which corresponds to a volume of 24.60 mm^3 and interfacial area of 39.24 mm^2.

Thus, with the results it is possible to accurately perform the tension tests with minimal noise ensuring that the drop will not detach over the aging time of the interfacial film

Acknowledgments

The authors thank to PRH 27.1 of the ANP/FINEP; Centro de Competências em Soluções Integradas Onshore; Núcleo de Estudos em Sistemas Coloidas ITP; Universidade Tirandentes (UNIT) and SENAI/CIMATEC for the support and for research incentives.

5. REFERENCES

1 A. P. G. Arthur W. Adamson, *Physical Chemistry of Surfaces*. 1997.

2 G. Castellan, “ISICO-QUIMI,” 1995.

3 J. Eggers, “Nonlinear dynamics and breakup of free-surface flows,” *Rev. Mod. Phys.*, vol. 69, no. 3, p. 865, 1997.

4 J. Eggers and E. Villermaux, “Physics of liquid jets,” *Reports Prog. Phys.*, vol. 71, no. 3, p. 36601, 2008.

5 J. Drelich, C. Fang, and C. L. White, “Measurement of interfacial tension in fluid-fluid systems,” *Encycl. Surf. colloid Sci.*, vol. 3, pp. 3158–3163, 2002.

6 E. H. Lucassen-Reynders and J. Lucassen, “Surface dilational rheology: past and present,” *Interfacial Rheol. Miller, R., Liggieri, L., Eds*, 2009.

7 J. D. Berry, M. J. Neeson, R. R. Dagastine, D. Y. C. Chan, and R. F. Tabor, “Measurement of surface and interfacial tension using pendant drop tensiometry,” *J. Colloid Interface Sci.*, vol. 454, pp. 226–237, 2015, doi: 10.1016/j.jcis.2015.05.012.

8 D. Myers, *Surfaces, interfaces, and colloids*, vol. 4. 1999.