

Article

Interfacial Tension Sensor for Low Dosage Surfactant Detection

Piotr Pawliszak ^{1,2}, Bronwyn H. Bradshaw-Hajek ² , Christopher Greet ³, William Skinner ^{1,2,†,‡}, David A. Beattie ^{1,2,†,‡}  and Marta Krasowska ^{1,2,*,†,‡} 

¹ Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia; piotr.pawliszak@mymail.unisa.edu.au (P.P.); William.Skinner@unisa.edu.au (W.S.); David.Beattie@unisa.edu.au (D.A.B.)

² UniSA STEM, University of South Australia, Mawson Lakes, SA 5095, Australia; Bronwyn.Hajek@unisa.edu.au

³ Research Laboratory, Magotteaux Australia Pty Ltd., Wingfield, SA 5013, Australia; Christopher.Greet@magotteaux.com

* Correspondence: marta.krasowska@unisa.edu.au

† ARC Centre of Excellence for Enabling Eco-Efficient Beneficiation of Minerals.

‡ ARC Training Centre for Integrated Operations for Complex Resources.

Abstract: Currently there are no available methods for in-line measurement of gas-liquid interfacial tension during the flotation process. Microfluidic devices have the potential to be deployed in such settings to allow for a rapid in-line determination of the interfacial tension, and hence provide information on frother concentration. This paper presents the development of a simple method for interfacial tension determination based on a microfluidic device with a flow-focusing geometry. The bubble generation frequency in such a microfluidic device is correlated with the concentration of two flotation frothers (characterized by very different adsorption kinetic behavior). The results are compared with the equilibrium interfacial tension values determined using classical profile analysis tensiometry.

Keywords: interfacial tension; frothers; microfluidics; bubble generation frequency



Citation: Pawliszak, P.; Bradshaw-Hajek, B.H.; Greet, C.; Skinner, W.; Beattie, D.A.; Krasowska, M. Interfacial Tension Sensor for Low Dosage Surfactant Detection. *Colloids Interfaces* **2021**, *5*, 9. <https://doi.org/10.3390/colloids5010009>

Academic Editor: Reinhard Miller

Received: 30 September 2020

Accepted: 28 January 2021

Published: 3 February 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The motion of gas bubbles is known to be affected by even the smallest amount of surface-active impurities, as these molecules adsorb at the gas-liquid interface and change the tangential mobility at the bubble surface [1–3]. In high-purity water (or surface-active molecule free) electrolyte solutions, in the low shear stress case (i.e., smaller bubbles or gas-liquid interface moving slowly), the gas-liquid interface deviates from being tangentially mobile [4–8]. For the higher shear stress (i.e., larger bubbles or gas-liquid interface moving fast) the gas-liquid interface stays tangentially mobile [9,10]. The immobilization of the gas-liquid interface of small bubbles due to adsorption of minute amounts of surface-active impurities makes them sensitive probes for low dosage surfactant detection.

The flotation process is a separation technique mainly used in mineral processing for the separation of valuable minerals from their host rock, and relies on bubbles selectively attaching to valuable mineral particles allowing them to be recovered from a slurry of valuable and gangue mineral particles [11]. Efficient separation is usually maximised by the use of surface-active chemicals (termed collectors and depressants) that preferentially adsorb at solid-liquid interface. These reagents reinforce or produce the required difference in hydrophobicity between the wanted and unwanted minerals, allowing for bubble attachment and recovery. Another group of surface-active flotation reagents are frothers. Frother molecules preferentially adsorb at the gas-liquid interface [12,13] and can be divided into five main subcategories based on their chemical composition i.e., aliphatic, cyclic, and aromatic alcohols, alkoxy paraffins, and polyglycol polymers [14]. Frothers lower gas-liquid interfacial tension affecting both the size and stability of bubbles generated

in the flotation tank. Bubble size decreases and stability increases (i.e., bubble coalescence is either delayed or prevented) with increasing frother concentration. This also results in a stable froth phase at the top of the flotation tank [15,16]. Although frothers improve flotation rate and recovery, too high concentration may have negative effects including a lower flotation recovery rate due to the decreased probability of bubble attachment to a hydrophobic particle as well as poorer selectivity [16,17]. Therefore, information about frother concentration could be crucial for more effective control of the flotation process.

The adsorption of frothers at the air-water interface may be studied by interfacial tension measurements. A number of approaches to the study of the kinetics of frother adsorption at the air-liquid interface as well as the equilibrium interfacial tension for different frothers have been reported [18–23]. Studies involve the application of various measurement techniques such as Wilhelmy plate [22], Du Noüy ring [23], or profile analysis tensiometry (with both a pendant drop and emerging bubble geometries used) [18,19,21,24]. However, all of these techniques rely on static conditions, in which the adsorption of frother molecules at the interfacial surface happens in the absence of flow, and may not reflect adsorption under dynamic conditions, i.e., such as in the flotation tank [24].

One of the technology platforms that has potential for deployment in industry to allow dynamic, in-line measurement of surfactant concentration is microfluidics. Microfluidic devices are optimized to handle small volumes (from pico- to micro-liters [25,26]) of fluids flowing through the channels (the channel's dimensions are usually in the range of several to tens of microns). The use of micron-sized channels results in laminar flow, which allows for easy and controlled formation of uniform bubbles and droplets [25,27]. In addition, the environment inside the channels is contaminant free, offering another advantage for fluid-liquid interfacial studies [28–30]. There are a number of considerations regarding the design of such a device to make it viable for interfacial studies. Bubble (or droplet) formation requires the presence of two immiscible phases: (i) the dispersed phase, which could be either gas or liquid and (ii) the continuous phase, which is a liquid that carries the bubbles or droplets. The influx of these two phases into the microfluidic device involves the use of pressure devices such as syringe pumps. After introduction of the phases into the chip, bubble (or droplet) formation depends on the local flow field that is mainly determined by the channel geometry and applied pressure [31,32]. Various microfluidic chip designs have been used for effective bubble or droplet generation. All the designs can be divided, according to the flow area at the contact point of the dispersed and continuous phases, into three categories: (i) cross-flow devices [31], (ii) flow-focusing devices [33], and (iii) co-flow devices [34]. Each of these types of flow categories has been adopted for interfacial tension measurement [35–39], however mostly for droplets. In cross-flow geometry tapered channels with T-junction geometry are often used [35,36]. Nguyen et al. [40] generated droplets at a cross-junction and used an optofluidic sensor detector, consisting of a laser and a photodiode, to measure the droplet formation frequency. However, one of the major drawbacks of using the T-junction configuration for experiments with surfactants is that the surfactant, depending on its nature, may also adsorb to the walls of the channel changing their wettability. Once the channel's walls become hydrophobic the bubbles will attach to them [37]. The current best approach for interfacial tension measurements is a co-flow configuration. Xu et al. [39] studied the effect of surfactant concentration on the liquid-liquid interfacial tension by means of a change in the droplet diameter. A flow-focusing microfluidic device was used by Lee et al. [38], where the authors tried to find the correlation between the liquid-liquid interfacial tension and the deformations of the generated droplets. However, all the reported studies focused on liquid-liquid interfacial tensions and high surfactant concentrations. In addition, the described devices were made of polydimethylsiloxane (PDMS), which makes them unsuitable for deployment in industry to allow dynamic, in-line measurement of the flotation frother's concentration.

In this paper we demonstrate a simple approach, developed for the determination of gas-liquid interfacial tension, using a co-flowing microfluidic geometry for bubble generation, and bubble generation frequency, as a means of frother concentration determination.

The bubble generation frequency as a function of surfactant concentration (for low concentration range) is measured for two commonly-used flotation frothers of different adsorption kinetics, e.g., methyl isobutyl carbinol and DowFroth 250. The influence of the continuous phase flow rate on the bubble generation frequency is also explored. The results obtained in a microfluidic chip are compared with the interfacial tension values obtained using profile analysis tensiometry.

2. Materials and Methods

2.1. Materials

All solutions were prepared using Milli-Q water (generated by an Advantage system A10, Millipore, USA). The gas-MilliQ water interfacial tension (measured at 22 °C) and the Milli-Q water resistivity were $72.4 \text{ mN}\cdot\text{m}^{-1}$ and $18.2 \text{ M}\Omega\cdot\text{cm}$, respectively. The total organic carbon was less than 4 ppb. Flotation frothers selected for microfluidic interfacial studies were: (i) methyl isobutyl carbinol (MIBC) and (ii) DowFroth 250. MIBC is a branched aliphatic alcohol with a molecular weight of $102.17 \text{ g}\cdot\text{mol}^{-1}$, and was sourced from Sigma-Aldrich (Australia). DowFroth 250 is polypropylene glycol monomethyl ether with an average molecular weight of $250 \text{ g}\cdot\text{mol}^{-1}$ (exact value $264.35 \text{ g}\cdot\text{mol}^{-1}$), and was supplied by The Dow Chemical Company (USA). Both frothers were of reagent grade (98% purity). The hydrophile-lipophile balance (HLB) is 6.05 and 7.83 for MIBC and DowFroth 250, respectively.

2.2. Methods

Microfluidic frother concentration determination experiments: The microfluidic device is based on a co-flowing geometry. It was fabricated using borosilicate Pyrex[®] glass in the South Australian node of the Australian National Fabrication Facility. The design of the chip consists of a central channel for a dispersed phase (gas) that meets two side channels allowing the flow of the continuous phase (frother solution). All the channels merge to form one large channel (Figure 1). The width of the dispersed phase channel is $25 \mu\text{m}$ while the width of the continuous phase channels is $300 \mu\text{m}$. The width of the merged channel is $500 \mu\text{m}$. The channels were fabricated using deep reactive-ion etching (DRIE). The microfluidic divide was then thermal bonded at $650 \text{ }^{\circ}\text{C}$. Nanoport[™] fittings (IDEX Health & Science, USA) made of polyether ether ketone (PEEK) were aligned with and attached to the inlets of the microfluidic device using adhesive rings (IDEX Health & Science, USA) and a curing time of 1 h (at $165 \text{ }^{\circ}\text{C}$). PEEK tubing (IDEX Health & Science, USA) with an inner diameter of $150 \mu\text{m}$ was used to connect the Nanoport[™] fittings to glass gastight syringes (Hamilton, USA) mounted in programmable and precisely-controlled syringe pumps (Cole-Palmer, USA) allowing for operations at constant and low flow rates of both phases. While the flow rate of the dispersed phase was kept constant ($0.4 \text{ mL}\cdot\text{h}^{-1}$), the flow rate of the continuous phase flow was varied, ranging from 1 up to $10 \text{ mL}\cdot\text{h}^{-1}$. Prior to actual measurement, the flow rates of both phases were allowed to stabilize for at least 15 min. To exclude environmental vibration effects, the experimental set-up was placed on an anti-vibration table Vision IsoStation (Newport, USA). To avoid temperature changes (and gradients) the microfluidic device was side illuminated by a cold light source with a halogen diode lamp (Bruker, USA). All experiments were carried out at $22.0 \pm 1.0 \text{ }^{\circ}\text{C}$.

The bubble generation frequency experiments in MilliQ water and in frother solutions of various concentrations were recorded using a high-speed camera SA3 Fastcam (Photron, USA) mounted on an inverted BXFM microscope (Olympus, Japan), as schematically shown in Figure 1. Depending on the surfactant concentration, the videos were recorded at a frame rate of either 250 fps or 1000 fps and with a resolution of $300 \text{ pixels} \times 300 \text{ pixels}$. All videos were recorded in a position capturing the merging of three channels, i.e., the point of bubble formation. Videos were converted to image (*.BMP) sequences and analyzed using ImageJ software [41] to determine the number of bubbles passing through the channel in a given time interval. The average bubble generation frequency was calculated as a function of frother concentration and flow rate ratio from three independent repeats.

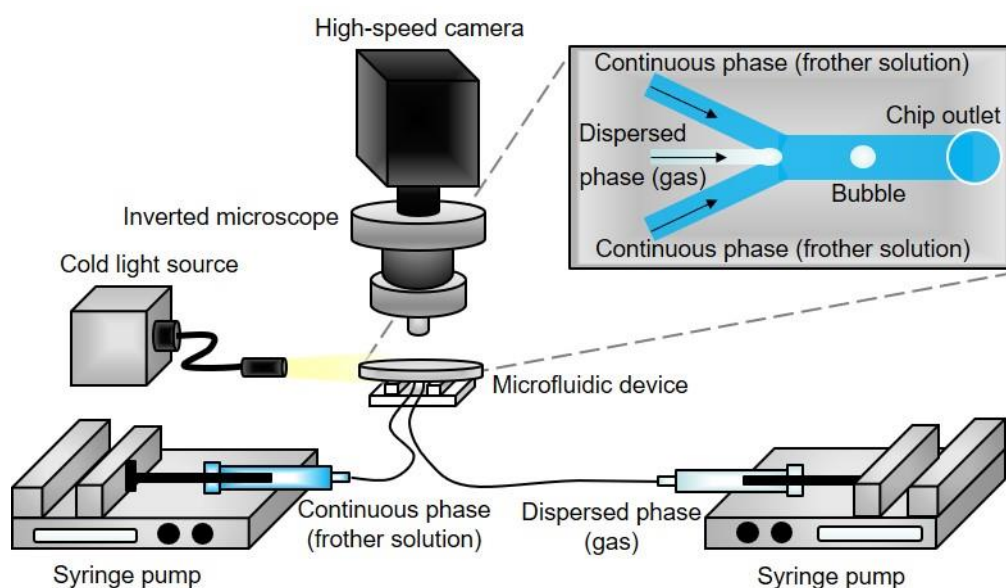


Figure 1. Left side, schematic representation of the experimental set-up; right top insert, schematic representation of the microfluidic device.

Profile analysis tensiometry experiments: Interfacial tension for all studied solutions was determined using profile analysis tensiometer, PAT1-M (Sinterface Technologies, Germany) placed on an anti-vibration table (Vision IsoStation, Newport, USA). The interfacial tension measurements (of static bubbles), as a function of adsorption time, were conducted using an emerging bubble geometry. A U-shaped stainless steel capillary (of a diameter of 2.935 mm) was used to generate air bubbles of a constant volume (17 μL). A 20 mL square optical glass cuvette was filled with the studied solution and closed with a lid to minimise solution evaporation. Profile analysis measurements were conducted for at least 30 min to ensure that the interfacial tension reached equilibrium. An average value of equilibrium interfacial tension was calculated from at least three independent measurements. A constant temperature of 22.0 ± 0.1 $^{\circ}\text{C}$ was maintained by a heating-cooling circulating bath.

Cleaning protocols: An optical glass cuvette (Hellma Analytics, Germany) used for profile analysis tensiometry. As well, all glassware used for the solution preparation was immersed in 2% aqueous Extran[®] (Merck Millipore, USA) solution for 40 min and rinsed with demineralized water. Then, the glassware was placed in a 2M KOH aqueous solution for further 40 min. This was followed by rinsing with copious amount of Milli-Q water until neutral pH and drying at 50 $^{\circ}\text{C}$ in an oven. An optical glass cuvette was additionally exposed to air plasma (Harrick, PDC-OD2, USA) for 90 s prior to the measurement.

The stainless steel capillary (Sinterface Technologies, Germany), polyether ether ketone (PEEK) tubing (IDEX Health & Science, USA), and gastight glass syringes (Hamilton, USA) were sonicated in 2% Mucosol[™] (Sigma-Aldrich, Australia) aqueous solutions for 15 min, followed by rinsing with demineralized water and sonicating in 100% undenatured ethanol (Chem-Supply Pty Ltd., Australia) for 15 min. Then, all the components were thoroughly rinsed and sonicated in Milli-Q water for 15 min, followed by drying in a nitrogen stream (99.999% purity, BOC, Australia). The cleaned syringes and the capillary were additionally air plasma cleaned for 90 s.

The Pyrex[®] glass microfluidic device was cleaned prior to the experiments by pumping 2% Mucosol[™] aqueous solution through the channels for 40 min, followed by extensive flushing with Milli-Q water, followed by 2M KOH aqueous solution for 40 min. Then, the microfluidic device was rinsed with Milli-Q water until neutral pH. All solutions were pumped at a constant flow rate of 1 $\text{mL}\cdot\text{h}^{-1}$. Finally, the microfluidic device was dried in a nitrogen stream and exposed to air plasma for at least 90 s.

3. Results and Discussion

3.1. Interfacial Tension Isotherms

Due to the difference in their molecular weight (and hence differences in surface activity and adsorption kinetics), MIBC and DowFroth 250 were chosen for our study. The equilibrium interfacial tension values as a function of the frother concentration are presented in Figure 2 (panel A for MIBC and Panel B for DowFroth 250). Both frothers' concentrations were chosen to obtain similar values of the air-solution interfacial tension.

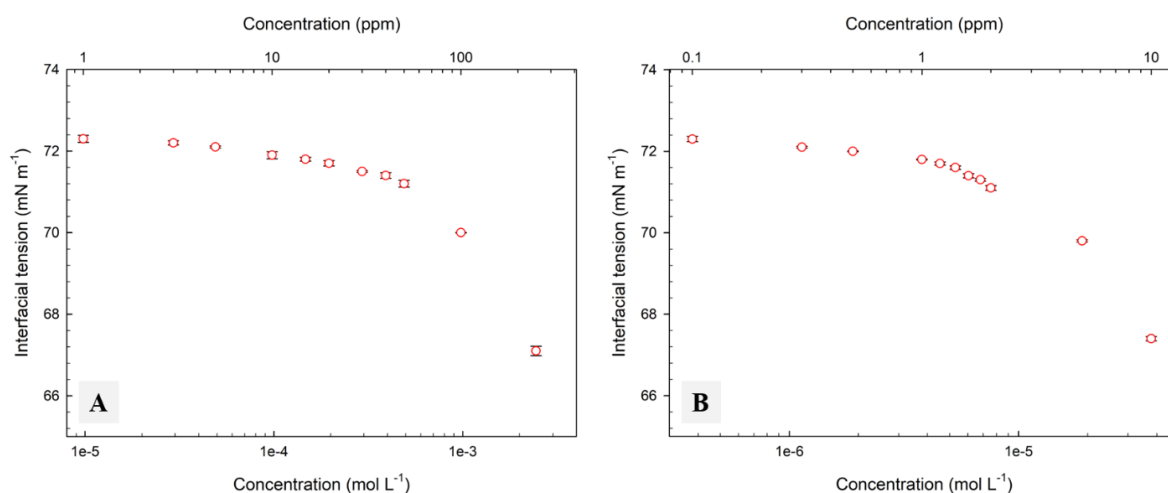


Figure 2. Equilibrium interfacial tension as a function of frother concentration. The average value taken from at least three independent measurements. (A) Methyl isobutyl carbinol MIBC and (B) DowFroth 250. Error bars shown.

The adsorption isotherm of MIBC (Figure 2A) resembles that of 1-hexanol, which is unsurprising given the similar carbon chain length and molecular weight [42]. Although there was no drastic reduction in the interfacial tension for the MIBC concentrations, the kinetics of adsorption was very fast, with the equilibrium values of the interfacial tension reached in a fraction of second for all studied MIBC concentrations. Such near-instantaneous adsorption is desirable in the flotation process [43]. It is important to note, that even at its highest concentration ($2.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, about 250 ppm), MIBC only lowers the interfacial tension of MilliQ water by $5.3 \pm 0.1 \text{ mN} \cdot \text{m}^{-1}$, with the equilibrium interfacial tension of $2.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ MIBC being $67.1 \pm 0.1 \text{ mN} \cdot \text{m}^{-1}$.

The adsorption isotherm for DowFroth 250, a frother belonging to the polyglycol ether family, is shown in Figure 2B. The isotherm shows that lower concentration of DowFroth 250 is required to achieve a similar decrease in the interfacial tension in comparison to MIBC. The concentration range of DowFroth 250 from 4×10^{-7} to $4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ (0.1 and 10 ppm) and resulted in equilibrium interfacial tension values between 72.3 and 67.4 mN m⁻¹, while for MIBC a concentration range of 1×10^{-5} to $2.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (1–250 ppm) was needed to reach the same values of interfacial tension. In spite of its branched structure, MIBC has a lower HLB in common with other aliphatic alcohols, and will likely structure in a semi-organised manner at the bubble surface, resulting in a smaller area per molecule occupied in comparison to the larger (in terms of molecular weight) and more structurally diverse DowFroth 250 [44]. Lower DowFroth 250 concentrations result in slower adsorption kinetics and hence a longer time is required to reach equilibrium interfacial tension (between 2500 and 3500 s for the concentration range used in this study).

3.2. Microfluidic Determination of Interfacial Tension

Our first target in the microfluidic experiments was the determination of microfluidic device working conditions for MilliQ water. All experiments were performed in the dripping flow regime, i.e., at low flow rates of dispersed ($0.4 \text{ mL} \cdot \text{h}^{-1}$) and continuous (1 up

to $10 \text{ mL}\cdot\text{h}^{-1}$) phases with the periodic generation of an individual bubble detaching from the tip of the dispersed phase channel [45].

The relation between viscous forces and capillary forces is described by a dimensionless number—the capillary number, Ca , as:

$$Ca = \frac{\mu_c U_c}{\gamma}$$

where μ_c is the continuous phase viscosity, U_c is the continuous phase velocity, and γ is the interfacial tension [45].

The bubble pinches off from the tip when the viscous drag forces overcome interfacial tension forces with the balance between these forces governing the size of the detaching bubble.

Figure 3A presents pictures of air bubbles formed in the microfluidic channel flowing Milli-Q water at different flow rates of the continuous phase, while the air bubble generation frequency as a function of Milli-Q water flow is plotted in Figure 3B. As can be seen in Figure 3A the size of the generated air bubbles decreases with increasing flow rate of the continuous phase (Milli-Q water). This is because the increase of the continuous phase flow rate leads to increased shear stress, causing formation of smaller air bubbles. At the same time, the generation frequency of air bubbles is higher.

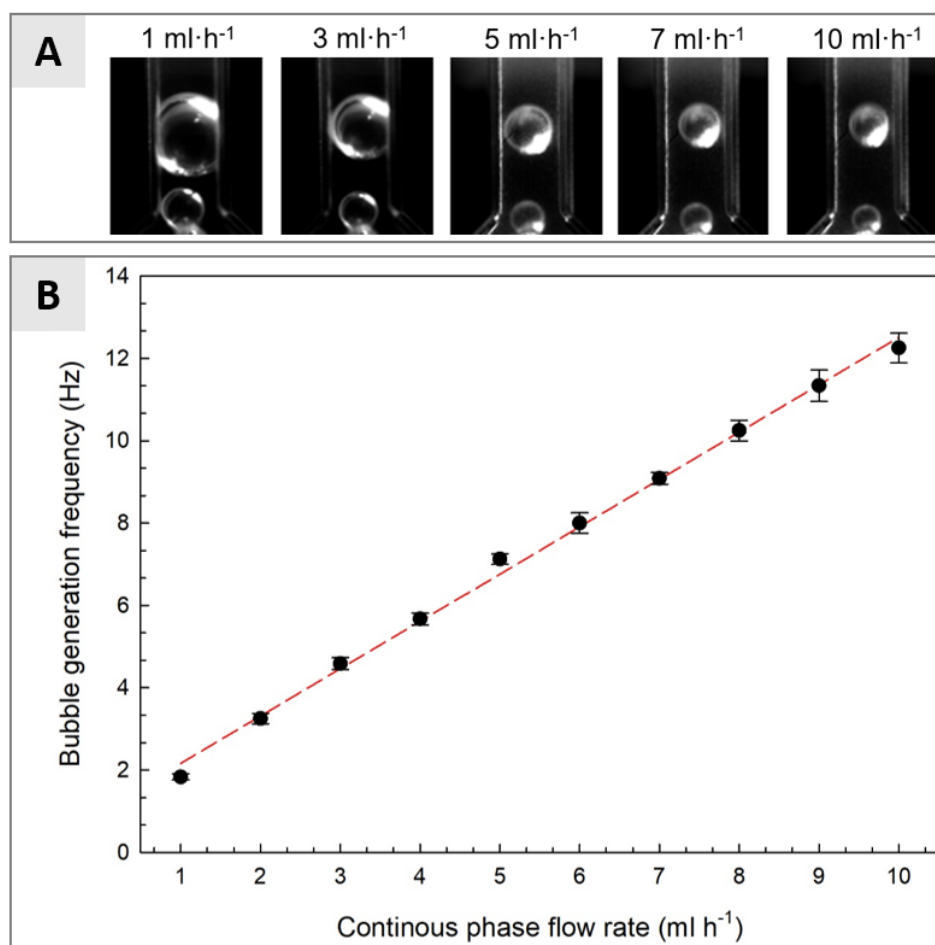


Figure 3. (A) Images of air bubbles generated in a microfluidic channel with Milli-Q water as the continuous phase is flowed at different flow rates (the flow rate of dispersed phase was kept constant at $0.4 \text{ mL}\cdot\text{h}^{-1}$) and (B) bubble generation frequency as a function of Milli-Q water flow rate. Average values calculated from at least three independent measurements (including error bars) are shown.

From data plotted in Figure 3B one can see that the frequency of generated air bubbles increases from 1.8 to 12.3 Hz as the continuous phase flow increases from 1 to 10 mL·h⁻¹, and that the relation between the frequency and the flow rate is linear (the coefficient of determination, R^2 , is 0.9969). The results are reproducible with the relative standard deviation, RSD, for three independent measurements not exceeding 3%. Hoeve et al. [46] predicted that the formation frequency, f , in a flow-focusing microfluidic device under the jetting regime and for constant flow rate is proportional to the flow rate of the continuous phase (Q_c), the radius of the dispersed phase channel (r_d), and the main channel, $f \propto Q_c/\pi r_d r^2$. However, in the dripping regime and for constant dispersed phase flow rate, the bubble generation frequency increases in a linear manner with increases in the continuous phase flow rate, as the viscosity is constant [47].

For the experiments with frothers, in order to avoid the situation when the bubble is 'squeezed' between the walls of the channel (and hence affecting uniform frother adsorption at the air-solution interface), we will focus on the following three continuous phase flow rates: 5, 7, and 9 mL·h⁻¹. Figure 4 presents the pictures of air bubbles generated in Milli-Q water and various concentrations of MIBC. The flow rates of both phases were kept constant with the dispersed phase flow rate being 0.4 mL·h⁻¹ and the continuous phase flow rate being 5 mL·h⁻¹. The presence of frother in the continuous phase results in adsorption of its molecules at the air-solution interface, which decreases the interfacial tension forces that keep the air bubble at the tip of the dispersed phase channel [19,45]. As a result, smaller bubbles (generated at the higher frequency) detached in surfactant solutions compared to the bubbles generated in Milli-Q water. The bubble size decreased and the bubble generation frequency increased with increases in the frother concentration, with the smallest and most frequently generated bubbles for 50 ppm MIBC solution (from the examples presented in Figure 4). Moreover, for higher concentrations (50 ppm and above) the generated air bubbles were 'pushed in contact' in downstream parts of the channel but we observed no coalescence. This is not surprising as 50 ppm is ~4.5–5 times higher than the critical coalescence concentration for MIBC [25,48].

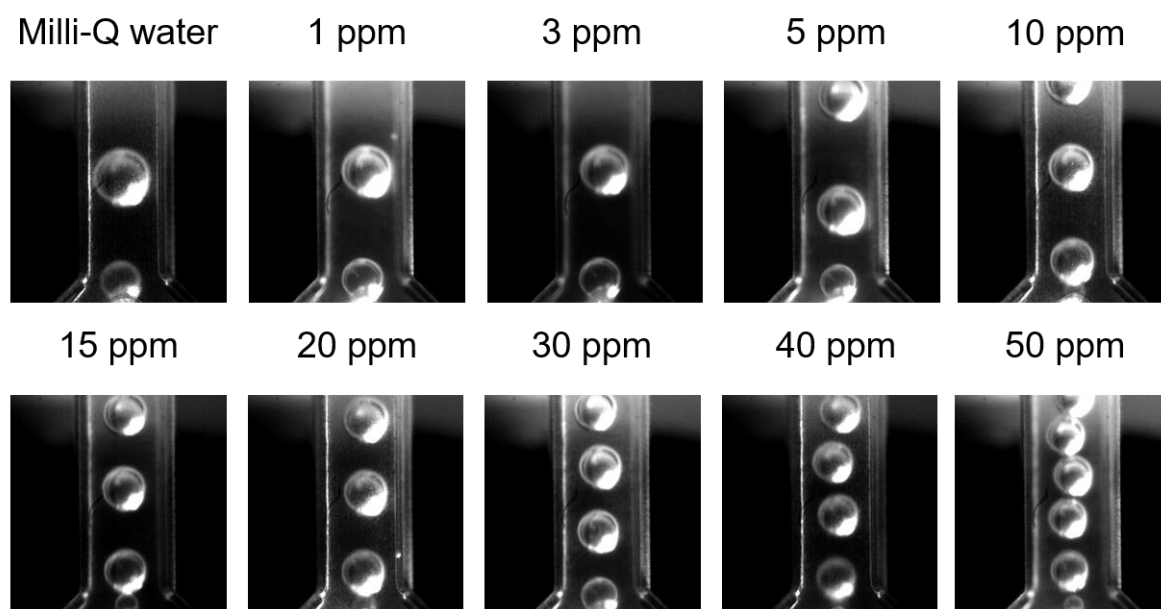


Figure 4. Images of air bubbles generated in a microfluidic channel with Milli-Q and MIBC solutions of various concentrations. The flow rate of the dispersed phase was 0.4 mL·h⁻¹, the flow rate of the continuous phase was 5 mL·h⁻¹.

The bubble generation frequency in MIBC and DowFroth 250 solutions of different concentrations for three different flow rates of the continuous phase is presented in Figure 5A,B, respectively. For the same continuous phase flow rate, as the concentration of MIBC and DowFroth 250 increased (and the interfacial tension counteracting viscous

drag decreased), the bubble generation frequency increased. For both MIBC and DowFroth 250, when the frother concentration was kept constant but the continuous phase flow rate increased (and the viscous drag counteracting constant interfacial tension increased) the bubble generation frequency increased.

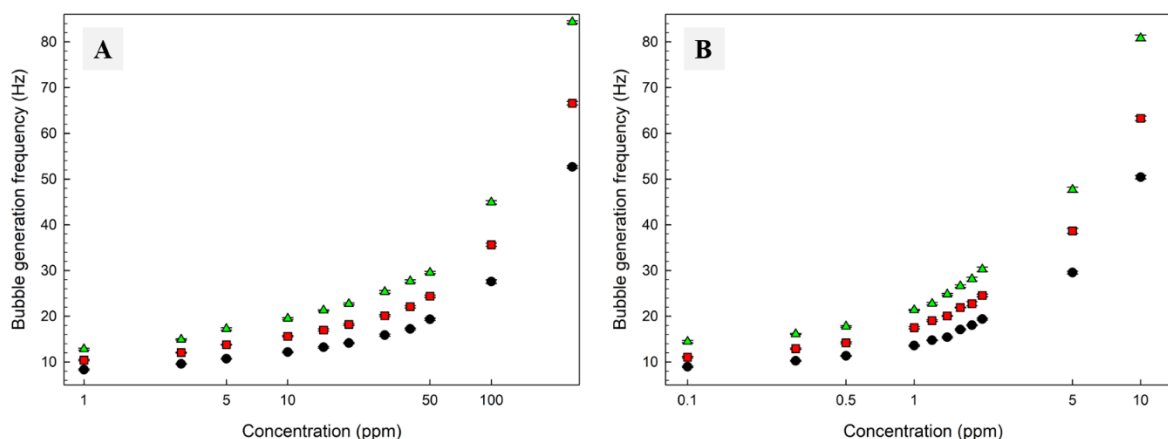


Figure 5. Bubble generation frequency as a function of frother concentration for three different flow rates of the continuous phase ($5 \text{ mL}\cdot\text{h}^{-1}$, black closed circles; $7 \text{ mL}\cdot\text{h}^{-1}$, red closed squares; and $9 \text{ mL}\cdot\text{h}^{-1}$, green closed triangles). Average values calculated from at least three independent measurements, with error bars shown. (A) MIBC and (B) DowFroth 250.

In Figure 5A (MIBC concentration ranged between 1 and 250 ppm or 1×10^{-5} and $2.5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) the lowest bubble generation frequency (8.3 Hz) was measured for 1 ppm ($1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) MIBC solution flowing at $5 \text{ mL}\cdot\text{h}^{-1}$, and the highest (84.3 Hz) was measured for 250 ppm ($2.5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) MIBC solution flowing at rate of $9 \text{ mL}\cdot\text{h}^{-1}$.

In Figure 5B (DowFroth 250 concentration ranged between 0.1 and 10 ppm or 4×10^{-7} and $4 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) the frequency of generated bubbles was the lowest (9.0 Hz) for 0.1 ppm ($4 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$) DowFroth 250 solution flowing at $5 \text{ mL}\cdot\text{h}^{-1}$ and the highest (80.8 Hz) for 10 ppm ($4 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) DowFroth 250 solution flowing at $9 \text{ mL}\cdot\text{h}^{-1}$. The increase in bubble generation frequency with the frother concentration increase was similar. For both frothers the results are reproducible with the RSD for three independent measurements not exceeding 1.8%.

The relationship between bubble formation frequency and interfacial tension in a T-junction microfluidic device was formulated by Nguyen et al. [49]. In their proposed model, the bubble formation frequency can be calculated using the following equation:

$$f = \frac{3D_c^2}{16([C_S/C_D]D_d)^{\frac{2}{3}}} \frac{\rho_c^{\frac{3}{2}} U_c^4}{\gamma^{\frac{3}{4}}}$$

where ρ_c is the continuous phase density, D_c is the diameter of the continuous phase channel, D_d is the diameter of the dispersed phase channel, and C_D and C_S are the coefficients for drag and interfacial tension, respectively. In the T-junction geometry, the flow rate and the formation frequency is characterized by non-linear dependency, as the bubble detachment is also affected by the interaction of the dispersed phase with the wall of microfluidic channel [34]. However, Nguyen et al. reported that for surfactant solution flowing through the microfluidic channel bubble formation frequency depended linearly on the interfacial tension, provided the continuous phase density was kept constant [40,48].

We cannot apply this equation to our data due to the different geometry of the channels, but we expect that there will be a similar dependency between bubble formation frequency and interfacial tension. Figure 6A,B present bubble generation frequency as a function of the interfacial tension for MIBC and DowFroth 250, respectively. For both frothers, at the constant continuous phase flow rate, the bubble generation frequency decreased linearly with increasing air-solution interfacial tension with R^2 for MIBC data being higher than 0.9978, and R^2 for DowFroth 250 data being higher than 0.9971. When the air-solution interfacial tension was kept constant, the bubble generation frequency increased with increasing continuous phase flow rate.

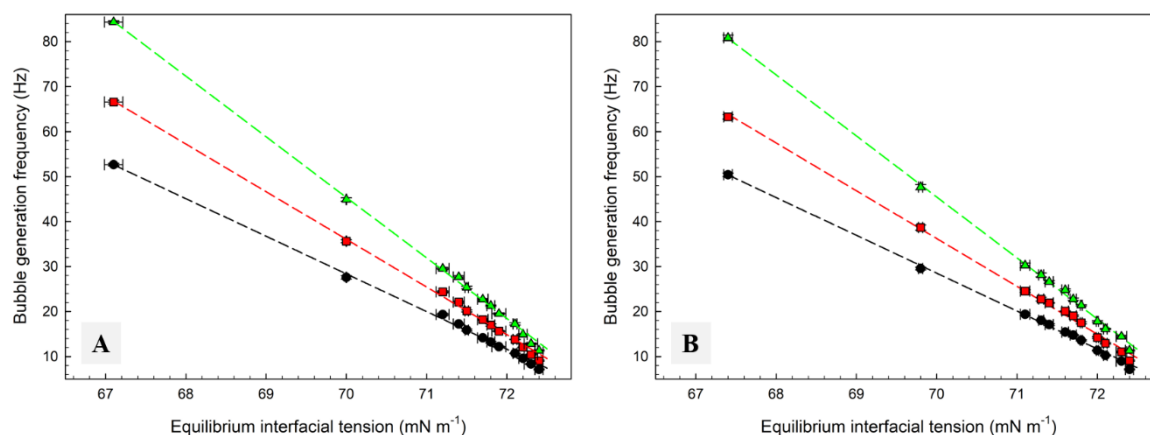


Figure 6. Bubble generation frequency as a function of the interfacial tension for three different flow rates of the continuous phase ($5 \text{ mL}\cdot\text{h}^{-1}$, black closed circles; $7 \text{ mL}\cdot\text{h}^{-1}$, red closed squares; and $9 \text{ mL}\cdot\text{h}^{-1}$, green closed triangles). Average values calculated from at least three independent measurements, with error bars shown. (A) MIBC and (B) DowFroth 250.

This frother sensing system based on bubble generation frequency is very sensitive—a drop in air-solution interfacial tension of $0.1 \text{ mN}\cdot\text{m}^{-1}$ causes an increase of 13–14% in bubble generation frequency, making it suitable for the detection of even minute amounts of frother molecules.

Figure 7 presents the scaled data from Figure 6A,B. The relative bubble generation frequency, f_r (i.e., the bubble generation frequency for frother solutions, f_f , normalised with respect to the bubble generation frequency for Milli-Q water, f_w , at a given flow rate: $f_r = f_f/f_w$), is plotted as a function of the drop in interfacial tension from Milli-Q water $\Delta\gamma = \gamma_w - \gamma_f$, with γ_w being the interfacial tension of Milli-Q water and γ_f being the interfacial tension of the frother solutions. The black closed circles are for MIBC while the red closed circles are for DowFroth 250.

The scaled frequency data for two frothers and bubbles generated at three different continuous phase flow rates can be fitted with a straight line (R^2 of 0.9979) for the entire range of considered frother concentrations. Therefore, after normalising with the bubble generation frequency for Milli-Q water, the bubble formation frequency is independent of the continuous phase flow rate and is only affected by changes (with respect to Milli-Q water) in the interfacial tension. Despite different adsorption kinetics, the relative bubble generation frequency is the same for MIBC and DowFroth 250 solutions of the same interfacial tension.

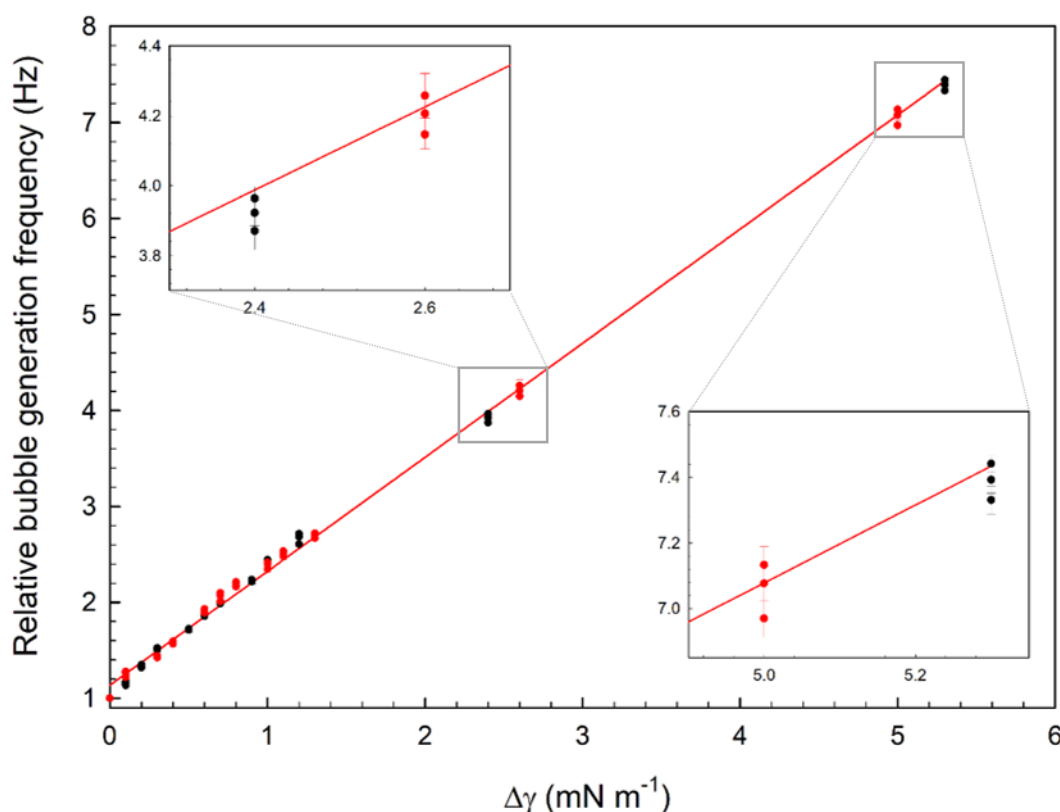


Figure 7. Relative bubble generation frequency as a function of a drop in Milli-Q water interfacial tension for all flow rates of the continuous phase. MIBC, black closed circles and DowFroth 250, red closed circles. Error bars shown.

4. Conclusions

In this work we present a microfluidic-based approach to determine gas-liquid interfacial tension for two flotation frothers of very different adsorption kinetics using bubble generation frequency measurements. We show that, in the dripping regime and at the constant dispersed phase flow rate, the bubble formation frequency in Milli-Q water linearly depends on the continuous phase flow rate. A drop in the air-solution interfacial tension as small as $0.1 \text{ mN} \cdot \text{m}^{-1}$ causes the bubble generation frequency to increase by 13–14%, making it a suitable device for the detection of even minute amounts of frother molecules. Moreover, for MIBC and DowFroth 250 solutions, despite the very different adsorption kinetics, the bubble generation frequency increases linearly with decreases in the equilibrium interfacial tension and increases in the continuous phase flow rate. Upon data scaling, all curves collapse onto a single line, despite different adsorption kinetics for MIBC and DowFroth 250. This is likely due to the continuous supply of the frother molecules to the gas-liquid interface. Moreover, a flow-focusing device offers a directional flow onto the bubble surface upon its generation, providing continuous supply of frother molecules.

Author Contributions: P.P., B.H.B.-H., D.A.B., and M.K. designed the experiments; P.P. performed the experiments; B.H.B.-H., D.A.B., and M.K. advised and oversaw the data analysis; P.P. analyzed the data; C.G., W.S., D.A.B., and M.K. secured the funding; all authors contributed to manuscript drafting as well as manuscript review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Joint Research Centre for In-Line Chemical and Mineral Sensing for Sustainable Mineral Processing Australia-China Fund (project JRCAF-55), administered by The Department of Industry, Innovation and Science, and by the SA Government through the PRIF RCP Mining Consortium ‘Unlocking Complex Resources through Lean Processing’.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Data available on request.

Acknowledgments: The authors warmly acknowledge the comments and critique on this work provided by habil. Reinhard Miller. The microfluidic devices for bubble generation were fabricated at the South Australian node of the Australian National Fabrication Facility, a company established under the National Collaborative Research Infrastructure Strategy to provide nano- and micro-fabrication facilities for Australia's researchers.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Malysa, K.; Zawala, J.; Krzan, M.; Krasowska, M. Bubbles rising in solutions; local and terminal velocities, shape variations and collisions with free surface. In *Bubble and Drop Interfaces*; Brill: Boston, MA, USA, 2011; pp. 251–300.
2. Liu, B.; Manica, R.; Xu, Z.; Liu, Q. The boundary condition at the air-liquid interface and its effect on film drainage between colliding bubbles. *Curr. Opin. Colloid Interface Sci.* **2020**. [\[CrossRef\]](#)
3. Krasowska, M.; Malysa, K.; Beattie, D.A. Recent advances in studies of bubble-solid interactions and wetting film stability. *Curr. Opin. Colloid Interface Sci.* **2019**, *44*, 48–58. [\[CrossRef\]](#)
4. Liu, B.; Manica, R.; Liu, Q.; Klaseboer, E.; Xu, Z.; Xie, G. Coalescence of bubbles with mobile interfaces in water. *Phys. Rev. Lett.* **2019**, *122*, 194501. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Pawliszak, P.; Ulaganathan, V.; Bradshaw-Hajek, B.H.; Manica, R.; Beattie, D.A.; Krasowska, M. Mobile or immobile? Rise velocity of air bubbles in high-purity water. *J. Phys. Chem. C* **2019**, *123*, 15131–15138. [\[CrossRef\]](#)
6. Carnie, S.L.; Del Castillo, L.; Horn, R.G. Mobile surface charge can immobilize the air/water interface. *Langmuir* **2019**, *35*, 16043–16052. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Vakarelski, I.U.; Lee, J.; Dagastine, R.R.; Chan, D.Y.; Stevens, G.W.; Grieser, F. Bubble colloidal AFM probes formed from ultrasonically generated bubbles. *Langmuir* **2008**, *24*, 603–605. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Zawala, J.; Niecikowska, A. “Bubble-on-demand” generator with precise adsorption time control. *Rev. Sci. Instrum.* **2017**, *88*, 095106. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Malysa, K.; Krasowska, M.; Krzan, M. Influence of surface active substances on bubble motion and collision with various interfaces. *Adv. Colloid Interface Sci.* **2005**, *114*, 205–225. [\[CrossRef\]](#)
10. Vakarelski, I.U.; Yang, F.; Thoroddsen, S.T. Free-rising bubbles bounce stronger from mobile than immobile water-air interfaces. *Langmuir* **2020**, *36*, 5908–5918. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Wills, B.A.; Finch, J.A. Chapter 12—Froth Flotation. In *Wills' Mineral Processing Technology (Eighth Edition)*; Wills, B.A., Finch, J.A., Eds.; Butterworth-Heinemann: Boston, MA, USA, 2016; pp. 265–380.
12. Pawliszak, P.; Zawala, J.; Ulaganathan, V.; Ferri, J.K.; Beattie, D.A.; Krasowska, M. Interfacial characterisation for flotation: 2. Air-water interface. *Curr. Opin. Colloid Interface Sci.* **2018**, *37*, 115–127. [\[CrossRef\]](#)
13. Krasowska, M.; Zawala, J.; Bradshaw-Hajek, B.H.; Ferri, J.K.; Beattie, D.A. Interfacial characterisation for flotation: 1. Solid-liquid interface. *Curr. Opin. Colloid Interface Sci.* **2018**, *37*, 61–73. [\[CrossRef\]](#)
14. Pearce, M. An overview of the use of chemical reagents in mineral processing. *Miner. Eng.* **2005**, *18*, 139–149. [\[CrossRef\]](#)
15. Gupta, A.K.; Banerjee, P.; Mishra, A. Effect of frothers on foamability, foam stability, and bubble size. *Coal Prep.* **2007**, *27*, 107–125. [\[CrossRef\]](#)
16. Gupta, A.K.; Banerjee, P.; Mishra, A.; Satish, P. Effect of alcohol and polyglycol ether frothers on foam stability, bubble size and coal flotation. *Int. J. Miner. Process.* **2007**, *82*, 126–137. [\[CrossRef\]](#)
17. Harvey, P.; Nguyen, A.; Jameson, G.; Evans, G. Influence of sodium dodecyl sulphate and Dowfroth frothers on froth stability. *Miner. Eng.* **2005**, *18*, 311–315. [\[CrossRef\]](#)
18. Jávora, Z.; Schreithofer, N.; Heiskanen, K. Micro- and nano-scale phenomena effect on bubble size in mechanical flotation cell. *Miner. Eng.* **2015**, *70*, 109–118.
19. Nguyen, A.V.; Phan, C.M.; Evans, G.M. Effect of the bubble size on the dynamic adsorption of frothers and collectors in flotation. *Int. J. Miner. Process.* **2006**, *79*, 18–26. [\[CrossRef\]](#)
20. Qu, X.; Wang, L.; Karakashev, S.I.; Nguyen, A.V. Anomalous thickness variation of the foam films stabilized by weak non-ionic surfactants. *J. Colloid Interface Sci.* **2009**, *337*, 538–547. [\[CrossRef\]](#)
21. Jávora, Z.; Schreithofer, N.; Heiskanen, K. Multi-scale analysis of the effect of surfactants on bubble properties. *Miner. Eng.* **2016**, *99*, 170–178.
22. Le, T.N.; Phan, C.M.; Nguyen, A.V.; Ang, H.M. An unusual synergistic adsorption of MIBC and CTAB mixtures at the air-water interface. *Miner. Eng.* **2012**, *39*, 255–261. [\[CrossRef\]](#)
23. Fong, C.; Greaves, T.L.; Healy, T.W.; Drummond, C.J. The effect of structural modifications on the solution and interfacial properties of straight and branched aliphatic alcohols: The role of hydrophobic effects. *J. Colloid Interface Sci.* **2015**, *449*, 364–372. [\[CrossRef\]](#) [\[PubMed\]](#)

24. Jávör, Z.; Schreithofer, N.; Heiskanen, K. Validity of critical coalescence concentration in dynamic conditions. *Int. J. Miner. Process.* **2014**, *127*, 16–22.
25. Bremond, N.; Bibette, J. Exploring emulsion science with microfluidics. *Soft Matter* **2012**, *8*, 10549–10559. [[CrossRef](#)]
26. Stone, H.A.; Stroock, A.D.; Ajdari, A. Engineering flows in small devices: Microfluidics toward a lab-on-a-chip. *Annu. Rev. Fluid Mech.* **2004**, *36*, 381–411. [[CrossRef](#)]
27. Jakiela, S.; Korczyk, P.M.; Makulska, S.; Cybulski, O.; Garstecki, P. Discontinuous transition in a laminar fluid flow: A change of flow topology inside a droplet moving in a micron-size channel. *Phys. Rev. Lett.* **2012**, *108*, 134501. [[CrossRef](#)]
28. Mazutis, L.; Griffiths, A.D. Selective droplet coalescence using microfluidic systems. *Lab A Chip* **2012**, *12*, 1800–1806. [[CrossRef](#)]
29. Baret, J.-C. Surfactants in droplet-based microfluidics. *Lab Chip* **2012**, *12*, 422–433. [[CrossRef](#)]
30. D’Apolito, R.; Perazzo, A.; D’Antuono, M.; Preziosi, V.; Tomaiuolo, G.; Miller, R.; Guido, S. Measuring interfacial tension of emulsions in situ by microfluidics. *Langmuir* **2018**, *34*, 4991–4997.
31. Xu, J.; Li, S.; Tan, J.; Wang, Y.; Luo, G. Preparation of highly monodisperse droplet in a T-junction microfluidic device. *AIChE J.* **2006**, *52*, 3005–3010. [[CrossRef](#)]
32. Nunes, J.; Tsai, S.; Wan, J.; Stone, H.A. Dripping and jetting in microfluidic multiphase flows applied to particle and fibre synthesis. *J. Phys. D Appl. Phys.* **2013**, *46*, 114002. [[CrossRef](#)]
33. Anna, S.L.; Bontoux, N.; Stone, H.A. Formation of dispersions using “flow focusing” in microchannels. *Appl. Phys. Lett.* **2003**, *82*, 364–366. [[CrossRef](#)]
34. Xiong, R.; Bai, M.; Chung, J.N. Formation of bubbles in a simple co-flowing micro-channel. *J. Micromech. Microeng.* **2007**, *17*, 1002. [[CrossRef](#)]
35. Zhou, H.; Yao, Y.; Chen, Q.; Li, G.; Yao, S. A facile microfluidic strategy for measuring interfacial tension. *Appl. Phys. Lett.* **2013**, *103*, 234102. [[CrossRef](#)]
36. Gu, H.; Duits, M.H.G.; Mugele, F. Interfacial tension measurements with microfluidic tapered channels. *Colloids Surf. A Physicochem. Eng. Asp.* **2011**, *389*, 38–42. [[CrossRef](#)]
37. Parhizkar, M.; Edirisinghe, M.; Stride, E. The effect of surfactant type and concentration on the size and stability of microbubbles produced in a capillary embedded T-junction device. *RSC Adv.* **2015**, *5*, 10751–10762. [[CrossRef](#)]
38. Lee, D.; Fang, C.; Ravan, A.S.; Fuller, G.G.; Shen, A.Q. Temperature controlled tensiometry using droplet microfluidics. *Lab A Chip* **2017**, *17*, 717–726. [[CrossRef](#)] [[PubMed](#)]
39. Xu, J.H.; Dong, P.F.; Zhao, H.; Tostado, C.P.; Luo, G.S. The Dynamic Effects of Surfactants on Droplet Formation in Coaxial Microfluidic Devices. *Langmuir* **2012**, *28*, 9250–9258. [[CrossRef](#)]
40. Nguyen, N.-T.; Lassemono, S.; Chollet, F.A. Optical detection for droplet size control in microfluidic droplet-based analysis systems. *Sens. Actuators B: Chem.* **2006**, *117*, 431–436. [[CrossRef](#)]
41. Schneider, C.A.; Rasband, W.S.; Eliceiri, K.W. NIH Image to ImageJ: 25 years of image analysis. *Nat. Methods* **2012**, *9*, 671–675. [[CrossRef](#)]
42. Le, T.N.; Phan, C.M.; Ang, H.M. Influence of hydrophobic tail on the adsorption of isomeric alcohols at air/water interface. *Asia-Pac. J. Chem. Eng.* **2012**, *7*, 250–255. [[CrossRef](#)]
43. Fainerman, V.B.; Miller, R. Dynamic Surface Tension Measurements in the Sub-millisecond Range. *J. Colloid Interface Sci.* **1995**, *175*, 118–121. [[CrossRef](#)]
44. Finch, J.A.; Zhang, W. Frother function–structure relationship: Dependence of CCC95 on HLB and the H-ratio. *Miner. Eng.* **2014**, *61*, 1–8. [[CrossRef](#)]
45. Utada, A.S.; Fernandez-Nieves, A.; Stone, H.A.; Weitz, D.A. Dripping to Jetting Transitions in Coflowing Liquid Streams. *Phys. Rev. Lett.* **2007**, *99*, 094502. [[CrossRef](#)] [[PubMed](#)]
46. van Hoeve, W.; Dollet, B.; Gordillo, J.M.; Versluis, M.; van Wijngaarden, L.; Lohse, D. Bubble size prediction in co-flowing streams. *EPL (Europhys. Lett.)* **2011**, *94*, 64001. [[CrossRef](#)]
47. Zhang, J.M.; Li, E.Q.; Thoroddsen, S.T. A co-flow-focusing monodisperse microbubble generator. *J. Micromech. Microeng.* **2014**, *24*, 035008. [[CrossRef](#)]
48. Nguyen, N.-T.; Lassemono, S.; Chollet, F.; Yang, C. Microfluidic sensor for dynamic surface tension measurement. *IEEE Proc. Nanobiotechnol.* **2006**, *153*, 102–106. [[CrossRef](#)]
49. Nguyen, N.; Lassemono, S.; Chollet, F.A.; Yang, C. Interfacial Tension Measurement With an Optofluidic Sensor. *IEEE Sens. J.* **2007**, *7*, 692–697. [[CrossRef](#)]