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<td>Author(s)</td>
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Microfluidic sensor for dynamic surface tension measurement

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Abstracts: A novel microfluidic sensor for measuring dynamic gas-liquid interfacial tension is reported. The device consists of a microfluidic 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. Owing to the fixed flow rate ratio used for the sensor, surface tension is the only parameter determining bubble formation frequency, which can be measured 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 cetyl trimethyl ammonium bromide. Surface tensions of these solutions were calibrated with a commercial tensiometer. The measurement results show a clear relation between surface tension and formation frequency. The sensor can be used to identify the critical micelle concentration 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.

1 Introduction

The 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 [1]:

- direct measurement using microbalance
- measurement of capillary pressure,
- analysis of capillary gravity forces,
- gravity distorted drop,
- reinforced distortion of drop.

All current commercially available systems are based on the above concepts. In the first group, surface tension is measured directly by a force sensor. Commercial systems use a plate or a ring that is made of platinum-iridium alloy or platinum. The plates or rings have standard dimensions, thus no calibration is required. In the second group, surface tension is derived from capillary pressure, which can be measured directly with a pressure sensor. The third group measures gravity rise or size of a droplet after detachment. In the fourth group, the shape of the droplet is distorted by surface tension and gravity, and measurement of the geometry of a pendant drop allows the determination of surface tension. This last method requires a CCD camera and a bulky computer for evaluation.

Besides the above-mentioned conventional techniques, there is a growing interest in interfacial tension measurement of small samples. The study of interfaces on very small particles and in finely dispersed systems is called microtensiometry. The main application fields of microtensiometry are criminology, biology and pharmaceutical microreactors. The two methods currently known for
microtensiometry are: micropipette technique and atomic force microscopy. In micropipette technique, a droplet is first captured at the tip of a micropipette. If the radian of curvature on both sides of the droplet is used, the surface tension can be calculated. This technique also requires bulky microscope and an image recording system. The second approach is based on direct force measurement, where a force sensor is needed. Both methods of microtensiometry have to deal with the problem of evaporation because the small sample droplet can quickly evaporate.

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 work is based on droplets formed between immiscible liquids. The flow pattern inside a moving droplet can improve mixing significantly. Microdroplets have been used for DNA analysis, protein crystallisation [4], analysis of human physiological fluids, encapsulation [5], and production of polymeric microbeads [6]. Uniform droplets can be prepared using a simple T-junction [7] or a cross junction [8]. All the above-mentioned work used two immiscible liquids to form droplets. To the best knowledge of the authors, no previous work used this concept for measuring the interfacial tension between the two liquids. Furthermore, the generation of microbubbles in a gas-liquid system was not mentioned in the recent reported work.

Olthuis et al. [9] reported microbubble generation based on electrolysis. Bubble formation was detected electrically. This method was limited to aqueous samples and the measurement of gas-liquid interfacial tension. The measured signals were
not stable owing 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 microscale, surface tension is dominant while volume-based buoyancy force becomes negligible. Thus, further miniaturization is not in favour of 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 polymethyl methacrylate (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 work 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 relationship 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. Details on fabrication and characterization of the sensor are described in the following. Surface tension values were calibrated using a commercial measurement system. Finally, the results are presented and discussed.

2 Sensor concept and fabrication

The sensor concept is based on the process of bubble formation in a microchannel; see Fig. 1. As bubble formation is a complex physical phenomenon, the following analytical model only serves the purpose of promoting the
relationships between key parameters: the formation frequency and the surface tension. The model assumes a fixed flow rate ratio between air and sample liquid $\alpha = \frac{\dot{Q}_s}{\dot{Q}_i}$. Further assumptions are small bubbles size ($\alpha \ll 1$) and incompressibility of air.

As bubbles in the model are formed at microscale 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 develops. The presence of the surface tension gradient leads to the Marangoni force 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:

$$F_{\text{drag}} = F_{\text{surface tension}}$$

$$\frac{1}{2} C_D \rho u_s^2 A_D = C_s \pi D_i \sigma$$

(1)

where $u_s$, $A_D$, $D_i$, and $\sigma$ 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 $C_D = 24/Re$. 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
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, owing to the continuous bubble growth the drag force is large enough to release the bubble. Substituting (2) into (1) results in the bubble diameter:

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

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

$$f = \frac{\dot{Q}_a}{V_b}$$ (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:

$$f = \frac{3\alpha D_s^2}{16(C_s D_i / C_D)^{3/2}} \frac{\rho^2 u_s^4}{\sigma^{3/2}}$$ (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 tensions such as those of diluted surfactants. In these solutions, the density change usually is of three to four orders less than the surface tension change.

Our microfluidic sensor consists of a microchannel network for bubble 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. 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 and detected by an optical sensor. A crossing air bubble changes the intensity of the laser. The change in laser intensity is recorded as a pulse in the output signal of the optical sensor.

We used Raytrace, an optical simulation tool (http://members.ozemail.com.au/~imesoft/) to confirm this detection concept. The laser is modelled by a number of light rays, whose number represents the laser intensity. Figure 2 depicts the typical number of rays arriving at the receiving side for different bubble positions. The positions are qualitatively depicted based on the grid number in the model. The two peaks caused by bubble entrance and bubble exit can be clearly observed in Fig. 2. Some of the rays are diffracted while passing through the curved interface between air and liquid. To enter the fibre core, the incident light must enter within a cone, which depends on the numerical aperture (NA) of the optical fibre, a value fixed by the refractive indices of the fibre core and its cladding. In our experiment, the optical fibre had a numerical aperture of NA=0.22, thus the maximum angle of the incident light should theoretically be $\alpha = \arcsin(NA) = 12.7^\circ$.

Our microfluidic device is made of PMMA, the microchannels are machined into the substrate using CO$_2$ laser. PMMA is one of the thermoplastic polymers that 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 visible spectrum. The CO₂ 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 W CO₂ laser and a maximum beam speed of about 640 mms⁻¹. 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 downstream 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 an 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 °C, the bonded stack is annealed at 80 °C 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.

3 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) are placed on a syringe pump (Cole-Parmer 74900-05, 0.2 μl h\(^{-1}\) to 500 ml h\(^{-1}\), accuracy of 0.5 %). As both syringes (Hamilton GasTight) are driven by the same stepper motor, the flow rate ratio can be adjusted by choosing syringes with a corresponding ratio of cross-sections. In our experiments, the volumetric flow rate ratio between air and sample liquid is kept at 1:4. Figure 4 shows the typical process of bubble formation at the injection port. In these images, diluted fluorescence (acid yellow 73) was used for a better contrast.

For detecting the micro bubbles, one optical fibre is positioned and aligned to a laser source (Melles Griot 58SDM101, 635nm), the other fibre is connected to an avalanche photodiode module (APD, C5460-01, Hamamatsu, Japan), Fig. 5. 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).
4 Results and discussions

Figure 6 shows the typical bubble signals detected by the APD at a sample flow rate of 4mLh\(^{-1}\) for the different sample concentrations. The results agree qualitatively well with the simulation results in Fig. 2. As optical simulation does not include the different absorbance behaviour of air and the sample liquid, the simulated pulse caused by the bubble is not as clear as in the measurement. 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 and the formation frequency fluctuates. This characteristic instability can be used to detect CMC. In the stable region up to CMC, the ratio of 1:5 between the pulse width and the period 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. In the following, only the formation frequency is evaluated and discussed.

Figure 7 depicts the measured frequency of bubble formation as a function of sample flow rate. The lines are fitting curves of the measured data. The signal is stable at low sample flow rate and high surface tensions.

The characteristics of bubble formation frequency against surface tension are shown in Fig. 8. Table 1 summarises the measured surface tension values of these sample solutions and the corresponding measured formation frequencies. The data shows that surface tension decreases with increasing concentration. The CMC is about 10\(^{-3}\) M, Fig. 8a. The results show that bubble formation frequency continues to increase beyond CMC. As the surface tension does not change significantly at concentration higher than CMC, the frequency increase could be caused by
Marangoni force. As the bubble grows 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 develops. The presence of the surface tension gradient leads to the Marangoni force acting on the bubble. If the surfactant solution is dilute, the Marangoni force is assumed to be negligible. The Mangaroni force is induced by non-uniform distribution of surfactant clusters that makes the formation and break-up of the bubbles unstable. Surface tension values were calibrated according to the data listed in Table 1. The calibration curve is shown in Fig. 8a. The error data were calculated as the standard derivation of the measured frequency values. The abrupt change of the formation frequency and the large error due to instability at CMC and above can be clearly observed in Fig. 8b. 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, the formation frequency can be used directly to determining the surface tension. As mentioned above, there is a sharp change in formation frequency beyond CMC. The two regions can be clearly observed in Fig. 8b. In both Fig. 7 and Fig. 8b, the lines represent the fitting curves of the measured data.

5 Conclusions

In this paper, we reported 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. Owing to the small changes in density, formation frequency depends only on the surfactant concentration or on the surface tension. As 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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References

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<tr>
<th>Concentration, M</th>
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<th>Formation frequency at 8 ml hr⁻¹, Hz</th>
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