Accepted Manuscript



Interfacial characterisation for flotation: 2. Air-water Interface

Piotr Pawliszak, Jan Zawala, Vamseekrishna Ulaganathan, James K. Ferri, David Beattie, Marta Krasowska

PII: S1359-0294(18)30010-4
DOI: doi:10.1016/j.cocis.2018.07.002
Reference: COCIS 1209

To appear in: *Current Opinion in Colloid & Interface Science*

Received date: 27 May 2018
Revised date: 18 July 2018
Accepted date: 18 July 2018

Please cite this article as: Piotr Pawliszak, Jan Zawala, Vamseekrishna Ulaganathan, James K. Ferri, David Beattie, Marta Krasowska , Interfacial characterisation for flotation: 2. Air-water Interface. Cocis (2018), doi:10.1016/j.cocis.2018.07.002

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

ACCEPTED MANUSCRIPT

Interfacial Characterisation for Flotation: 2. Air-Water Interface

Piotr Pawliszak[1,2], Jan Zawala[3], Vamseekrishna Ulaganathan[1], James K. Ferri[4], David Beattie[1,2], Marta Krasowska[1,2]*

[1] Future Industries Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes, SA 5095, Australia;

[2] School of Information Technology and Mathematical Sciences, University of South Australia, Mawson Lakes Campus, Mawson Lakes, SA 5095;

[3] Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul Niezapominajek 8, 30-239 Krakow, Poland;

[4] Department of Chemical and Life Sciences Engineering, Virginia Commonwealth University, Richmond, VA 23219, United States.

ACCEPTED MANUSCRIPT

* Corresponding author; Email: marta.krasowska@unisa.edu.au

ACCEPTED MANUSCRIPT

Abstract

The progress in recent years in characterizing the properties of the interface between air and water in the presence of commonly used surfactants in mineral flotation (termed frothers) is summarized. The focus of this review is on techniques that provide access to dynamic aspects of frother interactions at the interface between air and water, and those techniques that provide a unique perspective of equilibrium adsorbed layer properties. Profile analysis tensiometry (PAT) and other forms of interfacial tension measurement are described, and recent work highlighted. In addition, the methods of dilational interfacial rheology, which probes the viscoelastic properties of the air-water interface and the influence of dynamic adsorption processes, is discussed in relation to published work on flotation frother, as is work on measurement of rising bubble velocities, which allows probing of the dynamic adsorption layer (DAL). In addition to these more traditional measures of interfacial activity and effect, the study of the air-water interface with vibrational spectroscopy, and its relevance to flotation (with reference to recent published work), is described.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

1. Introduction

Mineral flotation is an industrial process used to separate and concentrate ores by exploiting the contrast in the surface wettability of mineral particles (and hence their ability to attach to air bubbles). Hydrophobic mineral particles attach to passing air bubbles and form aggregates of a density smaller than the suspension itself. The aggregates float to the top of the flotation cell and are collected. Hydrophilic particles do not attach to the air bubbles and they sediment to the bottom of the flotation cell [1]. The flotation process takes advantage of several classes of chemicals; some of them adsorb at the solid-water interface (see [2] for the interfacial characterization of such chemicals), while some preferentially adsorb at the air-water interface. This latter group of surface active molecules is called frothers [3]. Frothers not only affect bubble size and rise velocity, but most importantly they prevent bubble coalescence and improve the stability (and properties) of flotation froths [4-7], thus maximizing mineral recovery. The interplay between all these effects is quite complex. For example the effect of frothers on bubble size is a result of interfacial tension and the ability of the frother to prevent bubble coalescence. With increasing frother concentration the bubble size decreases, and at a certain frother concentration (called the critical coalescence concentration: CCC) bubble coalescence is completely inhibited and the bubble size does not decrease further [6, 8].

The interfacial activity of frothers, and their function in a complex multi-phase flotation mixture, is relatively unique in the area of surfactant science. However, there is still a need to understand their interaction with the air-water interface, as a first step in benchmarking their performance, and to understand observed differences in effectiveness in flotation.

This article aims to summarize and provide comments on the last 10 years of research in the area of frother studies at the air-water interface, with a specific emphasis on the use of techniques that can give information on dynamic aspects of chemical and physical processes. This emphasis is required in the study of frothers, as mineral flotation has steps that occur on very short timescales, and quiescent colloidal systems or attainment of thermodynamic equilibrium are not commonplace in the process.

2. Classical Tensiometry

One of the most commonly used techniques to study frother adsorption is the measurement of interfacial tension. Generally, a number of approaches are available for determination of gas-frother solution interfacial tension including Wilhelmy plate or Du Noüy ring methods [9, 10]. However, frothers are used at low (normally a few to a few tens of ppm) concentrations and some of them (of high molecular weight) exhibit slow diffusion. Therefore the most valuable information, including equilibrium interfacial tension as well as adsorption kinetics, can be gained from the time-dependent interfacial tension measurements using profile analysis tensiometry (in either pendant drop or emerging bubble geometry) [11]. Profile analysis

ACCEPTED MANUSCRIPT

tensiometry (PAT) relies on the shape analysis, using the Young-Laplace equation, of the pendant drop/emerging bubble and is widely used in frother adsorption studies [12-14].

Qu *et al*. [15] studied air-solution interfacial tension of some of the most commonly used frothers, including methyl isobutyl carbinol (MIBC), n-pentanol, n-octanol, and polypropylene glycol 400 (PPG-400), for a wide range of surfactant concentration (1×10^{-7} M up to 1×10^{-1} M) to correlate these data with foam film thickness. They found that within this range of concentrations, none of the studied frothers reached the critical micelle concentration, CMC, and that PPG-400 was the most surface active molecule, with its interfacial tension reaching 45 $mN\cdot m^{-1}$ for a 1×10^{-1}M solution. Park *et al*. [16] used the pendant drop configuration to determine the surface activity of methyl cyclohexanemethanol (MCHM) as a potential frother for collectorless coal flotation. They found that the molecules of MCHM occupied a larger surface area and were more surface active (as demonstrated by the larger decrease in the interfacial tension) than MIBC, which is widely used in flotation systems. Harvey *et al*. [17] compared the surface activity of a typical anionic surfactant sodium dodecyl sulphate (SDS) with two Dowfroth (polyglycol based) frothers (Dowfroth 250, and Dowfroth 400) and tried to correlate it with the bubble size, and foam surface shear viscosity. Both frothers were more efficient than SDS in lowering the interfacial tension and produced more stable foams of higher surface shear viscosity. Phan *et al*. [18] used pendant drop method to investigate the kinetics of adsorption of Dowfroth 250 and sodium dodecylbenzene sulphonate (SDBS) at the gas-liquid interface. They used two numerical models (the diffusion-controlled adsorption model and the kinetics-controlled adsorption model) to compare with the experimental data for both surfactants. While the SDBS adsorption was well described by the diffusion-controlled model, the adsorption-desorption rate for Dowfroth 250 was very slow and significantly differed from the predictions given by this model. Schreithofer *et al*. [19] explored the synergistic effect of frothers and depressants (molecules which preferentially adsorb at solid-liquid interfaces) on interfacial tension. They used Dowfroth 200 and two different depressants: Stypress 504 and Depramin 267. They observed that the measured interfacial tension was always lower for the frother-depressant system in comparison to pure Dowfroth 200 solution.

Emerging bubble is an alternative geometry for profile analysis tensiometry. This technique is more difficult to control due to the compressibility of air and hence the possible fluctuations in the bubble volume. However, it eliminates the evaporation issue and allows for adsorption studies at very low concentration [20]. Fainerman *et al*. [20] compared the adsorption of polyethylene glycol tert-octylphenyl ether (Triton X-100) with other non-ionic surfactants using emerging bubble and pendant drop method. They attributed the significant differences in equilibrium interfacial tension values obtained by two geometries to the depletion effects (for the small volume of a pendant droplet). Nguyen *et al*. [21] used emerging bubble to determine the frother and collector adsorption dependency on the bubble diameter. They compared theoretical analysis based on the transfer of surfactant by adsorption and diffusion for different bubble sizes with experimental dynamic interfacial tension data for small bubbles in Dowfroth 250 solutions.

ACCEPTED MANUSCRIPT

The authors concluded that for bubbles with the diameter of the order of 1 mm (a size which lies within the range of bubble sizes in flotation[1]) the size has a negligible effect on the dynamics of adsorption. Hence, the adsorption of frother onto the bubble surface in flotation can be described using the Ward and Tordai equation (derived from the diffusion equation for a planar interface). Phan *et al*. [22] investigating the dynamic adsorption of 1-octanol and other octanols found that 1-octanol is characterised by the highest interfacial activity and the slowest adsorption rate at the gas-liquid interface. They showed that a linear molecule with longer hydrophobic tail occupied less surface area and thus led to the increase in the packing density. Ozdemir *et al*. [23] studied the interfacial tension of MIBC in concentrated NaCl and KCl solutions. Salt solutions had concentrations close to their saturation and interfacial tensions were presented as a function of frother concentration. Initially, the presence of salt ions caused an increase in interfacial tension, however, after reaching MIBC concentration of 5×10^{-3} M the measured interfacial tension was lower than for corresponding aqueous MIBC solution without addition of salt. It is an important observation as salts are naturally present in flotation systems and it is important to understand how they interact with the flotation reagents. In another study dedicated to exploring the effect of process water composition on the interfacial activity of MIBC, Bournival *et al*. [24] used the process water composition from four different coal plants. They found that all types of process water had a negligible effect on the interfacial tension. They concluded that addition of salt in the amount of less than 1×10^{-3} M is insufficient to significantly affect the surface activity of frother molecules. We would like to note, however, that typical salt concentration in flotation circuits is usually higher than 1×10^{-3} M. Bournival *et al*. [25] studied the kinetics of adsorption of MIBC, n-pentanol, PPG-425 and tri(propylene glycol) methyl ether (TPM). They concluded that for the most of the frothers they used the emerging bubble technique had too low time resolution at the early stages of adsorption, as the equilibrium interfacial tension was reached already at the beginning of the measurement. The exception was PPG-425, which showed a decrease in interfacial tension in time due to slow diffusion of molecules. Moreover, this frother reached the lowest equilibrium interfacial tension.

An alternative approach, which provides the information about the kinetics of adsorption with higher time resolution for short measurement time, is the maximum bubble pressure technique. In this approach the pressure, p, inside the gas bubble is measured as a function of time. The pressure increases upon bubble expansion, reaching a maximum value, p_{max}, when the bubble has the completely hemispherical shape and its radius is exactly the same as the radius of the capillary by which it is formed. After the bubble passes the maximum pressure it grows quickly and due to buoyancy detaches from the capillary. The interfacial tension, γ, is calculated from the Young-Laplace equation taking the capillary radius as the radius of curvature, r: $p_{max} = \frac{2\gamma}{r}$. [26] This method is complementary to profile analysis tensiometry, and it cannot be used for long adsorption times [27]. Tan *et al*. [28] studied the adsorption kinetics of individual polyglycol frother solutions as well as a mixture of PPG-192 and PPG-1000 using maximum bubble pressure tensiometry. They reported that in the short time scale i.e. < 10 seconds, the frother

ACCEPTED MANUSCRIPT

mixture had interfacial tension considerably below the interfacial tension of the pure components of PPG 192 and PPG 100 indicating a greater surface elasticity.

Jávor *et al*. [29-32] extensively studied the interfacial behavior of n-pentanol, Nasfroth 240, Dowfroth 200 and 250, and PPG-425. They used maximum bubble pressure tensiometry to determine rapid adsorption (within the first few seconds) at a gas-liquid interface, while the emerging bubble technique allowed them to study the kinetics of frother adsorption at longer timescales. They found that Dowfroth 200 was less surface active than Nasfroth 240, even though they have the same molecular weight. Dowfroth 250 had the highest surface activity of these three frothers and the lowest concentration was required to reach the interfacial tension of 61 $mN \cdot m^{-1}$.

Although the most insight is gained from dynamic measurements some useful information can be found with static measurement. Fong *et al.* [33] investigated the effect of branching of a hydrocarbon chain on the interfacial (and solution) properties of short-chain aliphatic alcohols. They used the du Nouy ring method to determine the static interfacial tension of straight-chain and branched alcohols. They concluded that maximum adsorption densities at the air-solution interface, and the corresponding minimum surface areas per molecule for the C5–C8 straight-chain alcohols, show that at surface saturation the molecules of alcohol are not absolutely close packed.

Recently, Le *et al.* used the Wilhelmy plate technique to study the adsorption of MIBC and cetyl trimethyl ammonium bromide (CTAB) mixtures at the air–water interface. They observed an unusual synergistic behaviour, specifically the interfacial tension of MIBC–CTAB mixtures increased with concentration for a given (intermediate) concentration range. This positive synergism could not be explained by existing theoretical models, and Le *et al*. suggested it was due to the existence of two distinctive molecular arrangements at adsorption zone: one dominated by bulky structure of MIBC, the other dominated by CTAB [34].

3. Interfacial rheology

Depending on the concentration, molecular size, and surface activity of the frother, the interfacial tension decreases at a certain rate and reaches a value where it no longer decreases, i.e. the point where the adsorption/desorption processes of the surfactant has reached thermodynamic equilibrium [35, 36]. With tensiometry, the adsorption kinetics is measured at static or quiescent conditions. This makes it hard to correlate these studies with industrial processes such as flotation, where the conditions are highly dynamic [37]. It is also important to investigate the frother efficiency with the adsorption process at dynamic conditions. Adsorption kinetics of frothers depends on its diffusion coefficient, *D*, and as described in the previous section can be determined using classic tensiometry experiments and fitting Ward-Tordai model [18, 36, 38].

A frother should also provide enough stability to the freshly generated bubbles undergoing various mechanical stresses, which would directly affect the layer adsorbed at the bubble

ACCEPTED MANUSCRIPT

surfaces. Any surface deformation would create gradients in frother concentration at the bubble surface and, as a result, increases the chances of coalescence between deformed bubbles leading to froth instability[39, 40].

To understand the ability of frother molecules to compensate the change in the surface area it is important to characterise the frothers adsorbed at bubble surfaces under periodic compression and expansion cycles. The interfacial dilational rheology is such a technique which allows studying a change in the interfacial tension in response to area changes, by performing harmonic sinusoidal expansion and compression of the surface area [41, 42].

The complex surface dilational modulus, E, is given by $E = \frac{\mathrm{d}\gamma}{d\ ln\ A}$, where d$\gamma$ is the change in interfacial tension with respect to change in relative surface area A. It should be noted that E is also a function of a rate of area change under dynamic conditions [43]. The dilational rheology is performed as harmonic sinusoidal area perturbations and it is expressed as a complex function [44].

$$E = E' + iE'' = E' + i\omega\eta_{dil} \quad (1)$$

E' is the surface dilational elasticity, E'' is the imaginary part of E, which is product of ω and η_{dil}. η_{dil} is the surface dilational viscosity and ω is the radial frequency of oscillations. The E' as described above is a parameter which informs the relative change in interfacial tension in response to the change in the surface area. Whereas η_{dil} is a parameter which provides the information about the relative change in interfacial tension in response to a rate of area change. If E' increases and reaches a constant value over a range of frequencies then it would mean that at lower frequencies the system is able to respond to the area change but at higher frequencies, there is not enough time for molecules to adsorb/desorb to/from the interface. Therefore at higher frequencies, it behaves as an insoluble surfactant layer. The value of elasticity where it reaches a constant value with increasing ω is called limiting elasticity, E_0, and it is given as [35]:

$$E_0 = \frac{d\gamma}{d\ ln\Gamma} \quad (2)$$

Where Γ is the adsorbed amount at the interface in mol/m^2. Based on this, the E' and E'' can be defined as:

$$E' = E_0 \frac{1+\sqrt{\omega_0/\omega}}{1+\frac{2\omega_0}{\omega}+2\sqrt{\omega_0/\omega}} \quad (3)$$

$$E'' = E_0 \frac{\sqrt{\omega_0/\omega}}{1+\frac{2\omega_0}{\omega}+2\sqrt{\omega_0/\omega}} \quad (4)$$

The Equations 3 and 4 give rise to an important parameter ω_0, the characteristic frequency. This parameter is given by: $\omega_0 = \frac{D}{2}(\frac{dc}{d\Gamma})^2$. The parameter d$c$/d$\Gamma$ is obtained by fitting the surfactant adsorption isotherm to Langmuir adsorption model [35].

ACCEPTED MANUSCRIPT

Figure 1 shows the theoretical values of surface dilational elasticity and viscosity normalized to E_0, calculated for three different frothers: tridecyl dimethyl phosphine oxide (TDDMPO), nonanol and Triton-X100 with ω_0 obtained from [45].

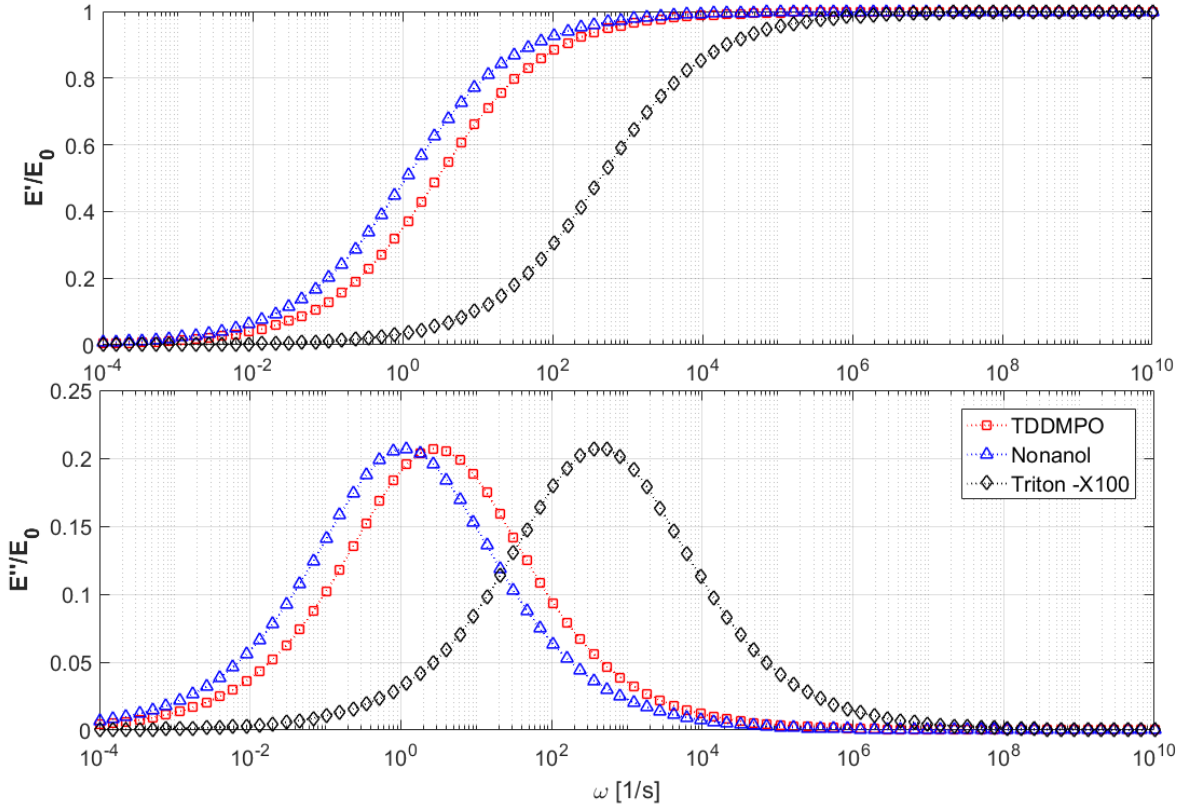


Figure 1. Theoretical (normalized to E_0) dilational elasticity and viscosity values calculated for TDDMPO (red empty squares), nonanol (blue empty triangles) and Triton-X100 (black empty diamonds) for frother bulk concentration of 5×10^{-5} M.

From Figure 1, one can see that with increasing ω, the E' increases until it reaches a constant value, described earlier as the limiting elasticity E_0. In case of E'', the values increase with ω and reach a maximum at its characteristic frequency ω_0 after which it starts to decrease. At higher ω the E' reaches E_0, the E'' reaches zero. This is because E'' relates to change in surface tension in response to 'rate of change of area' while E' relates to change in surface tension in response to change in area. In other words, when the adsorbed surfactant layer behaves as an insoluble one, it is not sensitive to the rate of area change.

Although it is possible to calculate the theoretical values for dilational visco-elasticities over a wide range of frequencies, experimental methods have a narrow range. Each experimental method for dilational rheology, the range of frequencies at which they operate, and a comparison

ACCEPTED MANUSCRIPT

with calculated visco-elasticities of different surfactants, are discussed in detail in an excellent review by Mucic *et al*.[35]

The surface elasticities or viscosities correlation with the foamability or foam stability can be often found in the literature [46-50]. The adsorption isotherms have been systematically studied for homologous series of n-alcohols [51], and from this one could calculate the theoretical elasticities and viscosities as given by Jávor *et al*. [29] Some studies with surface rheology have been done for these systems previously with oscillating bubble tensiometry and the elasticity values corresponded well with the frothability and froth stability [47, 52].

Fainerman *et al*. studied dilational rheology of the Triton-X series surfactants for the frequencies between 5×10^{-3} Hz and 2×10^{-1} Hz [53]. They showed that for low solution concentrations the Tritons with more ethylene oxide groups exhibited higher surface activity while for the concentrations higher than 1×10^{-6} M the Tritons with less ethylene oxide groups were more surfaces active. They attributed this behavior to the peculiar adsorption of the ethylene oxide chain at low surface pressure values and further gradual displacement from the surface layer into the bulk solution [20]. They used their theoretical model [20] together with the theory for the visco-elasticity of oscillating drops and bubbles proposed by Joos [54] to describe the experimental results. While the experimental dependency of the visco-elastic modulus on surfactant concentration at a fixed oscillation frequency showed one maximum for Triton-X45 and Triton-X100 solutions, two maxima appeared for Triton-X165 and Triton-X405. These maxima are caused by the reorientation and compression of the Triton molecules in the surface layer and are predicted by the theoretical model. There was also a good agreement between experiment and theory for the viscoelastic modulus and phase angle for Triton-X45 and Triton-X100 solutions, while an unsatisfactory agreement was observed for the Tritons with more ethylene oxide groups. This discrepancy was attributed to the fact that the Tritons are mixtures of homologues with different oxyethylation degree and thus should be treated as surfactant mixtures.

PPG of different molecular weights has been studied by Diez-Pascual *et al*., for a range of frequencies (1×10^{-3} Hz to 4×10^{2} Hz), using a combination of the oscillating drop, oscillating barrier, and electrocapillary wave experiments [55]. The dynamic elasticity of both spread and adsorbed layers were dependent on surface pressure and showed a small change in the frequency. They concluded that the frequency dependence of the elasticity was well described by the Lucassen-van den Tempel model [55]. In order to probe the effect of the block structure on the property of the branched block polyethers synthesized with tetraethylenepentamine (TEPA), Gong *et al*. studied the equilibrium and dynamic interfacial tension, as well as surface dilational viscoelasticity [56]. They observed that the surface dilational modulus was dependent on the concentration of polyether, with its maximum at different concentrations for different surfactants. They concluded that the structure has an important role on the dilational viscoelasticity of the branched block polyethers.

ACCEPTED MANUSCRIPT

An alternative approach to evaluate mechanical properties of the gas-liquid interface when surface molecules interact to form an elastic interfacial network was proposed by Ferri and collaborators [57-59]. In this axisymmetric drop shape analysis (ADSA) they treated the surface of pendant drop with adsorbed polymer molecules as an interface having an isotropic thermodynamic interfacial tension, γ, and elastic membrane tensions, T_1 and T_2, in the two surface directions. In the absence of deformation $T_1=T_2$ and the Young–Laplace equation describes the shape of such droplet. When the droplet is deformed (for example due to hydrostatic pressure) and this deformation gets more significant the surface stresses or tensions develop in response to stretching. A liquid-liquid interface is incapable of supporting an anisotropic distribution of stress, and hence will display small, but systematic deviations from the Young–Laplace equation prediction. During inflation (i.e. increasing the droplet volume), the sum of this deviation increases. Using the ADSA approach Ferri *et al.* were able to get the surface and bulk moduli values for thin (thickness less than 20 nm) polymeric films at gas-liquid interface [58, 59].

4. Bubble Terminal Rise Velocity

Bubble velocity in an unbounded liquid phase depends mainly on its size [60-64] liquid viscosity [65], density difference between liquid and gas phases (as it determines the magnitude of the buoyancy force) and the state of adsorption layer at the bubble surface [66-71]. Like any other physical object moving in a viscous medium, the rising bubble reaches its terminal velocity when the balance between viscous drag and lift (buoyancy) forces is established (under so-called steady-state conditions). In pure water, where the bubble surface is fully mobile (no adsorption layer), the time required to reach the steady-state conditions depends mainly on the bubble size. This is usually a very fast process, occurring just after a bubble formation, i.e. within milliseconds [72, 73], even for relatively large, i.e. mm size, bubbles, such as those encountered in flotation process [66]. In surfactant solutions, however, the time-scale of this phenomenon can be different because it depends on the kinetics of formation of the so-called dynamic adsorption layer (DAL) [66, 68, 74]. The formation of DAL, i.e. uneven distribution of surfactant molecules at the bubble surface, affects the fluidity of the gas-liquid interface, which leads to lowering the bubble rise velocity [66, 69, 75, 76]. During bubble motion, the top part of the bubble surface is depleted in surfactant molecules, while excessive accumulation of the surfactant occurs at the bottom part of the bubble. Such uneven surfactant distribution at the bubble surface leads to the formation of interfacial tension gradients and a tangential ‘Marangoni’ stress opposing the flow shear stress [66]. Depending on the degree of adsorption coverage with surfactant molecules, the bubble surface can be partially or completely immobilized, i.e. the hydrodynamic boundary conditions can be gradually shifted from full slip (for fully mobile surfactant free surface) to partial slip, to no slip [17, 68, 77]. The degree of bubble surface immobilization directly impacts the value of its terminal velocity.

ACCEPTED MANUSCRIPT

Existing experimental approaches do not allow for the direct observation of the DAL formation at a rising bubble surface. There is lack of experimental techniques to probe the bubble surface directly, hence a quantitative correlation between dynamic surface phenomena, properties of the adsorbed layers and the shape and velocity of the rising bubble cannot be established [75]. Different stage of the DAL development can be evaluated and followed only indirectly, using experimental as well as numerical approaches. In the experimental approach, an indirect evaluation of the DAL formation kinetics is usually achieved by analysis of dynamics of bubble motion, i.e. its shape and local velocity variations [69, 73, 74]. Recently a new experimental method for tracking the DAL formation, called bubble in a flow field, was proposed by Lotfi *et al*. [75] Influence of a liquid flow over surface of an air bubble fixed at the capillary tip on dynamic interfacial tension was determined using a capillary pressure tensiometer to reproduce the situation of bubble rising in surfactant solutions. The experiments were aimed at direct and quantitative determination of interfacial tension changes related to the DAL development. Unfortunately, no straightforward evidence for the DAL formation was found, most probably because the redistribution of adsorbed surfactant molecules does not seem significant or does not lead to a measurable pressure change, as it was concluded by the authors. If so, it seems that the value of the interfacial tension decrease, leading to the (partial) immobilization of a moving bubble interface is very small and unmeasurable with classical tensiometry methods. The presented results demonstrated also that monitoring the shape and velocity changes of a rising bubble is presently the most feasible experimental approach for indirect evaluation of the kinetics of DAL development as well as its structure [78]. Recently, Kosior and Zawala presented an interesting approach, in which they explored the effect of the initial degree of adsorption coverage at the surface of motionless bubble in surfactant solutions on the DAL formation and the kinetics of terminal velocity establishment [68]. They used a custom-made device (a so-called bubble trap) synchronized with a single bubble generator developed in their earlier studies [79]. This bubble-on-demand generator allows the precise control of the adsorption time of surfactant molecules at the bubble surface. The process of DAL formation was then tracked by monitoring the variations of the bubble local velocity (Figure 2A) and deformation (χ, i.e. the ratio between bubble horizontal and vertical axis – Figure 2B) in the solutions of n-octanol, CTAB, and Tween 80. For all surfactants, the higher the initial adsorption coverage, the faster was the establishment of steady-state conditions. Moreover, they saw that, despite the different initial adsorption coverage, once the DAL was established at the bubble surface, the bubble terminal velocity was practically identical. These findings indicate that the DAL development is associated not only with the characteristic redistribution of surfactant molecules but also with the initial adsorption kinetics, causing increase in the adsorption coverage, up to the limiting value for the steady-state conditions.

ACCEPTED MANUSCRIPT

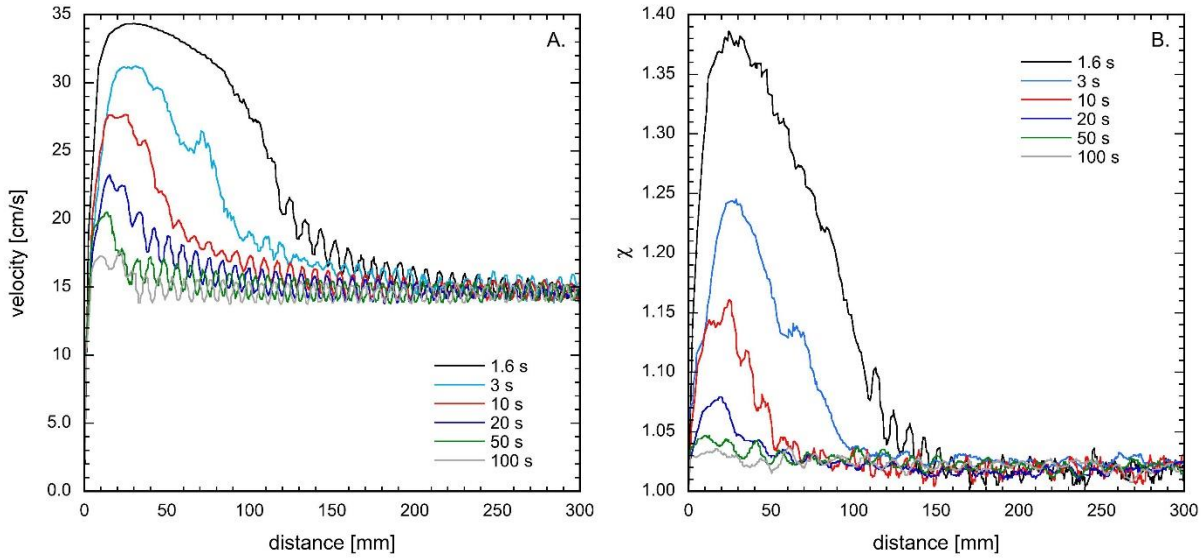


Figure 2. Experimentally measured variations of (A) bubble local velocities and (B) bubble deformation ratio (χ) as a function of distance from the bubble formation point in the solution of Tween80 of concentration 1×10^{-6} M and six different adsorption times as reported by Kosior and Zawala [68]. Reproduced with permission from the Royal Society of Chemistry.

In addition to experimental studies, numerous theoretical approaches regarding various aspects of the influence of surfactants on the bubble motion as well as the formation and properties of the DAL have been developed by Dukhin *et al*. [66] Present theories addressed only steady DAL, without the possibility of calculations of whole bubble velocity profile, i.e. its transition from zero in the moment of its detachment until it reaches the terminal velocity. The newest insight into the influence of surfactants on the bubble motion based on Direct Numerical Simulation was presented by Pesci *et al*. [80] Their developed numerical procedure allows one to reproduce quite accurately not only bubble rising velocity variations in surfactant solution over first few tens of centimeters but also bubble path instabilities and its terminal velocity, the time-scale required to establish a steady-state conditions and even visualizes an uneven distribution of surfactant molecules at the gas-liquid interface.

In papers from the group of Finch at McGill University in Canada the single bubble rise technique has been used to study effect of flotation frothers on the bubble shape, path of bubble rise and the velocity profiles [67, 81-88]. They concluded that the type of frother had a profound effect on the bubble velocity and shape variation. The oscillation in velocity of rising bubble matched bubble shape oscillation and the lowest velocity was reached for the most spherical bubbles. Dowfroth 250 and polyglycol F-150 had a strong effect on preserving a spherical shape of a bubble and, as the result, the bubbles rising in the solutions of these frothers had the lowest velocities. Bubbles in the solutions of MIBC and n-pentanol were less spherical and consequently their rise velocity was higher [81]. Furthermore, they significantly extended their analysis showing that the reduction of bubble rise (terminal) velocity, extracted from single bubble rise experiments, is a useful tool to quantify the performance of flotation frothers [89].

ACCEPTED MANUSCRIPT

Building upon the concept of critical coalescence concentration, CCC [90], they introduced the concentration at minimum velocity (CMV) parameter [67]. They determined the CMV for a range of frother structures, primarily from the two frother families: alcohols and diols of different carbon chain length and the position of the -OH group. They further extended their studies to include PPG (propylene, dipropylene and tripropylene) and PEG (ethylene, dietrylene and triethylene) glycols family [67, 89, 91]. They demonstrated that CMV decreased for alcohol and polyglycols as alkyl chain length increased, and for polyglycols as the number of propylene oxide and ethylene oxide groups was increased. In addition, the significant impact of the relative position of the -OH and $–CH_3$ groups in branched-alcohols was revealed [86, 89] and is schematically shown in Figure 3. Longer chain alcohols with the -OH group at the terminus and further away from the $–CH_3$ group were found to give the lowest CMV. Tan and Finch suggested this low rise velocity correlates with the structure of DAL, specifically high surfactant packing at the rear pole of the rising bubble and its effect on the interfacial tension gradients and H-bonding [86]. They also suggested, based on the lowest CMV, that 4-methyl-1-pentanol would be a superior frother to MIBC. They also found an excellent correlation between CMV and CCC for various frother families.

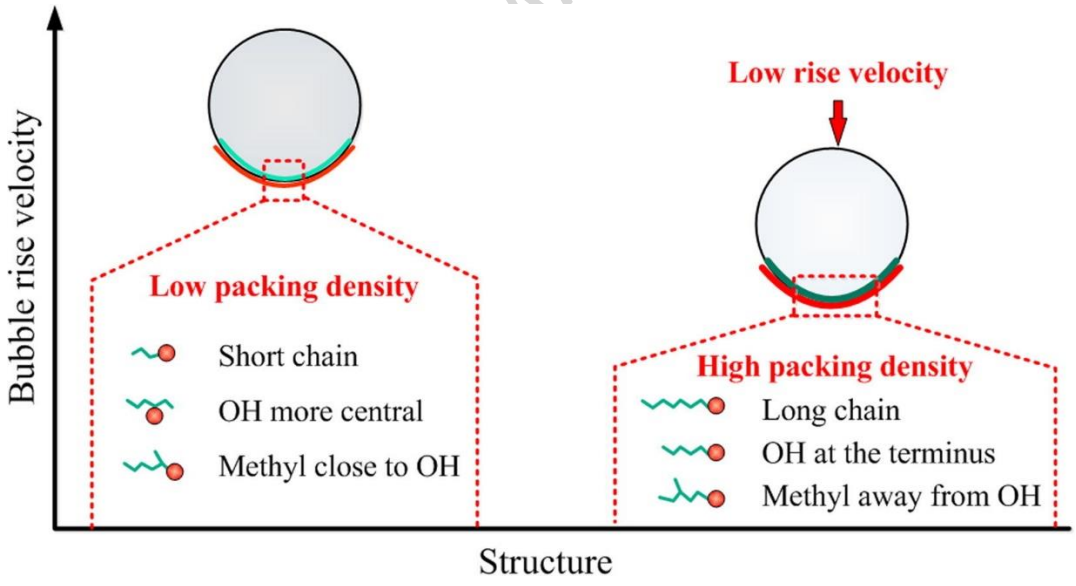


Figure 3. Schematic correlation between alcohol molecular structure, the structure of the DAL, and the bubble rise velocity as suggested by Tan and Finch [86]. Reproduced with permission from Elsevier.

The values of CMV for wide range of flotation frother were collected and analysed by Kowalczuk *et al*. [72]. They used experimental data of the terminal velocity of the bubble rising in various surfactant solutions determined by the research groups of Malysa at Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Poland and Finch at

ACCEPTED MANUSCRIPT

McGill University in Canada. By introducing the normalized bubble velocity and normalized CMV the empirical equation determining the bubble terminal velocity, *u*, *vs* frother concentration, *c*, as well as CMV value, was derived:

$$u = u_{min}(u_{max} - u_{min}) \cdot e^{-3(\frac{c}{CMV})^2} \quad (5)$$

where u_{min} is the bubble minimum terminal velocity for fully mobile bubble surface with slip hydrodynamic boundary condition at gas-liquid interface; u_{max} is the bubble maximum terminal velocity for fully immobilized bubble surface with no slip hydrodynamic boundary condition at gas-liquid interface. They showed that Equation 5 can accurately determine the CMV values for many different frother families (straight and branched alkyl chain aliphatic alcohols, 1,ω-diols, poly(propylene glycol) and poly(ethylene glycol) alkyl ethers, and many commercial frothers. An excellent agreement was observed between calculated and experimentally obtained CMV values. By using u_{min} and u_{max} as input parameters, this empirical approach can predict the terminal bubble velocity – frother concentration curve, as well as the values of CMV.

5. Vibrational Spectroscopy of the Gas-Liquid Interface

The two main techniques of vibrational spectroscopy that are applicable to studies of the gas-liquid interface are (i) external reflectance infrared (IR) spectroscopy [92], and (ii) vibrational sum frequency spectroscopy (VSFS) [93, 94]. Both techniques are heavily used in interfacial science and applied to a number of different interface types (solid-air for external reflectance IR; solid-air, solid-liquid, and liquid-liquid for VSFS). The techniques are very different from straightforward transmission IR and make use of the optical processes that occur when one reflects light off an interface, and the ability to control both light polarisation and incident angle.

For external reflectance IR, the presence of an adsorbed surfactant film at an interface causes an alteration in the reflectance of the IR beam specifically at energies that correspond to the molecular vibrations of the layer. The absorbance of particular wavelengths of light alters the optical parameters of the layer, which in turn alters the reflectance of light of that wavelength. This altered reflectivity is also a sensitive function of the polarisation of the incoming light and the angle of incidence, a feature of the technique that allows orientation information to be gleaned from spectra recorded with varying polarisation/incident angle [92].

VSFS is a much more complicated technique for obtaining a spectrum of an interfacial film. It makes use of the non-linear optical process of sum-frequency generation (SFG), whereby the interaction of two wavelengths of light within a non-centrosymmetric medium can result in the combination of those wavelengths to produce light with the sum of the two original light frequencies. An interface with an oriented layer of molecules is a non-centrosymmetric system and is able to give rise to SFG [95]. The magnitude of the SFG response is enhanced significantly when one or both incident wavelengths are resonant with a molecular energetic

ACCEPTED MANUSCRIPT

transition (either vibrational or electronic), with the result that if IR light is chosen, enhanced SFG is expected when the IR energy matches that of a particular vibration. Spectra are then obtained by either using a broadband (femtosecond) laser source of IR light, and collecting all sum frequency (SF) light and dispersing on a position sensitive detector like a charge-coupled device, or by using a narrowband (pico- or nano-second) laser source of IR, and scanning the energy of the IR beam while monitoring the intensity of the SF light.

As with external reflectance IR, the degree to which a signal can be detected with VSFS varies with the polarisations of the different light beams (incident IR, incident visible, and SFG visible), and the angles of incidence/generation of the light. Through careful modelling of SF intensities, it is possible to extract information of molecular orientation [96]. It is also straightforward to get a proxy measure of conformational order in surfactant systems by detecting the relative intensities of $-CH_2$ to $-CH_3$ vibrations of alkyl chains ($-CH_2$ groups have local centrosymmetry in an ordered all-trans configuration, i.e. when the alkyl chain is fully extended, and therefore gives no SF signal).

Curiously, it is the more complicated of these two techniques that has seen the most application in gas-liquid interface studies of relevance to flotation research. In an interesting study published by Wang *et al*, VSFS was used to study the water structure immediately adjacent to a wetting film between an air bubble and a silica surface, indicating the presence of ordered water in the stable film at the silica surface [97]. In a paper from the group of Nguyen at the University of Queensland, VSFS was used to study a complex system of two co-adsorbing surfactants at the air-water interface, with spectral information highlighting a potential synergistic effect in the observed structuring of surfactant hydrocarbon chains at the interface [98]. As many flotation systems contain surfactants used as frothers and different surfactants used as collectors, the potential for synergistic interactions needs to be considered when investigating the properties of the air-water interface.

In work of more direct relevance to flotation (in that the surfactant studied is an actual flotation frother) the same group published VSFS data that was used to analyse the presence and structure/orientation of MIBC, one of the most commonly used frothers in mineral processing, at an air-water interface [99-101]. In the first of these papers [99], the focus was on the fundamental science of adsorption of MIBC to the gas-liquid interface and, based on the obtained data, the authors were able to determine a tilt angle of the MIBC molecules of approx. 40° for the C-O bond of the molecule relative to the surface normal (this was also determined in one of the later papers, using more complex analysis of the SF intensities [100]). Furthermore, in combination with Wilhelmy plate interfacial tension measurements, the spectral evidence relating to measurements performed beyond the solution concentration yielding saturation coverage indicate that there could be continued association of MIBC molecules at the interface immediately below the initial monolayer. These molecules were not components of an ordered bilayer, as no diminishment of sum frequency intensity was observed (which occurs when surfactants form bilayers at interfaces, due to the formation of a plane of inversion symmetry).

ACCEPTED MANUSCRIPT

In later work, the authors extended this investigation of extended interfacial layers (initial monolayer and associated underlayer) to two short-chain alcohols (1-hexanol and 1-pentanol; commonly studied as frother molecules) [101]. The VSFS data was critical in identifying the attainment of initial monolayer saturation coverage in all three cases, which when combined with interfacial tension, interfacial rheology, and thin film balance measurements, indicated clearly that such simple surfactants (which do not display a CMC) form a saturated monolayer and then an underlayer that contributes to further lowering of interfacial tension (see Figure 4). The associated measurements using more traditional probing of gas-liquid interfacial properties highlighted the effect of this underlayer on foam stability.

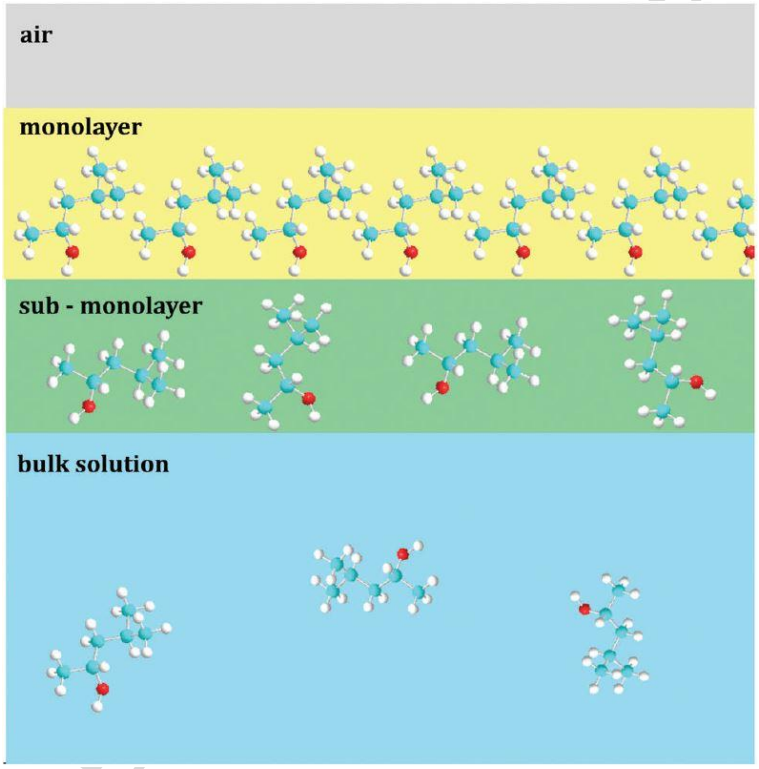


Figure 4. Schematic diagram of the proposed MIBC interfacial structure (monolayer and underlying associated adsorption layer, postulated based on combined analysis of an air-water interface, involving interfacial tension determination and sum frequency spectroscopy, as reported by Shahir *et al*. [99] Reproduced with permission from the Royal Society of Chemistry.

Although there is a distinct lack of external reflectance IR studies on flotation frothers, there does exist in the literature some exceptionally relevant investigations of dynamic gas-liquid interfaces. The majority of interfacial vibrational spectroscopy of the gas-liquid interface is performed for adsorbed layers at equilibrium. This is far from the real system in flotation, where bubbles have residence times in the seconds/minutes time regime within flotation cells, and the adsorption layer of surfactants varies in composition at different sections of the bubble [78]. However, there is one methodology for reflectance FTIR that allows one to access the gas-liquid

ACCEPTED MANUSCRIPT

interface as a function of interface age: the overflowing cylinder [102, 103]. This methodology has been adapted by the group of Colin Bain to study surfactant adsorption at the gas-liquid interface using external reflectance infrared [104-107]. To date, there have been no investigations on common frother molecules, but the applicability is clear. The overflowing cylinder allows one to interrogate adsorption timescales of 0.1 to 1 s, which is of significant relevance for bubble formation and bubble rise in flotation cells.

The paucity of investigations in the flotation area may be due to the inherent complexity in both acquisition and analysis of the data obtained from such experiments. However, the need for unambiguous chemical composition and structure information for surfactant layers in flotation research is clear, and it is likely that more work will be done in this area in the future. Flotation involves multiple reagents and often with competing or complementary interactions at the gas-liquid and solid-liquid interfaces. Determining the identity of surfactant species present at the gas-liquid interface will help significantly in connecting reagent characteristics with flotation outcomes and understanding/identifying potentially deleterious effects. Mixed surfactant systems can be characterised using other methodologies and information inferred/determined relating to the composition of the adsorbed layer (such as dynamic interfacial tension measurements), but vibrational spectroscopy has significant potential to give relatively clear information on layer composition.

Another area where vibrational spectroscopy may have a significant role to play in studying flotation frother interfacial layers is in the area of bubble-mineral interactions and particle attachment. The interactions between two bubbles in flotation rarely occurs with bubbles unladen with particles, and therefore the link between frother structure and orientation and bubble-bubble interactions is less important than that between bubbles and particles/solid surfaces. An appreciation of composition and structure may well prove insightful when one considers the initial interaction forces, wetting film rupture, and initial spreading (dewetting) of a bubble against a mineral particle. As mentioned above, there has been some work in this area from the group of Jan Miller, using VSFS to characterise the interface between a bubble and a solid surface [97], but this work was not done in the presence of frothers or collectors in solution.

6. Future Perspective

It is clear that there is wealth of data being generated on the influence of frothers on the properties of the air-water, with new insights being revealed using techniques that probe the dynamic aspects of adsorption and bubble characteristics. It is also encouraging that data is beginning to be generated for systems that include the presence of not one but two types of flotation reagents (e.g. frothers and depressants). In many instances, molecules like depressants (often large organic polymers) do not associate with the neat air-water interface, but the possibility is there for co-adsorption when a frother has already populated the interface. The implications of this co-adsorption on bubble properties and air-water interface characteristics

ACCEPTED MANUSCRIPT

(including interfacial layer composition) can be determined using the techniques reviewed above. The next step would be to the correlate this information with flotation outcomes, a necessary step in relating this fundamental colloid and interface science with the targeted industry application. Only when the link through to process outcomes is established can one rationally determine reagent choice, or indeed consider design/synthesis of new reagents.

Another critical step that needs to be made in regards to the air-water interface, frothers, and flotation is the move to study the attachment and spreading of bubbles onto solid surfaces with frothers present in the system. Although the properties of individual bubbles is important in the study of the air-water interface in flotation, the natural next step to consider foams and foam stability (as one would do in some other areas of science) is not as useful as it may appear. Flotation involves the formation of froths – particle laden foams, with the particles attached to the air-water interface. Traditional measures of foam stability, and the connection to the properties of layers of surfactants, are of interest in flotation, but ultimately represent a slight departure from the real system. However, there is much that can be (and should be) learned about the influence of frother adsorbed layers on bubble-particle attachment. The question of how frother choice affects the bubble-particle collision process, thin film drainage and rupture, and dewetting of a mineral particle has yet to be answered to any satisfactory extent. All of the abovementioned techniques have a central role to play in such investigations, as they provide the detailed information of the properties of the interface prior to collision. As with multiple reagent investigations, considering the influence of frother choice (i.e. determining interfacial tension, the properties of the DAL, and interfacial elasticity) on particle collection efficiencies will be valuable in optimizing flotation outcomes.

Lastly, it is appropriate to highlight a move toward interfacial tension measurements in non-traditional devices. Microfluidic devices are currently under investigation for interfacial tension measurements of liquid-liquid interfaces [108]. The use of such devices in the study of air-water interfacial tension is likely to proceed in the coming years, but to become useful in studies of frothers, these devices will need to be able to function at low surfactant concentrations and with high sensitivity for small changes in interfacial tension.

References

[1] Wills BA, Napier-Munn T. Chapter 12: Froth Flotation. Wills' mineral processing technology: an introduction to the practical aspects of ore treatment and mineral recovery. 8th ed. London: Elsevier; 2016.
[2] Krasowska M, Zawala J, Bradshaw-Hajek BH, Ferri JK, Beattie DA. Interfacial characterisation for flotation: 1. Solid-liquid interface. Current Opinion in Colloid & Interface Science. 2018;37:61-73.
[3] Bulatovic SM. Handbook of flotation reagents: chemistry, theory and practice. 1st ed. Boston: Elsevier; 2007.
[4] Cho YS, Laskowski JS. Effect of flotation frothers on bubble size and foam stability. International Journal of Mineral Processing. 2002;64:69-80.

ACCEPTED MANUSCRIPT

[5] Finch JA, Nesset JE, Acuña C. Role of frother on bubble production and behaviour in flotation. Minerals Engineering. 2008;21:949-57.
[6] Grau RA, Laskowski JS, Heiskanen K. Effect of frothers on bubble size. International Journal of Mineral Processing. 2005;76:225-33.
[7] Subrahmanyam TV, Forssberg E. Froth stability, particle entrainment and drainage in flotation - A review. International Journal of Mineral Processing. 1988;23:33-53.
[8] Corona-Arroyo MA, López-Valdivieso A, Laskowski JS, Encinas-Oropesa A. Effect of frothers and dodecylamine on bubble size and gas holdup in a downflow column. Minerals Engineering. 2015;81:109-15.
[9] Nguyen CV, Phan CM, Ang HM, Nakahara H, Shibata O, Moroi Y. Molecular dynamics investigation on adsorption layer of alcohols at the air/brine interface. Langmuir. 2015;31:50-6.
[10] Dey S, Pani S, Singh R. Study of interactions of frother blends and its effect on coal flotation. Powder Technology. 2014;260:78-83.
[11] Zholob SA, Makievski AV, Miller R, Fainerman VB. Optimisation of calculation methods for determination of surface tensions by drop profile analysis tensiometry. Advances in Colloid and Interface Science. 2007;134-135:322-9.
[12] Zholob S, Makievski A, Miller R, Fainerman V. Optimisation of calculation methods for determination of surface tensions by drop profile analysis tensiometry. Advances in colloid and interface science. 2007;134:322-9.
[13] Kairaliyeva T, Mucic N, Spasojevic L, Bucko S, Katona J, Aksenenko E, et al. Surface Tension Measurements with the Drop Profile Analysis Tensiometry—Consideration of the Surfactant Mass Balance in a Single Drop. Colloids and Interfaces. 2017;1:1.
[14] Berry JD, Neeson MJ, Dagastine RR, Chan DYC, Tabor RF. Measurement of surface and interfacial tension using pendant drop tensiometry. Journal of Colloid and Interface Science. 2015;454:226-37.
[15] Qu X, Wang L, Karakashev SI, Nguyen AV. Anomalous thickness variation of the foam films stabilized by weak non-ionic surfactants. Journal of Colloid and Interface Science. 2009;337:538-47.
[16] Park H, Wang J, Wang L. A comparative study of methyl cyclohexanemethanol and methyl isobutyl carbinol as frother for coal flotation. International Journal of Mineral Processing. 2016;155:32-44.
[17] Harvey PA, Nguyen AV, Jameson GJ, Evans GM. Influence of sodium dodecyl sulphate and Dowfroth frothers on froth stability. Minerals Engineering. 2005;18:311-5.
[18] Phan CM, Nguyen AV, Evans GM. Dynamic adsorption of sodium dodecylbenzene sulphonate and dowfroth 250 onto the air–water interface. Minerals Engineering. 2005;18:599-603.
[19] Schreithofer N, Wiese J, McFadzean B, Harris P, Heiskanen K, O'Connor C. Frother-depressant interactions in two and three phase systems. International Journal of Mineral Processing. 2011;100:33-40.
[20] Fainerman VB, Lylyk SV, Aksenenko EV, Makievski AV, Petkov JT, Yorke J, et al. Adsorption layer characteristics of Triton surfactants: 1. Surface tension and adsorption isotherms. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2009;334:1-7.
[21] Nguyen AV, Phan CM, Evans GM. Effect of the bubble size on the dynamic adsorption of frothers and collectors in flotation. International Journal of Mineral Processing. 2006;79:18-26.
[22] Phan CM. Dynamic adsorption of octanols at air/water interface. The Canadian Journal of Chemical Engineering. 2010;88:688-92.
[23] Ozdemir O, Karakashev SI, Nguyen AV, Miller JD. Adsorption and surface tension analysis of concentrated alkali halide brine solutions. Minerals Engineering. 2009;22:263-71.
[24] Bournival G, Muin SR, Lambert N, Ata S. Characterisation of frother properties in coal preparation process water. Minerals Engineering. 2017;110:47-56.
[25] Bournival G, Ata S, Karakashev SI, Jameson GJ. An investigation of bubble coalescence and post-rupture oscillation in non-ionic surfactant solutions using high-speed cinematography. Journal of Colloid and Interface Science. 2014;414:50-8.
[26] Benedetto FE, Zolotucho H, Prado MO. Critical Assessment of the Surface Tension determined by the Maximum Pressure Bubble Method. Materials Research. 2015;18:9-14.

ACCEPTED MANUSCRIPT

[27] Ritacco H, Langevin D, Diamant H, Andelman D. Dynamic Surface Tension of Aqueous Solutions of Ionic Surfactants: Role of Electrostatics. Langmuir. 2011;27:1009-14.
[28] Tan SN, Pugh RJ, Fornasiero D, Sedev R, Ralston J. Foaming of polypropylene glycols and glycol/MIBC mixtures. Minerals Engineering. 2005;18:179-88.
[29] Jávor Z, Schreithofer N, Heiskanen K. Multi-scale analysis of the effect of surfactants on bubble properties. Minerals Engineering. 2016;99:170-8.
[30] Jávor Z, Schreithofer N, Heiskanen K. Micro- and nano-scale phenomena effect on bubble size in mechanical flotation cell. Minerals Engineering. 2015;70:109-18.
[31] Jávor Z, Schreithofer N, Heiskanen K. The effect of bubble release techniques on their behaviour at the initial stages of rise. Minerals Engineering. 2012;36-38:254-61.
[32] Jávor Z, Schreithofer N, Heiskanen K. Fast adsorption phenomena at air/liquid interfaces. XXV International Mineral Processing Congress, Brisbane2010. p. 2015-23.
[33] Fong C, Greaves TL, Healy TW, Drummond CJ. The effect of structural modifications on the solution and interfacial properties of straight and branched aliphatic alcohols: The role of hydrophobic effects. Journal of Colloid and Interface Science. 2015;449:364-72.
[34] Le TN, Phan CM, Nguyen AV, Ang HM. An unusual synergistic adsorption of MIBC and CTAB mixtures at the air–water interface. Minerals Engineering. 2012;39:255-61.
[35] Mucic N, Javadi A, Kovalchuk N, Aksenenko E, Miller R. Dynamics of interfacial layers—experimental feasibilities of adsorption kinetics and dilational rheology. Advances in colloid and interface science. 2011;168:167-78.
[36] Dukhin SS, Kretzschmar G, Miller R. Dynamics of adsorption at liquid interfaces: theory, experiment, application: Elsevier; 1995.
[37] Malysa K, Lunkenheimer K. Foams under dynamic conditions. Current Opinion in Colloid & Interface Science. 2008;13:150-62.
[38] Ward A, Tordai L. Time-dependence of boundary tensions of solutions I. The role of diffusion in time-effects. The Journal of Chemical Physics. 1946;14:453-61.
[39] Yeo LY, Matar OK, de Ortiz ESP, Hewitt GF. Film drainage between two surfactant-coated drops colliding at constant approach velocity. Journal of colloid and interface science. 2003;257:93-107.
[40] Chan DY, Klaseboer E, Manica R. Film drainage and coalescence between deformable drops and bubbles. Soft Matter. 2011;7:2235-64.
[41] Ravera F, Loglio G, Kovalchuk VI. Interfacial dilational rheology by oscillating bubble/drop methods. Current Opinion in Colloid & Interface Science. 2010;15:217-28.
[42] Miller R, Ferri JK, Javadi A, Krägel J, Mucic N, Wüstneck R. Rheology of interfacial layers. Colloid and Polymer Science. 2010;288:937-50.
[43] Tempel Mvd, Lucassen J, Lucassen-Reynders E. Application of surface thermodynamics to Gibbs elasticity. The Journal of Physical Chemistry. 1965;69:1798-804.
[44] Lucassen-Reynders E, Cagna A, Lucassen J. Gibbs elasticity, surface dilational modulus and diffusional relaxation in nonionic surfactant monolayers. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2001;186:63-72.
[45] Wantke K-D, Fruhner H, Fang J, Lunkenheimer K. Measurements of the surface elasticity in medium frequency range using the oscillating bubble method. Journal of colloid and interface science. 1998;208:34-48.
[46] Koelsch P, Motschmann H. Relating foam lamella stability and surface dilational rheology. Langmuir. 2005;21:6265-9.
[47] Malysa K, Lunkenheimer K, Miller R, Hartenstein C. Surface elasticity and frothability of n-octanol and n-octanoic acid solutions. Colloids and Surfaces. 1981;3:329-38.
[48] Małysa K, Miller R, Lunkenheimer K. Relationship between foam stability and surface elasticity forces: Fatty acid solutions. Colloids and Surfaces. 1991;53:47-62.
[49] Wang L, Yoon R-H. Effects of surface forces and film elasticity on foam stability. International Journal of Mineral Processing. 2008;85:101-10.

ACCEPTED MANUSCRIPT

[50] Georgieva D, Cagna A, Langevin D. Link between surface elasticity and foam stability. Soft Matter. 2009;5:2063-71.
[51] Wüstneck R, Miller R. The adsorption behavior of solutions containing sodium dodecyl sulfate and different n-alkanols. Colloids and Surfaces. 1990;47:15-21.
[52] Małysa K, Lunkenheimer K, Miller R, Hempt C. Surface elasticity and dynamic stability of wet foams. Colloids and surfaces. 1985;16:9-20.
[53] Fainerman V, Aksenenko E, Lylyk S, Makievski A, Ravera F, Petkov J, et al. Adsorption layer characteristics of Tritons surfactants: 3. Dilational visco-elasticity. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2009;334:16-21.
[54] Joos P. Dynamic surface phenomena: VSP; 1999.
*[55] Díez-Pascual AM, Monroy F, Ortega F, Rubio RG, Miller R, Noskov BA. Adsorption of water-soluble polymers with surfactant character. Dilational viscoelasticity. Langmuir. 2007;23:3802-8.
Dilational surface viscoelastic properties of adsorbed and spread polymeric surfactants at the air-water interface studied for broad frequency range (and by different techniques). Surface pressure values prove the dynamic equivalence of adsorbed and spread surfactant layers.
[56] Gong H, Xu G, Ding H, Shi X, Tan Y. Aggregation behavior of block polyethers with branched structure at air/water surface. European Polymer Journal. 2009;45:2540-8.
*[57] Ferri J, Fernandes P. Axisymmetric Drop Shape Analysis with Anisotropic Interfacial Stresses: Deviations from the Young-Laplace Equation. Bubble and Drop Interfaces: Brill; 2011. p. 61-74.
A new approach to evaluate mechanical properties of the gas-liquid interface when surface molecules interact to form an elastic interfacial network based on axisymmetric drop shape analysis.
[58] Ferri JK, Fernandes PA, McRuiz JT, Gambinossi F. Elastic nanomembrane metrology at fluid–fluid interfaces using axisymmetric drop shape analysis with anisotropic surface tensions: deviations from Young–Laplace equation. Soft Matter. 2012;8:10352-9.
[59] Cramer AD, Dong W-F, Benbow NL, Webber JL, Krasowska M, Beattie DA, et al. The influence of polyanion molecular weight on polyelectrolyte multilayers at surfaces: elasticity and susceptibility to saloplasticity of strongly dissociated synthetic polymers at fluid–fluid interfaces. Physical Chemistry Chemical Physics. 2017;19:23781-9.
*[60] Klaseboer E, Manica R, Hendrix MH, Ohl C-D, Chan DY. A force balance model for the motion, impact, and bounce of bubbles. Physics of Fluids. 2014;26:092101.
Development of a theoretical force balance model predicting the terminal velocity of bubble (in sub-millimeter size range) rising in water under buoyancy.
[61] Legendre D, Zenit R, Velez-Cordero JR. On the deformation of gas bubbles in liquids. Physics of Fluids. 2012;24:043303.
[62] Manica R, Klaseboer E, Chan DY. The hydrodynamics of bubble rise and impact with solid surfaces. Advances in colloid and interface science. 2016;235:214-32.
[63] Tripathi MK, Sahu KC, Govindarajan R. Dynamics of an initially spherical bubble rising in quiescent liquid. Nature communications. 2015;6:6268.
[64] Jiang L, Krasowska M, Fornasiero D, Koh P, Ralston J. Electrostatic attraction between a hydrophilic solid and a bubble. Physical Chemistry Chemical Physics. 2010;12:14527-33.
[65] Premlata A, Tripathi MK, Sahu KC. Dynamics of rising bubble inside a viscosity-stratified medium. Physics of Fluids. 2015;27:072105.
*[66] Dukhin S, Kovalchuk V, Gochev G, Lotfi M, Krzan M, Malysa K, et al. Dynamics of Rear Stagnant Cap formation at the surface of spherical bubbles rising in surfactant solutions at large Reynolds numbers under conditions of small Marangoni number and slow sorption kinetics. Advances in colloid and interface science. 2015;222:260-74.
The analysis of local velocity profile of rising bubbles using an analytical theory for a quasi-steady growth of rear stagnant cap.
[67] Dukhin S, Lotfi M, Kovalchuk V, Bastani D, Miller R. Dynamics of rear stagnant cap formation at the surface of rising bubbles in surfactant solutions at large Reynolds and Marangoni numbers and for

ACCEPTED MANUSCRIPT

slow sorption kinetics. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2016;492:127-37.
*[68] Kosior D, Zawala J. Initial degree of detaching bubble adsorption coverage and the kinetics of dynamic adsorption layer formation. Physical Chemistry Chemical Physics. 2018;20:2403-12
The study of the effect of the initial surface coverage at the bubble surface on profiles of its rising velocities and shape variations.
[69] Ulaganathan V, Gochev G, Gehin-Delval C, Leser M, Gunes D, Miller R. Effect of pH and electrolyte concentration on rising air bubbles in β-lactoglobulin solutions. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2016;505:165-70.
[70] Wang S, Guo T, Dabiri S, Vlachos PP, Ardekani AM. Effect of surfactant on bubble collisions on a free surface. Physical Review Fluids. 2017;2:043601.
[71] Krasowska M, Kolasinska M, Warszynski P, Malysa K. Influence of polyelectrolyte layers deposited on mica surface on wetting film stability and bubble attachment. Journal of Physical Chemistry C. 2007;111:5743-9.
[72] Kowalczuk PB, Zawala J, Drzymala J. Concentration at the Minimum Bubble Velocity (CMV) for Various Types of Flotation Frothers. Minerals. 2017;7:118.
[73] Tan Y, Rafiei A, Elmahdy A, Finch J. Bubble size, gas holdup and bubble velocity profile of some alcohols and commercial frothers. International Journal of Mineral Processing. 2013;119:1-5.
[74] Ulaganathan V, Krzan M, Lotfi M, Dukhin S, Kovalchuk V, Javadi A, et al. Influence of β-lactoglobulin and its surfactant mixtures on velocity of the rising bubbles. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2014;460:361-8.
*[75] Lotfi M, Bastani D, Ulaganathan V, Miller R, Javadi A. Bubble in flow field: A new experimental protocol for investigating dynamic adsorption layers by using capillary pressure tensiometry. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2014;460:369-76.
New experimental method for direct measurements of dynamic interfacial properties of a bubble surface using the capillary pressure tensiometry under liquid flow conditions.
[76] Manica R, Hendrix MH, Gupta R, Klaseboer E, Ohl C-D, Chan DY. Effects of hydrodynamic film boundary conditions on bubble–wall impact. Soft Matter. 2013;9:9755-8.
[77] Zawala J, Kosior D, Dabros T, Malysa K. Influence of bubble surface fluidity on collision kinetics and attachment to hydrophobic solids. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2016;505:47-55.
[78] Malysa K, Zawala J, Krzan M, Krasowska M. Chapter 11: Bubbles rising in solutions, local and terminal velocities, shape variations and collisions with free surface. Bubble and Drop Interfaces: Brill; 2011. p. 243-93.
[79] Zawala J, Niecikowska A. "Bubble-on-demand" generator with precise adsorption time control. Review of Scientific Instruments. 2017;88:095106.
*[80] Pesci C, Weiner A, Marschall H, Bothe D. Computational analysis of single rising bubbles influenced by soluble surfactant. arXiv preprint arXiv:171205224. 2017.
Novel insights about the influence of soluble surfactants on bubble flows obtained by Direct Numerical Simulation (DNS).
[81] Kracht W, Finch JA. Effect of frother on initial bubble shape and velocity. International Journal of Mineral Processing. 2010;94:115-20.
[82] Zhang Y, McLaughlin JB, Finch JA. Bubble velocity profile and model of surfactant mass transfer to bubble surface. Chemical Engineering Science. 2001;56:6605-16.
[83] Maldonado M, Quinn JJ, Gomez CO, Finch JA. An experimental study examining the relationship between bubble shape and rise velocity. Chemical Engineering Science. 2013;98:7-11.
[84] Tan YH, Rafiei AA, Elmahdy A, Finch JA. Bubble size, gas holdup and bubble velocity profile of some alcohols and commercial frothers. International Journal of Mineral Processing. 2013;119:1-5.
[85] Tan YH, Finch JA. Frother structure–property relationship: Effect of alkyl chain length in alcohols and polyglycol ethers on bubble rise velocity. Minerals Engineering. 2016;95:14-20.

ACCEPTED MANUSCRIPT

*[86] Tan YH, Finch JA. Frother structure-property relationship: Aliphatic alcohols and bubble rise velocity. Minerals Engineering. 2016;96-97:33-8.

A bubble rise velocity concentration at minimum velocity (CMV) concept is used to underpin frother structure–property relationship.

[87] Zawala J, Kosior D, Malysa K. Formation and influence of the dynamic adsorption layer on kinetics of the rising bubble collisions with solution/gas and solution/solid interfaces. Advances in colloid and interface science. 2015;222:765-78.

[88] Niecikowska A, Zawala J, Miller R, Malysa K. Dynamic adsorption layer formation and time of bubble attachment to a mica surface in solutions of cationic surfactants (CnTABr). Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2010;365:14-20.

[89] Tan YH, Finch JA. Frothers and gas dispersion: A review of the structure-property-function relationship. Physicochemical Problems of Mineral Processing. 2018;54:40-53.

[90] Cho Y-S, Laskowski J. Effect of flotation frothers on bubble size and foam stability. International Journal of Mineral Processing. 2002;64:69-80.

[91] Tan YH, Zhang W, Finch JA. Frother structure-property relationship: Effect of polyethylene glycols on bubble rise velocity. Minerals Engineering. 2018;116 56-61.

[92] Mendelsohn R, Mao G, Flach CR. Infrared reflection–absorption spectroscopy: Principles and applications to lipid–protein interaction in Langmuir films. Biochimica et Biophysica Acta (BBA) - Biomembranes. 2010;1798:788-800.

[93] Beattie DA, Bain CD. Sum-Frequency Spectroscopy. In: Chalmers JM, Griffiths PR, editors. Handbook of Vibrational Spectroscopy. Chichester: Wiley; 2002. p. 801-11.

[94] Williams CT, Beattie DA. Probing buried interfaces with non-linear optical spectroscopy. Surface Science. 2002;500:545-76.

[95] Shen YR. Basic Theory of Surface Sum-Frequency Generation. The Journal of Physical Chemistry C. 2012;116:15505-9.

[96] Wang HF, Gan W, Lu R, Rao Y, Wu BH. Quantitative spectral and orientational analysis in surface sum frequency generation vibrational spectroscopy (SFG-VS). International Reviews in Physical Chemistry. 2005;24:191-256.

[97] Wang X, Yin X, Nalaskowski J, Du H, Miller JD. Molecular features of water films created with bubbles at silica surfaces. Surface Innovations. 2015;3:20-6.

[98] Nguyen KT, Nguyen TD, Nguyen AV. Strong Cooperative Effect of Oppositely Charged Surfactant Mixtures on Their Adsorption and Packing at the Air–Water Interface and Interfacial Water Structure. Langmuir. 2014;30:7047-51.

*[99] Shahir AA, Nguyen KT, Nguyen AV. A sum-frequency generation spectroscopic study of the Gibbs analysis paradox: monolayer or sub-monolayer adsorption? Physical Chemistry Chemical Physics. 2016;18:8794-805.

Novel study that uses a combination of spectroscopic and surface tension data to gain insight into the nature of the adsorbed layer of a common flotation frother.

[100] Nguyen KT, Shahir AA, Nguyen AV. Probing the Molecular Orientation of Methyl Isobutyl Carbinol at the Air–Water Interface. Journal of Surfactants and Detergents. 2017;20:969-76.

[101] Asadzadeh Shahir A, Arabadzhieva D, Petkova H, Karakashev SI, Nguyen AV, Mileva E. Effect of Under-Monolayer Adsorption on Foamability, Rheological Characteristics, and Dynamic Behavior of Fluid Interfaces: Experimental Evidence for the Guggenheim Extended Interface Model. Journal of Physical Chemistry C. 2017;121:11472-87.

[102] Bergink-Martens DJM, Bos HJ, Prins A. Surface dilation and fluid-dynamical behavior of newtonian liquids in an overflowing cylinder. ii. surfactant solutions. Journal of Colloid And Interface Science. 1994;165:221-8.

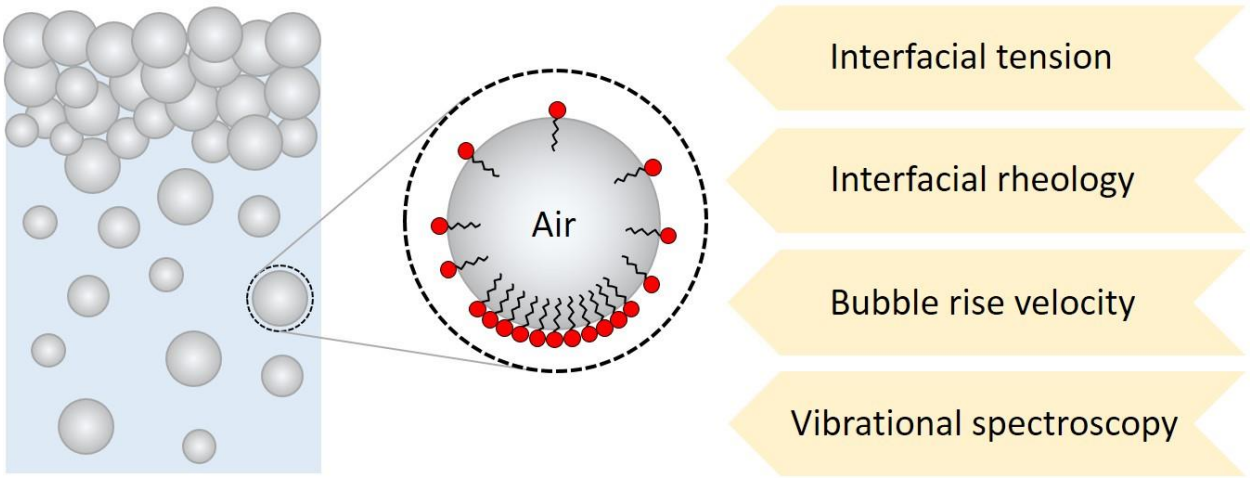
[103] Bergink-Martens DJM, Bos HJ, Prins A, Schulte BC. Surface dilation and fluid-dynamical behavior of newtonian liquids in an overflowing cylinder. I. Pure liquids. Journal of Colloid And Interface Science. 1990;138:1-9.

ACCEPTED MANUSCRIPT

[104] Campbell RA, Bain CD. External-reflection FT-IR spectroscopy of C10E8 at an expanding water surface. Vibrational Spectroscopy. 2004;35:205-11.
[105] Campbell RA, Parker SRW, Day JPR, Bain CD. External reflection FTIR spectroscopy of the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) on an overflowing cylinder. Langmuir. 2004;20:8740-53.
[106] Campbell RA, Day JPR, Bain CD. External reflection fourier transform infrared spectroscopy of surfactants at the air-water interface: Separation of bulk and adsorbed surfactant signals. Applied Spectroscopy. 2005;59:993-1001.
*[107] Day JPR, Campbell RA, Russell OP, Bain CD. Adsorption kinetics in binary surfactant mixtures studied with external reflection FTIR spectroscopy. Journal of Physical Chemistry C. 2007;111:8757-74.
The study of a mixed surfactant system at the air-water interface, with chemical/spectroscopic information allowing composition of the adsorbed layer to be determined.
[108] D'Apolito R, Perazzo A, Preziosi V, D'Antuono M, Tomaiuolo G, Miller R, et al. Measuring interfacial tension of emulsions in situ by microfluidics. Langmuir. 2018;34 4991–7.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT



Graphical abstract

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Highlights:

- Review of the application of advanced surface characterisation techniques to systems of relevance for mineral flotation, specifically for surfactant (frother) adsorption
- Emphasis on techniques that enable determination of interfacial properties of the air-water interface at early adsorption times, and with the interface under dynamic conditions
- Interfacial tension, interfacial rheology, rising bubble terminal velocity, and interfacial vibrational spectroscopy allow for a near-complete picture of surfactant adsorption processes

ACCEPTED MANUSCRIPT