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Determining liquid–liquid interfacial tension from a submerged meniscus

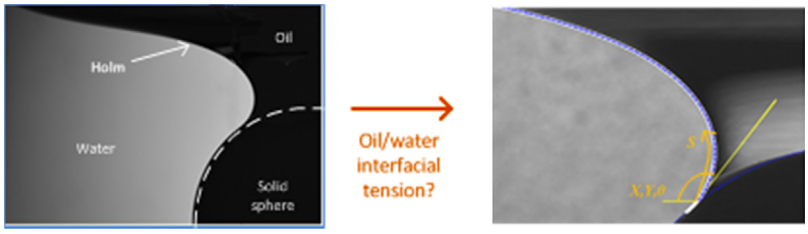
Anita Hyde, Chi Phan*, Gordon Ingram

Department of Chemical Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

HIGHLIGHTS

- Liquid–liquid interfacial tension was determined from submerged holm meridian.
- The interfacial tension was obtained successfully for four oil-water interfaces
- The method is applicable for a density difference as low as 10 kg/m^3.

GRAPHICAL ABSTRACT



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ABSTRACT

Liquid–liquid interfacial tension plays a crucial role in multiphase systems in the chemical industry. The available measurement methods for liquid–liquid interfacial tension are poorly suited to low bond number systems, which are often found in industrial processes. This study developed and verified a new method of calculating the interfacial tension of liquid–liquid systems by using the "submerged holm" meniscus. The holm meridian was experimentally formed around a solid object submerged at the interface. A program was developed in MATLAB to calculate the interfacial tension from the submerged holm meridian. The interfacial tension calculated by the new method was found to be consistent with available data for multiple oil–water systems. This is the first time the submerged holm meniscus has been used successfully for determining interfacial tension. More importantly, the method is applicable to liquid–liquid systems with a small density difference between the two phases. As a demonstration, the interfacial tension of silicone oil (1000 cP) – water was measured, where the difference in density was less than 30 kg/m^3 (3%). The method is potentially suitable for processes involving hazardous or unstable chemicals, elevated pressure or temperature.

1. Introduction

Liquid–liquid interfacial tension is an important physical parameter affecting multiphase systems throughout a range of processes, such as separation and emulsification. Consequently, it impacts through the chemical industry, from food to cosmetics and chemical processing. In the literature, there are a number of methods for measuring interfacial tension as reviewed by [1]. However, most of these methods are only applicable to gas–liquid systems. For example, the common tensiometric methods based on force measurement, such as the Du Noüy ring and the Wilhelmy plate, are not practical for analysis of liquid–liquid systems. The measurement of liquid–liquid interfacial tension relies predominantly on optical analysis, such as the pendant drop, sessile drop and spinning drop techniques.

The pendant drop method, which employs Axisymmetric Drop Shape Analysis (ADSA), has remained the most practical method for the tensiometric analysis of liquid–liquid systems. ADSA methods make use of specialized analysis software and high-resolution images to match experimental drop profiles with

* Corresponding author. Tel. +61 892667571.
E-mail address: c.phan@curtin.edu.au (C. Phan).

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solutions to the Young–Laplace equation of capillarity. This typically involves a combination of numerical integration, for solving the Young–Laplace equations, with multivariate optimization to find the best-fit parameters defining the drop boundary. The optimal fitting parameters are then used to determine the interfacial tension. Several variations on ADSA programs have been developed to facilitate the analysis of pendant and sessile drops and their phase-inverted counterparts: emergent and constrained bubbles. These are presented in several papers [2–6].

While the ADSA technique can be applied to both gas–liquid and liquid–liquid interfaces, the ability to form and maintain the droplet or bubble remains a physical limitation of the method, particularly for systems requiring a long equilibration time. Additionally, droplets are typically formed and maintained by a micro-pump. For oil–water measurements, the fluid phase in the droplet is usually the oil due to its non-transparency. Pumping and maintaining an adequately sized droplet is extremely difficult for some viscous oils, such as crude oils. Additionally, in the case of certain oil–water systems, particularly where the density difference is small, the interfacial tension dominates the gravitation effect, leading to near-spherical drops. These systems are characterized by a low Bond number, which often results in large errors in the estimation of interfacial tension [7]. Recently, magnetic resonance images, instead of optical images, were combined with ADSA to overcome the oils' non-transparency and allow the oil to be used as the bulk fluid [8]. Nevertheless, the method is expensive and requires very strong magnetic fields.

The spinning drop method is another technique strongly dependant on interfacial distortion, although caused by centrifugal instead of gravitational forces. As with ADSA, the technique is restricted to high Bond number systems [9] due to a practical limit on the spinning speed, less than 20,000 rpm. Although the method can measure systems with interfacial tensions below 0.1 mN/m [10], it requires a significant density difference between the two fluids. As before, the method requires depositing a small oil droplet by a syringe, which is impractical for highly viscous oils.

For systems with a density difference of less than 5%, it can be extremely difficult to determine a reliable interfacial tension using these methods. However, such systems are common in many chemical and petroleum processes. A recent paper [11] describes a method capable of determining the interfacial tension of silicone oil (20 cS) (PDMS) and water, for which the density difference is 3–4%. In brief, the method avoids the use of the Young–Laplace equation by basing the calculation on the force balance acting on the bubble cap. While this method appears more reliable than pendant or sessile drop techniques for the measurement of systems with a low density difference, it instead relies on highly accurate pressure measurements. Additionally, this method is still affected by the limits to precision which constrain all methods based on image analysis. In this paper, we present a method that exploits the principles of ADSA to calculate the interfacial tension of low Bond number systems using a simple experimental method that is easily applied even to viscous oils.

The pendant and sessile meridians are two of the four gravitational shapes classified by [12], each associated with a phase-inverted counterpart. The other two meridian shapes, liquid bridges and holms, have not been widely used so far for surface tension analysis. A recent addition to the ADSA family, ADSA-NA (No Apex) [6] can be used with fluid bridges as well as sessile drops. However, to the best of the authors' knowledge, there has been no method to date which uses the holm meridian for the calculation of interfacial tension. The present study developed and verified a method for calculating the interfacial tension of liquid–liquid systems by using the submerged holm meridian. The meniscus was formed around a solid sphere partially submerged at the fluid interface and could be easily produced and maintained for a range of liquid–liquid systems. In an adaptation of the ADSA methodology, a program was developed in MATLAB to numerically fit the theoretical Young–Laplace curves to the experimental interfacial profile. Ultimately, this study aimed to develop a new and effective method of determining interfacial tension for low Bond number liquid–liquid systems.

2. Theoretical

2.1. Fundamentals of interfacial deformation

Capillary systems such as pendant or sessile drops are axisymmetric fluid bodies where surface curvature changes with vertical position due to gravitational effects. A series of eight interfacial configurations have been identified [12]. All eight meridians are described by the Young–Laplace equation, which can be expressed as a system of three ordinary differential equations:

$$\frac{d\phi}{dS} + \frac{\sin\phi}{X} = 2(\lambda H - Y) \tag{1a}$$

$$\frac{dX}{dS} = \cos\phi \tag{1b}$$

$$\frac{dY}{dS} = \sin\phi \tag{1c}$$

In Eq. (1) above, S is the dimensionless distance along the drop surface and the meridian angle, ϕ, is measured from the horizontal plane. The 'contact angle' is defined as the meridian angle at the point where the meridian contacts the supporting object. For pendant drops, this would be the capillary tube. For the case we present of the submerged holm, it is the angle at which the holm contacts the solid sphere. The shape factor, H, describes the shape and curvature of the bubble or droplet, while the parameter λ takes on different values depending on the drop type (pendant drop, sessile drop, holm, etc.). The coordinates X and Y are the dimensionless radial and vertical coordinates, normalized by the capillary length $a = \sqrt{g \cdot \Delta\rho/\gamma}$. The interfacial deformation is characterized by the Bond number, which is the ratio of gravitational to surface forces. In Eq. (2), $\Delta\rho$ is the difference in density between the two fluids, g is the gravitational acceleration, R is the characteristic length of the system and γ is the interfacial tension.

$$Bo = \frac{\Delta\rho g R^2}{\gamma} \tag{2}$$

Like the coordinate system, the shape factor H is typically based on the capillary constant or Bond number, although a range of

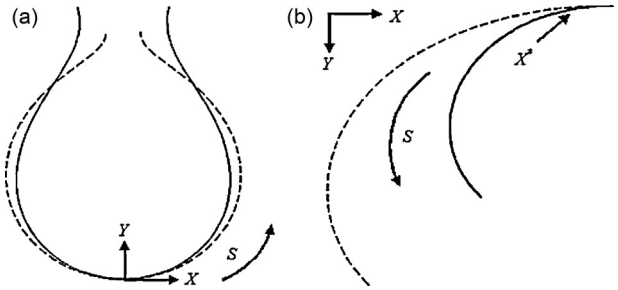

Fig. 1. Theoretical configurations observed for axisymmetric fluid–fluid interfaces in a gravitational field: (a) pendant drop with shape factor 0.5, solid line; and 0.2, dashed line. (b) Submerged holm meridian with shape factor 0.020, solid line and 0.015, dashed line. The curves were generated as solutions to the Young–Laplace equation by numerical integration using the shape factors given above. While (b) was integrated from the sphere side (left extreme: contact angle 130°) as we use in our method, it has been annotated to show the 'shape factor' X^* used in the common method of integration from the boundary condition at the horizontal asymptote (right extreme). Note that the vertical axis direction of (b) has been reversed, as the depth below the undisturbed interface is of interest.