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Surface Tension Measurement with an Optofluidic Sensor

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Abstract

This paper reports a novel microfluidic sensor for measuring dynamic gas/liquid interfacial tension. The device consists of a mirofluidic chip with a microchannel network and an optical detection system. The sample is introduced into a main channel, while air is injected through a T-junction. A simple analytical model was established to identify the parameters, which can be used for measuring the surface tension. Due to the fixed flow rate ratio used for the sensor, bubble formation frequency is the only parameter, which can be measured easily by optical detection. While the bubble is represented by a pulse in the output signal, the formation frequency is simply the frequency of the output signal. Measurements were carried out for aqueous solutions with different concentrations of the ionic surfactant CTAB (Cetyl Trimethyl Ammonium Bromide). Surface tensions of these solutions were calibrated with a commercial tensiometer (FTA200, First Ten Angstrom). The measurement results show a clear relation between surface tension and formation frequency. The sensor can be used to identify the critical micelle concentration (CMC) of surfactant. The sensor potentially allows the use of a minute amount of sample compared to the relatively large amount required for existing commercial systems.

Keywords: microfluidics, surface tension, lab on a chip

1 Introduction

Dynamic surface tension of an aqueous solution is an important parameter in many industrial and domestic applications. Dynamic surface tension depends on the surfactant concentration in the solution. Up to a certain concentration, surface tension is inversely proportional to the surfactant concentration. Above this concentration, surfactant molecules start to cluster and form micelles, surface tension remains almost constant. This critical concentration is called the critical micelle concentration (CMC). Conventional measurement methods of surface tension can be categorized in five groups: direct measurement using microbalance, measurement of capillary pressure, analysis of capillary gravity forces, gravity distorted drop, reinforced distortion of drop [1]. All these techniques require a relatively large amount of sample.

Monodisperse droplets have traditional applications in the fields of food science, cosmetics, and pharmaceutics. Recently, The formation of droplets and bubbles in microchannels attracts the interest of microfluidics community [2]. The main focus for this phenomenon is its application in microreaction technology [3]. Most of the previous works are based on droplets formed between immiscible fluids. The flow pattern inside a moving droplet causes chaotic advection and improves mixing significantly. Microdroplets have been used for DNA analysis, protein crystallisation [4], analysis of human physiological fluids, encapsulation [5], and production of polymeric micro beads [6]. Uniform droplets can be prepared using a simple T-junction [7] or a cross junction [8]. All the above-mentioned works used two immiscible liquids to form droplets. To the best knowledge of the authors, no previous works used this concept for measuring the interfacial tension between the two liquids. Furthermore, the generation of micro bubbles in a gas/liquid system was not mentioned in the recent reported works.

Olthuis et al. [9] reported microbubble generation based on electrolysis. Bubble formation was detected electrically. This method was limited by aqueous sample, and gas/liquid interfacial tension. The reported results show a bad reproducibility of bubble formation due to the large numbers of bubbles evolving at the same time from the electrode surface. Furthermore, bubble detachment and formation rely entirely on the balance between surface tension and buoyancy force. In micro scale, surface tension is dominant while volume-based buoyancy force becomes negligible. Thus, further miniaturization is not in favour for this concept.

This paper presents a microfluidic sensor for dynamic surface tension measurement. The sensor chip has two functions: generation and detection of air bubbles in a sample flow. The microfluidic sensor was fabricated on a PMMA substrate by laser machining and direct thermal bonding. The bubbles are formed at a T-

junction between a large channel for the sample liquid and a smaller channel for injection of the air bubble. The T-configuration has been widely used for droplet formation in the works mentioned above. Our experiments also showed that this configuration results in reliable and reproducible generation of air bubbles. The generated air bubbles are detected optically using a pair of optical fibres positioned on both sides of the sample channel. The characterization results show a clear relation between the surface tension and the formation frequency of the bubbles, which can be easily determined from the output signal of the optical detection system.

Following, we first discuss a simple analytical model for the relations between surface tension and the formation frequency of the bubbles. The model also helps to identify other parameters of the sample liquid, which may affect the bubble formation frequency besides surface tension. Next, details on fabrication and characterization of the sensor are described. Surface tension values were calibrated using a commercial measurement system. Finally, the results are presented and discussed.

Even though accurate and simple, the system is far from perfect. Its working principle results in two fundamental limitations. First, the detection based on difference of refractive indexes of air and liquid makes it not possible to measure gas. Second, it can only measure average flow so not suitable for online monitoring.

2 Theoretical model

Figure 1 depicts a simple model of bubble formation. Since bubble formation is a complex physical phenomenon, this model only serves the purpose of understanding the relations between key parameters such as bubble size, formation frequency, sample flow rate, and most importantly surface tension. The model assumes a fixed flow rate ratio between air and sample liquid ($\alpha = \dot{Q}_a / \dot{Q}_s$). Further assumptions are small bubbles size ($\alpha << 1$) and incompressibility of air. Since bubbles in the model are formed in micro scale and the flows are in steady state, mass related forces such as inertial force, momentum force and buoyancy force are neglected. As the growing bubble is present in a flowing surfactant liquid, the surfactant concentration at the bubble surface is not uniformly distributed and thus a gradient of surface tension on the bubble surface is developed. The presence of the surface tension gradient leads to the Marangoni force

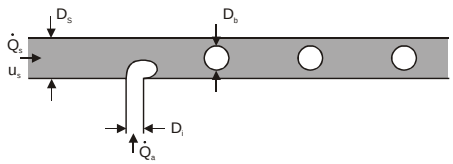

Figure 1: A simple model of bubble formation.

acting on the bubble. If the surfactant solution is dilute, the Marangoni force is assumed to be negligible, and thus the force balance equation including only the drag force of the sample flow and the surface tension at the injection port is expressed as:

$$F_{\text{drag}} = F_{\text{surface tension}}$$
$$\frac{1}{2} C_D \rho u_s^{\,2} A_D = C_s \pi D_i \sigma \tag{1}$$

where u_s, A_D, D_i, and σ are the average velocity of the sample flow, the effective drag surface, the diameter of the injection opening, and the surface tension, respectively. In addition, C_D and C_s are the drag coefficient and the coefficient for the surface tension. The drag coefficient of a sphere at a low Reynolds number Re is calculated as $C_D = 24/\text{Re}$. The coefficient C_s depends on the contact angle and the shape of the injection port. In this model C_s is assumed constant. The effective drag surface A_D grows with the bubble. If the bubble is a sphere, the effective drag surface at the detachment moment is:

$$A_D = \frac{\pi D_b^{\,2}}{2} \tag{2}$$

where D_b is the diameter of the bubble. Initially the bubble is small, the surface tension is large enough to keep the bubble at the injection port. At the detachment moment, due to the continuous bubble growth the drag force is large enough to release the bubble. Substituting (2) into (1) results in the bubble diameter:

$$D_b = 2\sqrt{\frac{C_s}{C_D} D_i \frac{\sigma}{\rho_s u_s^{\,2}}} \tag{3}$$

The formation frequency can be estimated from the air flow rate $\dot{Q}_a$ and the bubble volume V_b as:

$$f = \dot{Q}_a / V_b \tag{4}$$

Using the bubble diameter D_b and the relation $\dot{Q}_a = \alpha \dot{Q}_s$, the formation frequency in (4) can be expressed as:

$$f = \frac{3\alpha D_s^{\,2}}{16\left(C_s D_i / C_D\right)^{\frac{3}{2}}} \frac{\rho^{\frac{3}{2}} u_s^{\,4}}{\sigma^{\frac{3}{2}}} \tag{5}$$

From (5), the surface tension can be measured based on the formation frequency f, if all other parameters are constant. The density of the liquid has the same impact on the formation frequency as the surface tension. Thus, this method is only suitable for solutions with constant density and varying surface

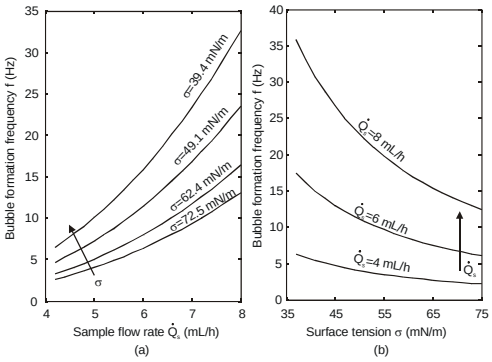

Figure 2: Characteristics of bubble formation

tensions such as those of diluted surfactants. In these solutions, the density change usually is of 3 to 4 orders less than the surface tension change. Equation (5) also shows a nonlinear relation between the formation frequency and the average sample velocity ($f \propto u_s^4$) or sample flow rate ($f \propto \dot{Q}_s^4$). Figure 2 (a) shows this relation graphically. The characteristics of bubble formation frequency versus surface tension at different sample flow rates are depicted in Fig. 2(b). Furthermore, if the Marangoni force is considered in equation (1) when the surfactant concentration is high, there will be an additional term for such force in the numerator of (5), resulting in a higher frequency.

3 Sensor concept and fabrication

Our microfluidic sensor consists of a microchannel network for droplet formation and an optical system for bubble detection. The configuration of the microchannel network is depicted in Figure 1. Air bubbles are injected through a small microchannel, while the sample liquid comes through a larger microchannel. The two channels form a T-junction, at which bubble formation occurs. The influence of channel diameters D_i and D_s on the formation frequency is apparent in (5).

After being generated and stabilised in the long sample channel, the bubbles are detected at a downstream position. Bubble detection is based on an optical concept. Laser light is guided into the microchannel by an optical fibre. After passing across the main channel, the light is received on the other side by a second optical fibre, which leads it to an optical sensor. The passing-by bubbles changes the intensity of the laser due to diffraction and absorption. Thus, the bubble can be well recorded as a pulse in the output signal of the optical sensor.

Our microfluidic device is made of polymethyl methacrylate (PMMA), the microchannels are machined into the substrate using CO_2 laser. PMMA is one of the thermoplastic polymers, which are usually linear-linked and will soften when heated above glass transition temperature. PMMA has a non-crystalline structure and therefore possesses good optical properties with a 92 % transmittance in the

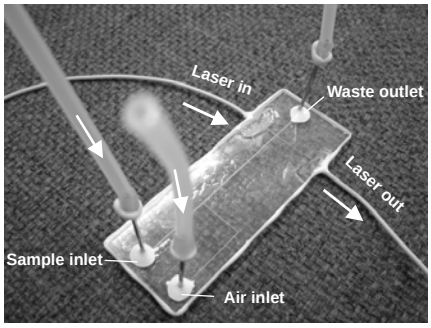

Fig. 3: The completed microfluidic sensor for dynamic surface tension measurement.

visible spectrum. CO_2 laser has a relatively long characteristic wavelength of 10.6 µm. Therefore, the ablation process depends more on thermal energy, which in turn has the same distribution as the laser intensity. We used the commercial Universal M-300 Laser Platform (Universal Laser Systems Inc.). The system has a 25 Watt CO_2 laser and a maximum beam speed of about 640 mm/s. The cross section of the engraved microchannel depends on the intensity distribution of the laser beam, its moving speed, the laser power and the thermal diffusivity of substrate material. The intensity of the laser beam has a Gaussian distribution, thus the cross section of the channel also has a Gaussian shape. The injection channel and the guides for inserting the optical fibres are both 175 µm in width and 205 µm in depth. The larger microchannel for sample flow has a width of 340 µm and a depth of 340 µm.

The guides for the two optical fibres are engraved at a down stream position. The optical fibres (AFS105/125Y, THORLABS Inc.) have a core diameter of 105 µm, a clad diameter of 125 µm, a buffer diameter of 250 µm, and a numerical aperture of 0.22. After positioning the fibres into the guides, the PMMA part with microchannels, optical fibres, and access holes is covered by a second PMMA part. The PMMA stack is then placed between a hotplate and a aluminium plate. The bonding pressure can be adjusted by putting weights on top of the upper plate. For a better surface flatness of the PMMA parts, two polished silicon wafers are placed on both sides of the PMMA-stack. Prior to the bonding process, the PMMA parts were carefully cleaned and rinsed in ethanol and DI-water. After bonding at 165 ºC, the bonded stack is annealed at 80 ºC for relieving stress. The bonding pressure was kept at about 20 kPa. The total fabrication process took about 4 hours. Finally, stainless steel needles were glued to the access holes. The completed device is shown in Fig. 3.

4 Experiments

In our experiments, the sample liquid is introduced into the main channel, while air joins through the smaller injection channel. A syringe filled with the sample liquid and an empty syringe (filled with air)

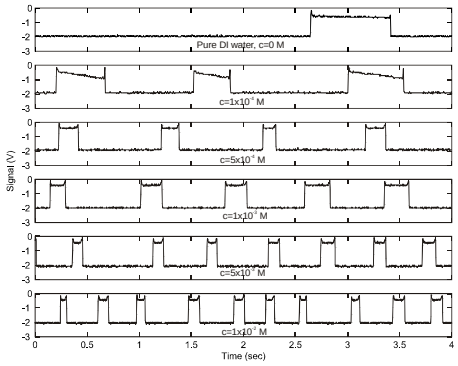

Figure 4: Typical bubble signals detected by the APD at an air flow rate of 1 ml/h (constant flow rate ratio α=1:4)

are placed on a syringe pump (Cole-Parmer 74900-05)

Since both syringes are driven by the same stepper motor, the flow rate ratio can be adjusted by choosing syringes with a corresponding ratio of cross sections. Small flow rate ratios as assumed in the analytical model leads to relatively unstable droplet formation process. In our experiments, the volumetric flow rate ratio between air and sample liquid is kept at 1:4. For detecting the micro bubbles, one optical fibre is positioned and aligned to a laser source (laser diode, 635 nm), the other fibre is connected to an avalanche photodiode module (APD, C5460-01, Hamamatsu, Japan). The output signal from the APD is recorded by a digital oscilloscope (TDS220, Tektronix), which in turn is connected to a personal computer (PC) over a serial cable. Thus, the bubble signal can be recorded and analyzed later on the PC.

Cetyl trimethyl ammonium bromide (CTAB, $C_{19}H_{42}BrN$) was used as surfactant to vary surface tension values. Samples with different concentration ranging from 10^{-4} M to 10^{-2} M were tested. For calibration, the surface tension of the samples was measured using the tensiometer FTA200 (First Ten Angstrom). Table 1 summarises the measured surface tension values of these sample solutions. The data shows that surface tension decreases with increasing concentration. The CMC is about 10^{-3} M.

Table 1 Measured surface tensions of aqueous solution of CTAB.

Concentration (M)	Surface tension (mN/m)
0	72.5
1×10^{-4}	62.4
5×10^{-4}	49.1
1×10^{-3}	39.4
5×10^{-3}	38.7
1×10^{-2}	38.6

5 Results and Discussions

Figure 4 shows the typical bubble signals detected by the APD at a sample flow rate of 4mL/h for the different sample concentrations. The bubbles are

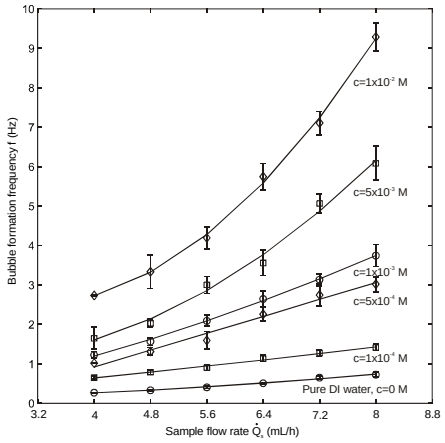

Figure 5: Measured bubble formation frequency as function of surface tensions at air flow rates of 1 mL/h and 2 mL/h.

represented by the pulses. The results here clearly show that the bubble becomes smaller and the formation frequency is higher with increasing surfactant concentration or decreasing surface tension. Beyond the CMC of about 1×10^{-3} M, the formation process becomes unstable, the formation frequency fluctuates. This instability characteristic can be used to detect CMC. In the stable region up to CMC, the pulse width ratio of 1:5 is consistent with the fixed flow rate ratio of 1:4 between air and sample liquid. Thus, the formation frequency also contains information about the pulse width or the bubble size. Following, only the formation frequency are evaluated and discussed.

Figure 5 depicts the measured frequency of bubble formation as a function of sample flow rate. From the theory, the expected non-linear relation can be observed clearly. The signal is stable and consistent at low sample flow rate and high surface tensions.

The characteristics of bubble formation frequency versus surfactant concentration are shown in Fig. 6. The results show that droplet formation frequency continues to increase beyond CMC. Since the surface tension does not change significantly at concentration higher than CMC, the frequency increase could be caused by Marangoni force as indicated in the theoretical model.

Figure 7 shows the formation frequency as a function of surface tension. Surface tension values were calibrated according to the data listed in Table 1. For diluted solutions with low surfactant concentrations, the curves agree well with the general characteristics predicted by the theory and shown in Fig. 2(b). The abrupt change of the formation frequency at CMC can be clearly observed in Fig. 7. Up to CMC, bubble formation and detachment is dominated by the drag force, the formation frequency decreases almost linearly with increasing surface tension. In this range, formation frequency can be used directly for determining the surface tension. Beyond CMC, there

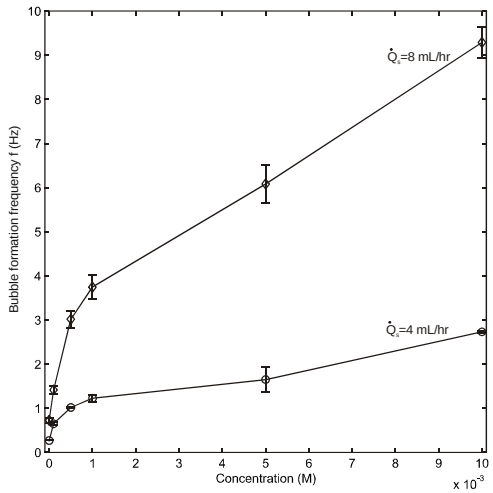

Figure 6: Measured bubble formation frequency as function surface tension.

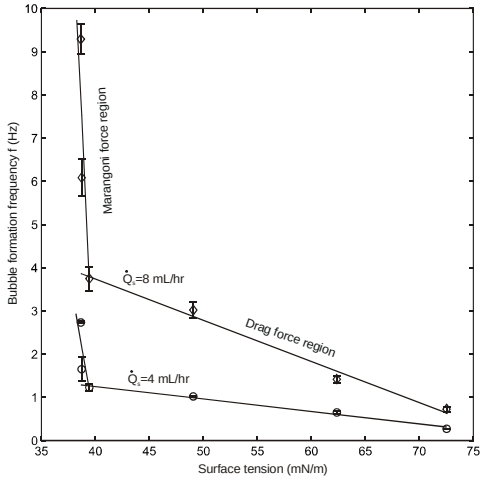

Figure 7: Measured bubble formation frequency as function surface tension.

is a sharp change in formation frequency. The Marangoni force caused by surface tension gradient on the bubble surface becomes dominant in this range and contributes to the increase of formation frequency.

6 Conclusions

In this paper, we presented a microfluidic device for bubble formation and detection. The device has a microchannel network to form the bubbles. The bubbles are detected by two optical fibres. A bubble passing by the detection point diffracts a part of the incoming laser light. The change in intensity can be detected by the optical fibres placed on the other side of the channel. Due to the small changes in density, formation frequency depends only on the surfactant concentration or on the surface tension. Since the frequency increases monotonously with the concentration, bubble formation frequency can be related directly to the surfactant concentration. Up to CMC, the relation between surface tension and formation frequency is almost linear. Thus, formation frequency can be used to measure surface tension. Beyond CMC, the frequency changes sharply. Detecting the sharp changes may allow the sensor to determine this critical value of a surfactant solution.

Acknowledgments

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