Pendant drop tensiometry of milk-water solutions

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Abstract

The surface tension of liquids were measured using the pendant drop tensiometry technique, which only requires the use of a needle, a camera, and a diffused light source. For certain liquids with known literature surface tension values, the experiment results agree well with the expected ones. We examine the effect of changing the concentrations of whole, low fat, and no fat milk to the surface tension of milk-water solutions. Low fat milk decreases the surface tension of the solution fastest in comparison with the other two. For all milk types, the solution surface tension decreased exponentially, which implies that the effect is greater at lower concentrations (< 50 %) than at higher concentrations. This phenomenon can be described by the Gibbs-Thomson equation, which relates surface tension, concentration, and surface adsorption.

Keywords: Surface tension (68.03Cd), Drops (47.55D-), Image processing (47.80.Jk)

1 Introduction

Surface tension, denoted by γ, describes the amount of energy per unit area needed for a liquid to resist atmospheric force on its surface, taking the unit Joules per square meter (J/m^2) or the more commonly used Newtons per meter (N/m) [1, 2]. Berry and company proposed the method pendant drop tensiometry in measuring surface tension through image processing. By measuring the dimensions of a liquid droplet suspended from a needle, they were able to calculate the surface tension of the liquid. The Young-Laplace equation relates the surface pressure between two media to the measure of their interfaces' curvature and surface tension γ [1, 3], and is given by

$$\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \Delta P \equiv \Delta P_o - \Delta\rho g z \tag{1}$$

where R_1 and R_2 are the principal radii of curvature, and $\Delta P \equiv P_{\text{in}} - P_{\text{out}}$ is the Laplace pressure across the interface. All variables are defined on Fig. 1C. In the case of a pendant drop, medium 2 is the atmosphere whose pressure is constant and the right hand side becomes $\Delta P_o - \Delta\rho g z$ where ΔP_o is a reference pressure at z = 0 and $\Delta\rho = \rho_d - \rho$ is the density difference across the drop and the atmosphere [3].

In this paper, pendant drop tensiometry was used to measure the surface tension of liquids with known surface tension values to confirm the accuracy of the method. It was then used to measure the surface tension of three kinds of milk: whole, low fat, and no fat milk at different concentrations. Knowing the surface tension of these solution allows us to deduce surface level properties of the liquid and to carefully conduct future experiments which take surface tension into account (e.g., three-dimensional reconstruction of surface waves via the diffusing light imaging technique [4]).

2 Methodology

The experiment setup is shown in Fig. 1A. It is composed only of a light source, a diffuser, a syringe with a blunt needle, and a camera. However, in spite of the simplicity there are factors that must be maintained: the needle must be absolutely parallel to gravity, and the air currents passing through and around the droplet must be reduced [1].

Fig. 1B shows the frame that holds the syringe. Acrylic glass was cut into four pieces with dimensions $15.24 \times 15.24 \times 4.5$ cm^3. The pieces were glued together to form a lidless glass box, which serves as a cuvette to prevent air currents from affecting the droplet shape. Two blocks of wood with dimensions $15.24 \times 8.89 \times 2.54$ cm^3 were screwed together and half cylinders were carved from each block on the surface where they meet, which serves as a clamp to hold the syringe in place.

The syringe was filled with water and a video was taken as water was slowly released from the syringe forming droplets at the end of the needle. Each frame of the video was extracted and converted to an image file. Selection of the images to be processed was done manually. To be able to take accurate values

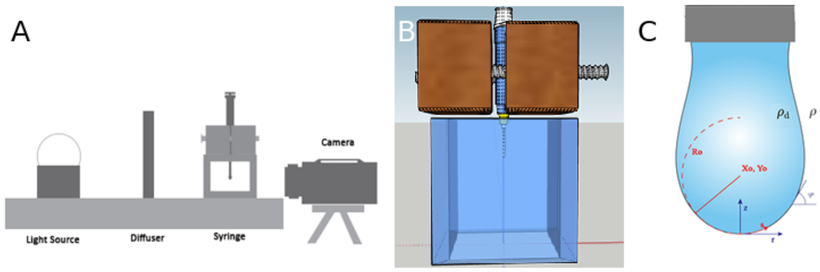

Figure 1: (A) Experiment set-up. (B) SketchUp model for the syring clamp and the cuvette. (C) Schematic diagram of the droplet [1]

of γ, the image of the droplet must be at a few seconds before detaching from the needle. Samples of droplets that will give accurate results are Figs. 2C and 2D. Figs. 2A and 2B will give inaccurate γ values. The chosen images were fed to the program, OpenDrop 11, provided by Berry and company in their paper [1].

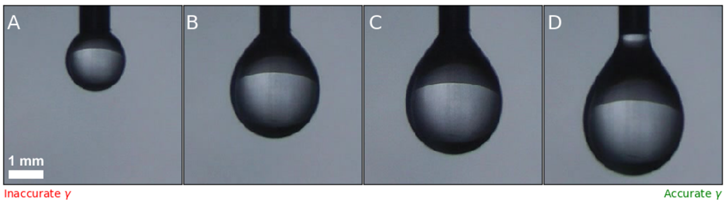

Figure 2: Sample droplet images from captured video.

OpenDrop 11 processes the image after the user selects the region of the needle (Fig. 3A), and of the drop (Fig. 3B). It measures the value of γ ($\frac{\mathrm{mN}}{\mathrm{m}}$), volume of the drop ($\mu$L), and surface area ($\mathrm{m}^2$) by fitting the Laplace equation onto the droplet (Fig. 3C), analyzing the droplets' dimension (Fig. 3D), and solving for the different values. Only γ was measured in this paper.

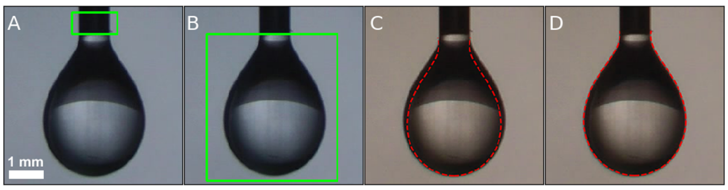

Figure 3: Opendrop 11 Interface (A) Needle region selection. (B) Droplet region selection. (C) Initial fitting guess. (D) Final fit.

The data collection and processing were repeated for other liquids, such as 70% Isopropyl alcohol, baby oil, whole milk, low fat milk, no fat milk, Ilfotol (surfactant used for photographic processing), and at different concentrations of milk-water solutions for the three different kinds of milk (with brand Nestlé).

3 Results and Discussion

The measured surface tension values of water, alcohol, baby oil, and Ilfotol are shown in Table 1. The given literature values are not the exact values for each substance. These values were taken from substances of similar composition: 70% 2-propanol for Isopropyl alcohol, mineral oil for baby oil, and Tergitol surfactant for Ilfotol. This explains the error reaching up to 18%. However, it still shows that the pendant drop method is an effective tool to measure surface tension.

For every type of milk (whole, low fat, and no fat), surface tension at different concentrations of milk in water from $0 - 100\%$ at 5% intervals were measured. The results are shown in Fig. 4.

Adding small amounts of milk to water significantly lowered the surface tension, true for all kinds of milk. As milk concentration is increased, the effect on surface tension slowly decrease shown by an initially steep slope gradually decreasing into an almost horizontal line. Each plot seems to show an

Table 1: Surface tension of common liquids.

Substance	Surface Tension ($\frac{mN}{m}$)	Estimated Literature Value	Percent Error (%)
Water	72.52 ± 134	72.0 [5]	0.7
Isopropyl alcohol	26.55 ± 0.29	22.68 (70% 2-propanol) [6]	14
Baby Oil	32.48 ± 0.88	32.3 (mineral oil) [7]	0.5
Ilfotol	29.79 ± 0.55	36.0 (Tergitol surfactant) [8]	17.25

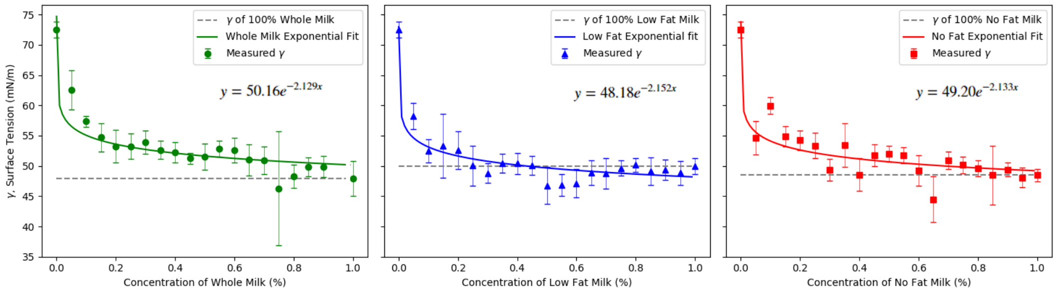

Figure 4: Plot of concentration v surface tension for whole (left), low fat (center), and no fat (right) milk-water solutions.

exponential decay from the surface tension of water towards the surface tension of milk. The best-fit equation for the curves are shown in Fig. 4, where x is concentration and y is the surface tension.

Our results are in accordance to Fessenden's [9] results where he mentioned a study on energy relationships in solutions. It states that adding small amounts of substance B to A where $\gamma_A > \gamma_B$ decreases the solution's surface tension with respect to γ_A significantly. On the other hand, if $\gamma_A < \gamma_B$, the solution's surface tension does not change significantly with respect to γ_A. Percival [10] and Fessenden [9] say this is caused by the presence of protein in milk. It also matches Percival's results, in his case on different forms of proteins, where adding small amounts of these proteins greatly decreased the surface tension but increasing the concentration only slightly decreases the surface tension. The change in surface tension approaches zero as the concentration reaches the limiting value or saturation. The effect of the added substance on increasing or decreasing the surface tension of the solution can be qualitatively described in a formula developed by Gibbs and Thomson independently [9], which is given by

$$\mathrm{u} = -\frac{c}{\mathrm{RT}} \cdot \frac{\mathrm{d}\gamma}{\mathrm{dc}} \tag{2}$$

where u is the excess or defect in the concentration of the dispersed phase in the surface layer, c is the concentration, R is the gas constant, T is the absolute temperature, and $\frac{\mathrm{d}\gamma}{\mathrm{dc}}$ is the rate of change of the surface tension with respect to changes in concentration. The values of c, R, and T are always positive, which means that when $\frac{\mathrm{d}\gamma}{\mathrm{dc}}$ is positive, u is negative, and when $\frac{\mathrm{d}\gamma}{\mathrm{dc}}$ is negative, u is positive. This means that for substances that increase the surface tension, it will be less concentrated in the surface layer than in the rest of the system. Meanwhile, for substances that decrease the surface tension, it will be more concentrated in the surface layer than in the rest of the system [9]. The equation shows that a small amount of the added substance can decrease the surface tension greatly, or increase it very slightly [9].

Fessenden [9] also mentions that two among his references state that protein and fat cause changes in surface tension, but another stated fat has little influence on surface tension. The protein contents of the milk used in this paper are more or less the same with 8.8 g, 9.0 g, and 8.8 g for every 250 mL of whole milk, low fat milk, and no fat milk, respectively. On the other hand, their fat contents are 8.7 g, 3.7 g, and 0.5 g, respectively. It can therefore be said that the differences in surface tension of the three different kinds of milk are not due to the protein content but due to the fat content. Looking at Table 2, the surface tension of each milk is more or less equal with each other. It also shows that low fat milk reached saturation fastest where γ no longer decrease at around $10-15\%$, followed by no fat milk at around $25-30\%$, and the slowest, whole fat milk at around $40-45\%$. Their rates of decay do not follow any trend in relation to their fat content. Comparing their best fit equations in Fig. 4, their decay constant slightly differs from each other at only ± 0.01 differences. It may be then said that fat content has little to no effect in the surface tension or to the rate of decay of the surface tension of the milk-water solution, confirming the results of Percival [10]. It is possible that the low fat milk indeed decreases the surface tension fastest but there might be other components present in milk which cause this result.

Table 2: Surface tension of different concentrations of milk.

	Surface Tension ($\frac{\mathrm{mN}}{m}$)		
Concentration (%)	Whole Milk	Low Fat Milk	No Fat Milk
0 (water)	72.52	72.52	72.52
5	62.57	58.22	54.69
10	57.36	52.45	59.96
15	54.71	53.32	54.83
20	53.24	52.57	54.24
25	53.23	50.03	53.35
30	53.94	48.81	49.40
35	52.65	50.44	53.40
40	52.21	50.43	48.55
45	5125	50.06	5177
50	5156	46.77	5196
55	52.89	46.84	5174
100 (milk)	47.96	49.96	48.47

4 Conclusions

To test the accuracy of the pendant drop tensiometry method, it was used to measure the surface tension of substances with known surface tension. The values obtained deviated by $0.5 - 18\%$ from the literature values taken from substances of similar composition. The method is therefore an effective tool to measure surface tension.

Adding different concentrations of milk to water lowers the surface tension exponentially. As milk concentration is increased, the change on the surface tension decreases until it reaches zero at saturation, obeying the Gibbs-Thomson equation.

Low fat milk decreases the surface tension fastest, followed by no fat milk, then whole milk. Since they do not follow the trend on fat content it may be that their difference is caused by some other component, or the small difference indicates that their rates of decrease are more or less the same.

Acknowledgments

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