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MEASUREMENT OF SURFACE INTERFACIAL TENSION AS A FUNCTION OF TEMPERATURE USING PENDANT DROP IMAGES

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Accurate and reliable measurements of surface tension at the interface of immiscible phases are crucial to understanding various physico-chemical reactions taking place between those. Based on the pendant drop method, an optical (graphical)-numerical procedure was developed to determine surface tension and its dependency on the surrounding temperature. For modeling and experimental verification, chemically inert and thermally stable perfluorocarbon (PFC) oil and water was used. Starting with geometrical force balance, governing equations were derived to provide non-dimensional parameters which were later used to extract values for surface tension. Comparative study verified the accuracy and reliability of the proposed method.

Keywords: droplet microfluidics, interfacial tension, perfluorocarbon oil, pendant drop method, thermocapillary

1. INTRODUCTION

For most fluids, surface (interfacial) tension decreases with the increase of temperature. Surface tension gradients created as a result of thermal gradients give rise to fluid motion, which is generally known as thermocapillary flow. Motion of bubbles and droplets (dispersed phase) in other fluids (continuous phase) due to gradients of temperature is an example of such flows (Young et al. 1959; Bratukhin 1975; Balasubramaniam et al. 1996; Xie et al. 2005). It has been shown that droplets of water resting at the air-liquid interface of a shallow layer of an immiscible liquid can be set in motion in the direction of increasing or decreasing temperature based on the configuration of droplets at the interface (Greco and Grigoriev 2009; Yakhshi-Tafti et al. 2010). Vela et al. (2009) used infra red laser-induced thermocapillary-driven flow to manipulate objects on a liquid platform, where the local surface/interfacial tension varies due to the radiative heating. Knowledge of the interfacial tension at the air-liquid and liquid-liquid interfaces, and especially the temperature dependency of tension values are essential in the study of thermocapillary phenomena. A comprehensive theory capable of predicting surface tension and its dependency

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NOMENCLATURE

β	dimensionless parameter expressed by $\rho g b^2 / \sigma$ where b is length scale	ρ	density, kg/m^3
g	gravitational acceleration, $9.8 \text{ m}^2/\text{sec}$	σ	surface tension, N/m
ΔP	differential pressure, N/m^2	φ	angle that R_1 makes with z axis
R_1, R_2	principal radii of curvature	E_w	work of adhesion between two phases
		Ψ	correction factor

on temperature does not exist and semi empirical methods and equations are used (Eotvos and van der Waals-Guggenheim equations) (Tropea et al. 2007).

In this study we measured the temperature-dependency of surface (interfacial) tension of a perfluorocarbon (PFC) liquid (FC-43 – Perfluorotributylamine) in air and in water. Due to chemical inertness and thermal stability, PFC liquids have broad applications ranging from electronic cooling to biomedical applications, and recently have been used as working fluids in multiphase droplet-based microfluidic devices (Selimovic et al. 2009). In multiphase applications, it is mostly likely that PFCs would have interfaces with water and/or air; therefore, the method and data provided in this article is of benefit for practical applications and modeling purposes. For example, droplet based microfluidic platforms are used in the study of artificial cells because small scale droplets act as self-contained carriers of cells and are convenient for controlling and manipulating quantitative chemical experiments (Takinoue and Takeuchi 2011). Droplet-based micro systems have been used for generating discrete reactors ranging from nano- to femtoliters, synthesizing particles, and encapsulating biological entities for biomedicine and biotechnology applications (Shia-Yen et al. 2008). The performance of these systems is strongly dependent on the surface/interfacial tension of the fluids involved. Considering widespread interest in the aforementioned applications, the availability of a simple but accurate measurement technique for surface/interfacial tension based on commonly accessible experimental tools is in great demand. In most multiphase (liquid/liquid) configurations, there is an aqueous phase (dispersed) and a non-aqueous phase (carrier liquid), which is to be chemically inert, electrically insulating and thermally stable. PFCs are well-suited for this purpose. Based on the pendant drop method, an optical (graphical)-numerical procedure is described for measuring the interfacial tension of PFC-air and PFC-water as a function of temperature.

Variations of the pendant drop method have been reported and used for the measurement of surface/interfacial tension (Lopez de Ramos et al. 1993; Schreyeck and Marie 1999). The method has been proven to be versatile and with enough accuracy for measurements even for extremely low surface-tension liquids ($\sim 0.06 \text{ mN/m}$). Based on this concept, a simple, yet accurate procedure is described in this work for measuring temperature dependent surface (interfacial) tension of a fluorocarbon oil.

2. THEORETICAL MODEL

2.1. Pendant Drop Method

More than 40 methods have been documented for measuring surface (interface) tension at the liquid-fluid and solid-fluid boundaries (Rusanov and Prokhorov 1996).

Among the various techniques, the drop (bubble) profile analysis tensiometry has been most frequently used in customized measurement setups. While the general aspects of the pendant drop shape method are well-understood and straightforward, the collections of hardware and software involved are usually proprietary (Woodward 1984; Rotenberg et al. 1983; Cheng et al. 1990) or require expertise in programming and image analysis. A laboratory technique that can be easily deployed using commonly available image processing/mathematics software, hardware and laboratory equipment, is provided here.

A pendant drop is formed in air or in another immiscible liquid. The profile of the droplet is captured by imaging the droplet and using backlighting. Based on the *Young-Laplace* equations, the shape of a pendant droplet can be found theoretically. By comparing the actual droplet curvature and the theoretically-predicted shape, the appropriate value for surface (interface) tension can be determined.

2.2. Governing Equations

Bashforth and Adams first developed the drop-shape method by numerically solving the theoretical equations describing the shape of a static droplet in a gravitation field (Bashforth and Adams 1883). Consider R_1 and R_2 to be the principal radii of curvature at point P on the surface, R_1 corresponds to the curvature in a drop cross section that includes the z axis and R_2 is measured in a plane perpendicular to the former (x - z) (Figure 1). The equations that describe the interface curve (drop shape) are derived in the following manner.

$$\sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P = \Delta \rho g z + C \quad (1)$$

This equation describes the balance of pressure difference (ΔP), between the inside of the droplet and the surrounding, with the interfacial tension at the surface. The

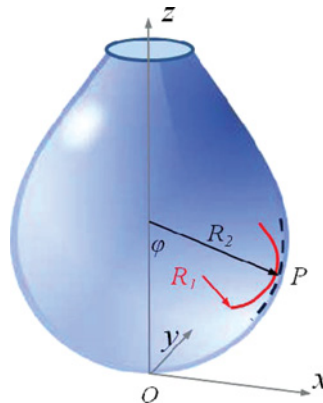


Figure 1. Drop shape. R_1 and R_2 are the principal radii of curvature at P on the surface. ϕ (ϕ) is the angle the drop axis makes with the normal of the surface at point P (color figure available online).

hydrostatic pressure depends on the different in density of the droplet and the surrounding ($\Delta\rho$) and gravity (g); the constant (C), depends on the location of the origin, from which the vertical distance is measured (z parallel to gravity). At the droplet apex, O ($z=0$), $R_1=R_2=b$ therefore $C = \frac{2\sigma}{b}$ and since $R_2 = \frac{x}{\sin\varphi}$:

$$\frac{1}{R_1} + \frac{\sin\varphi}{x} = \frac{\Delta\rho g z}{\sigma} + \frac{2}{b} \quad (2)$$

φ is the angle between the drop axis and normal of the surface for a given point P .

2.3. Parameterization

Using $x^* = \frac{x}{b}$, $z^* = \frac{z}{b}$, $R_1^* = \frac{R_1}{b}$ and grouping physical properties and constants in the gravitational parameter, $\beta \equiv \frac{\Delta\rho g b^2}{\sigma}$ the dimensionless differential equation is found as follows:

$$\frac{1}{R_1^*} + \frac{\sin\varphi}{x^*} = \beta z^* + 2 \quad (3)$$

R_1 and $\sin\varphi$ can be replaced in the following manner to achieve a differential equation that describes the curve in the form $z=f(x)$.

$$\begin{aligned} \frac{1}{R_1} &= \frac{\frac{d^2z}{dx^2}}{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{\frac{3}{2}}} \\ \sin\varphi &= \frac{\frac{dz}{dx}}{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{\frac{1}{2}}} \\ \frac{d^2z}{dx^2} + \left[1 + \left(\frac{dz}{dx}\right)^2\right] \frac{1}{x} \frac{dx}{dx} &= (2 + \beta z) \left[1 + \left(\frac{dz}{dx}\right)^2\right]^{\frac{3}{2}} \end{aligned} \quad (4)$$

It is noted that the form of the curve (droplet shape) only depends on the magnitude of the gravitational parameter β . The first boundary condition is: $x=0$: $z=0$. The other boundary condition is not apparent and results from examining equation 3 at the apex of the drop ($z^*=0$, $x^*=0$), $R_1^*=1$ ($R_1=b$), therefore the term, $\lim_{x^* \rightarrow 0} \left(\frac{\sin\varphi}{x^*}\right) = 1$. This formulation is not suitable for solving the second order differential equation using a numerical solver. Another approach is to form a set of first order differential equations (for x , z and φ) as function of the curve length, s , starting from the apex (origin). In this way boundary conditions can be set explicitly.

From the definition of $\sin\varphi$ it can be seen that $\frac{1}{R_1} = \frac{d}{dx}(\sin\varphi) = \frac{d\varphi}{ds}$ since the differential curve length is written as: $ds = R_1 d\varphi$; similarly $\frac{dx}{ds} \cos\varphi$ and $\frac{dz}{ds} = \sin\varphi$.

Considering equation 3, and the auxiliary equations for the coordinates, the set of first order differential equations that are solved simultaneously to give the drop

shape is as follows:

$$\begin{aligned}\frac{d\alpha}{ds} &= 2 - \beta z - \frac{\sin \varphi}{x} \\ \frac{dx}{ds} &= \cos \varphi \\ \frac{dz}{ds} &= \sin \varphi \\ s = 0 : x = 0, z = 0, \varphi = 0\end{aligned}\quad (5)$$

Fourth order Runge-Kutta solver was used to numerically solve the set of differential equations that would give the theoretically-predicted interface (droplet) shape.

3. EXPERIMENTAL RESULTS

3.1. Test Setup

The experimental setup shown in (Figure 2) is used to take images of pendant drops. A pendant drop is formed at the tip of a precision needle in the fluid medium of interest (air or water) in a transparent chamber with temperature control. The profile of the droplet is captured by imaging the droplet using backlighting. The droplet is imaged using a digital camera (ProSilica GE680, Allied Vision Technologies GmbH, Germany) with a normal magnifying lens (Navitar Macro 7000 Video Lens, Navitar, Inc., USA). The 10X Macro Zoom lens allows a close-up image capture without extension tubes or close-up lenses and the up-to-10X magnification variable zooming capability allows small objects to be expanded for close-up observation. Backlighting using a diffuse light source makes the detection of the curvature

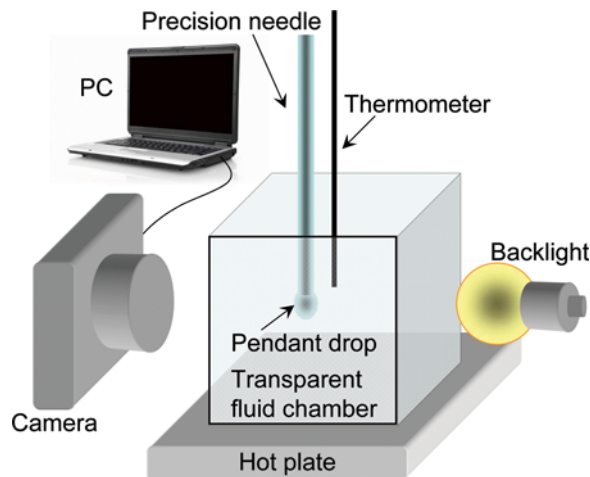


Figure 2. Experimental setup: Images of pendant drops formed in a fluidic chamber are transferred to a computer for processing (color figure available online).

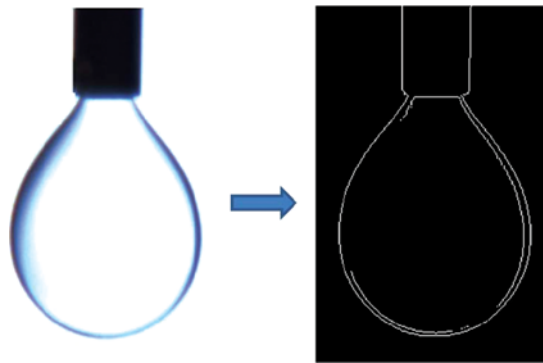


Figure 3. *Left*) Actual image of a pendant drop; *Right*) Binary image resulting from edge detection (color figure available online).

of the drop convenient since both the drop liquid (FC43, $n = 1.291$) and the surrounding fluid (water, $n = 1.333$) are transparent.

Imaging the pendant drop of FC43 formed in air or water using a diffuse light source for backlighting results in the profile image of a droplet with a sharp edge (Figure 3 *left*). This could be achieved using available *edge detection* routines (for example, MATLAB's image processing toolbox, Photoshop, etc.). The image processing procedure consists of converting the indexed "RGB" image to "GrayScale," enhancing the contrast and applying an edge detection routine. The resulting data from edge detection is a binary file which is stored in a matrix containing 0 and 1 values, representing values of the edge pixels (black) and transparent pixels (white), respectively (Figure 3 *right*). The x and z coordinates of the edge curve correspond to the row (z) and column (x) values of the edge pixels, which are found and stored in vectors by scanning the matrix for 1 (white edge pixels). The outer edge is compared to the theoretical curve in order to back calculate the surface/interface tension. Five droplet images per a given condition were taken on an average for calculation.

Based on the Young-Laplace equations developed in the previous section, the shape of a pendant droplet can be predicted theoretically. By comparing the actual droplet curvature and the theoretically-predicted shape, the appropriate value for surface (interface) tension can be determined. A computer code reads the image files and detects the boundaries; the drop is then rescaled for plotting. A comprehensive shape comparing procedure known as "axisymmetric drop shape analysis-profile (ADSA-P) has been developed by Neumann and coworkers (Rotenberg et al. 1983; Cheng et al. 1990), where the calculated theoretical (Laplacian) curve is compared to the actual drop profile until the specified overall is achieved. The surface tension is obtained from the gravitational parameter that results in the closest overlap between the theoretical curve and the actual drop profile (Figure 4).

3.2. Sensitivity, Accuracy and Reproducibility

The measured surface (interface) tension is highly sensitive to the gravitational parameter β used in the graphical fitting (overlapping) procedure $\left(\frac{d\sigma}{d\beta} \propto \frac{1}{\beta^2}\right)$. For

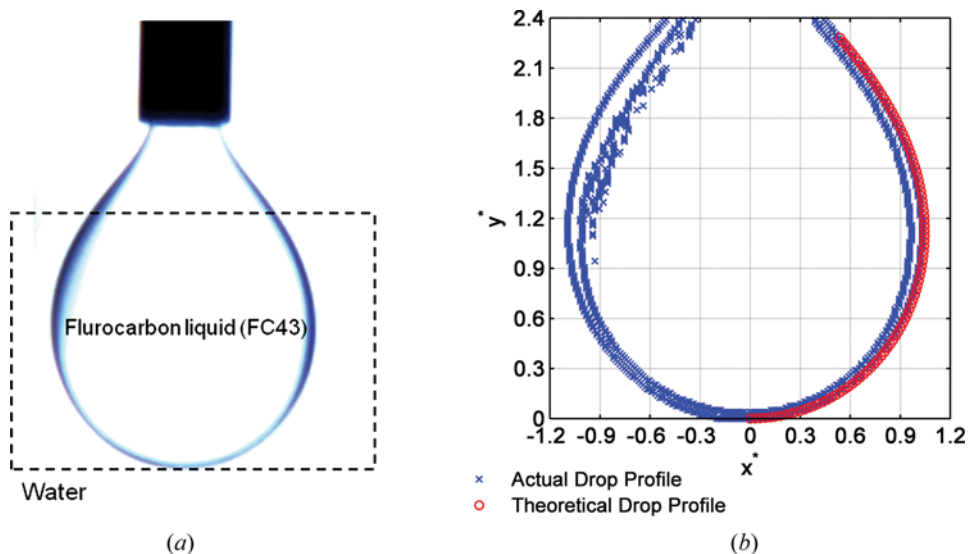


Figure 4. *Left*) Actual image of a pendant oil drop immersed in water (transparent); *Right*) By choosing an appropriate value of interfacial tension, s , the theoretical and actual drop profile overlap. The interfacial tension calculated for oil in water drops was found to be 52 dyne/cm (color figure available online).

example, the measured interfacial tension for FC43 drops formed in water can vary 2 mN/m as a result of 0.01 increment in the corresponding gravitational fitting parameter. Figure 5 shows the sensitivity of the graphical method to the gravitational parameter.

Consistency, accuracy and reproducibility of results based on this method was verified by comparing the measurements with data for water available in references, as well as measurements made by a commercially-available tensiometer (SITA bubble pressure tensiometer, SITA Messtechnik GmbH, Germany) as shown in Figure 6. The tensiometer can measure surface tension over a range of 10–100 mN/m and temperature range of 0–100°C, with a resolution of 0.1 mN/m. The tensiometer operates based on the following mechanism: air is pumped through a capillary into the liquid, forming bubbles that grow in size until they burst and break away from the capillary. During this process the pressure inside decreases as the bubble radius increases. The surface tension is calculated by correlating the maximum pressure to the smallest radius of curvature (radius of the capillary) using the Young-Laplace equation.

In the graphical method used here, the unknown interfacial tension between the oil (FC-43) and water at room temperature was extracted in multiple runs at identical conditions which yielded the result with less than 5% in repeatability error. It should be noted that the performance of the developed system matches with that of commercially available products, while being far less expensive and having the capability of providing the linear rate at which surface (interfacial) tension decreases with increasing temperature. In experiments, the temperature was increased in increments from room temperature up to 85°C in the imaging chamber. Images were taken when steady temperatures were reached. Figure 7 shows the measurements

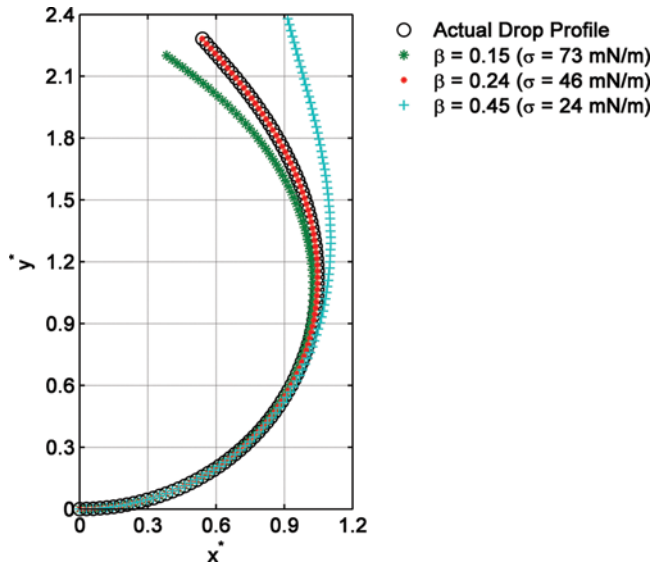


Figure 5. Effect of the gravitational parameter ($\beta = \frac{\Delta\rho gb}{\sigma}$) on the theoretical curve calculated for a pendant drop of FC-43 in water ($T = 55^\circ\text{C}$) (color figure available online).

obtained for temperature dependent surface tension (liquid-air) and interfacial tension (liquid-water) for FC43 perfluorocarbon liquid. For liquid-liquid pairs, e.g., FC43 droplets in water, at higher temperatures, convective currents inside the fluid

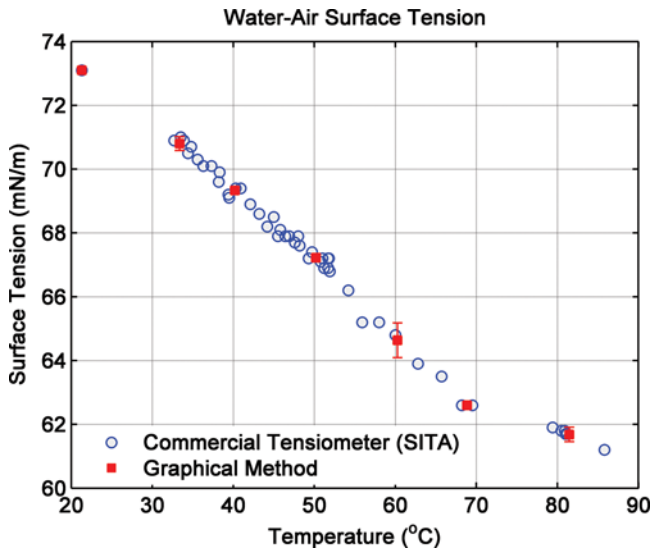


Figure 6. Surface tension of water as a function of temperature measured by commercially available tensiometer (SITA bubble pressure tensiometer) and the in-house graphical method ($d\sigma/dT = -0.203 \text{ mN/m}/^\circ\text{C}$) (color figure available online).

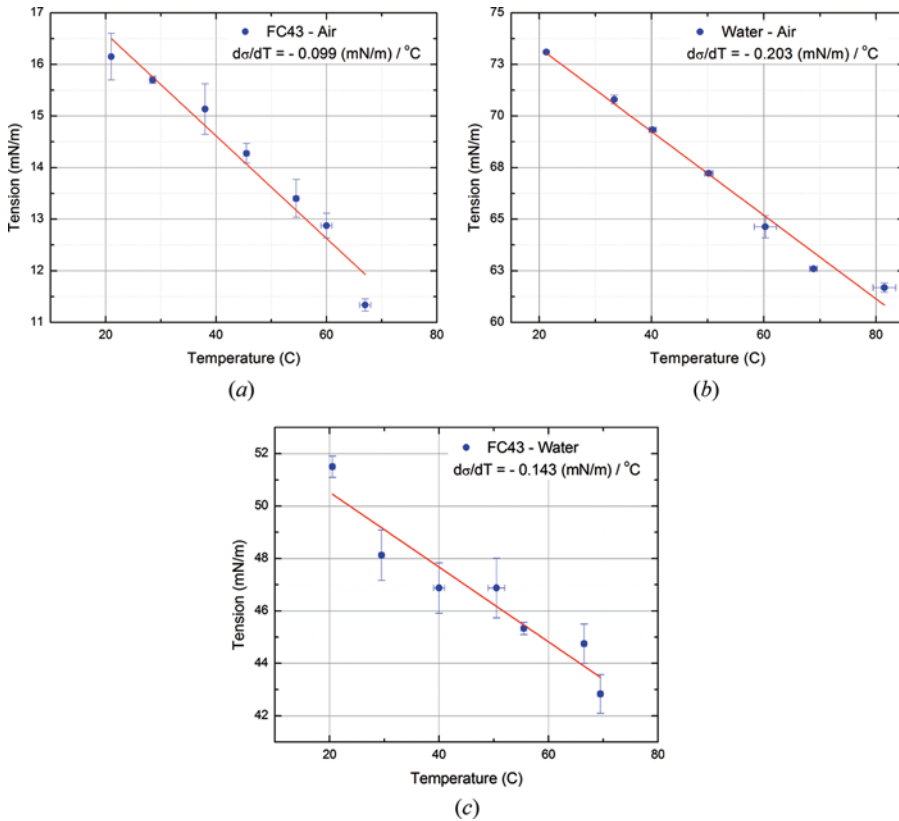


Figure 7. Variation of surface tension with temperature of fluid-medium pairs (FC43-air, water-air, FC43-water) (color figure available online).

chamber caused refractive index changes resulting in blurred edges. At such high temperatures, the graphical method starts losing accuracy.

Girifalco and Good (1957) provided an equation that related the free energy of cohesion of separate dense phases to the free energy of adhesion of each of the phases; i.e., the relationship between the interfacial tension among to two phases (σ_{AB}) to the surface tension of each phase (σ_A , σ_B).

$$\sigma_{AB} = \sigma_A + \sigma_B - E_w \quad (6)$$

E_w is the work of adhesion between two phases. Considering the surface tension of each liquid to include the effect of dispersive forces (London-van der Waals) and non dispersive (polar) forces, the work of adhesion has been given in the following form (Owens and Wendt 1969):

$$E_w = 2\Psi\sqrt{\sigma_a\sigma_b}$$

$$\Psi = \sqrt{\frac{\sigma_a^d\sigma_b^d}{\sigma_a\sigma_b}} + \sqrt{\frac{\sigma_a^p\sigma_b^p}{\sigma_a\sigma_b}} \quad (7)$$

Superscripts d and p stand for dispersive force and polar effects, respectively. For water (polar) and FC43 at 21°C, our measurements resulted in $\psi = 0.548$, which is close to the reported value 0.55, for water in non-polar liquids including n-hexane, n-heptane, n-octane, and n-heptane (Tropea et al. 2007). We also found that only dispersive forces contributed to the surface tension of FC43 ($\sigma_{FC43}^p = 0$) and confirmed the non polar nature of this fluid.

4. CONCLUSION

A graphical-numerical procedure based on the pendant drop method was developed for making temperature dependent measurement of surface and interfacial tension of fluids. Measurements using this method were compared to those made by the commercially available tensiometer. Results are accurate and reproducible with 5% error. Specifically, surface tension (FC43-Air) and interfacial tension (FC43-Water) was measured as a function of temperature. As expected, tension values decreased linearly with increasing temperature. The linear slopes for FC43-Air and FC-43-Water interfacial tension were found to be -0.099 and -0.143 mN/m/°C, respectively. As droplet-based microfluidic transport platforms are currently being studied and developed more widely, the information and methods described in this article are of practical importance for the design and modeling of such systems.

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SUPPLEMENTARY MATERIAL

“*TensionCalculator.xmcd*” is a MathCad spreadsheet including the procedure for solving the theoretical drop curve equations. For a given pair of fluids, the surface (interfacial tension) is found from the gravitation parameter that results in the best overlap between the actual drop profile and the theoretical curve. “*Binary-Image.dat*” is a sample input file generated from applying *edge detection* to drop images.

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