**EFFECT OF FLOTATION FROTHERS ON BUBBLE SIZE
AND FOAM STABILITY**

by

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ABSTRACT

The experiments described herein indicate that the frothers control the size of bubbles in flotation systems by controlling bubble coalescence. The ability of frothers to prevent bubble coalescence is well characterized by the Critical Coalescence Concentration (CCC).

At frother concentrations C lower than CCC, the bubble size is determined by coalescence. At frother concentrations that exceed CCC, bubble size is no longer determined by coalescence but depends on the sparger geometry and hydrodynamic conditions. The efficiency of different spargers can thus be compared only when the experiments are carried out at frother concentrations exceeding CCC.

Flotation experiments carried out using small-scale flotation devices (e.g. Hallimond tube, etc.) equipped with either a single capillary or a porous frit may be very difficult to compare. They may give different flotation kinetics because of bubble coalescence in the latter case at $C < \text{CCC}$ hence resulting in much larger bubble sizes.

The tests revealed that foam stability measured under dynamic conditions is determined by bubble coalescence.

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CHAPTER 1

INTRODUCTION

Froth flotation is the most extensively used method of mineral separation. The process of selective separation by froth flotation depends mainly on differences in flotation kinetics of various mineral species.

Flotation kinetics involve a number of mass transfer processes with some taking place in the pulp phase (particle-bubble collision and attachment, transport of particle-bubble aggregate to the froth phase) and some in the froth phase (recovery of particle from the froth phase to concentrate launder). All of these sub-processes depend strongly on bubble size and froth stability.

In a flotation process, frothers are utilized to enhance generation of fine bubbles and to stabilize the froth. According to Leja – Schulman's penetration theory (Leja and Schulman, 1954), surface active molecules (frother) accumulate preferentially at the water/gas interface and actively interact with collector molecules adsorbed onto mineral particles at the moment of the particle to bubble collision and attachment.

Froth is an important part of the flotation system. Yet, despite the importance of the froth phase, relatively few studies have been conducted to examine the impact of froth behavior on the performance of conventional and column flotation cells. If the froth phase is not sufficiently stable, mineralized bubbles that enter the froth layer rupture prematurely, causing valuable mineral particles to drop back into the pulp. On the other hand, too stable a froth may result in nonselective entrainment of excessively large amounts of gangue particles in turn reduces the product grade.

Recent measurements of bubble size, dynamic foamability index, and surface tension for a series of flotation frothers by Sweet et al. (1997) showed (Fig. 1) that bubble

size and dynamic foamability index are sensitive to minor changes in frother concentration. However, surface tension is only affected when frother concentrations is increased tenfold. Since the existing equations relate the size of generated bubbles to surface tension, and the surface tension does not seem to change much at very low frother concentrations, the question of why the bubble size depends on frother concentration therefore arises. In order to answer such a question, a series of experiments was carried out in which specially designed spargers were used and the size of the bubbles was measured over a broad concentration range for different frothers. In concomitant experiments the dynamic foamability index and the surface tension were measured for the same frothers.

Figure. 1. Normalized retention time, Sauter mean bubble diameter, and surface tension of n-hexanol and MIBC. (Sweet et al., 1997)

Bubbles are commonly produced by sparging, that is by pumping gas through a capillary or frit into the bulk liquid. In mechanical flotation cells fine bubbles are produced by cavitation at the trailing edge of an impeller blade or by using shearing forces to cut the air supplied under pressure (Grainger-Alley, 1970). Since bubble size is the primary factor determining the efficiency of gas-liquid contactors, spargers efficiency is frequently evaluated using this parameter. This usually involves measuring the size distributions of bubbles produced by different spargers (Yoon and Luttrell, 1989) and a silent assumption that the size of the generated bubbles is determined by the sparging mechanism and not by secondary processes (for instance, bubble coalescence). This is a critical point that is further discussed in this thesis.

CHAPTER 2

OBJECTIVES

The objectives of this study were to determine:

- (i) Why bubble size depends on frother concentration in a flotation cell.
- (ii) What is the mechanism that determines the size of the generated bubbles.
- (iii) What are the conditions under which the bubble size measurement could characterize the efficiency of sparging systems.

CHAPTER 3

LITERATURE REVIEW

3.1. Flotation frothers

3.1.1. Classification

Frothers are commonly classified according to their chemical composition. The mineral industry employs five main groups of frothing reagents (Table 1).

3.1.1.1. Alcohol-type frothers

(a) Aliphatic alcohols (ROH)

Both straight (C6 to C9) and branched (C6 to C16) chain compounds are used. These frothers produce fine-textured, fairly selective froths that are brittle and therefore do not give problems with entrainment or excessive launder stability. They generally have limited solubility in water but can easily be dispersed. This category of frothers includes iso-amyl alcohol, hexanol, cyclo-hexanol, heptanol, MIBC (methyl-iso-butyl carinol) and 2 – ethyl hexanol.

(b) Cyclic alcohols

The main types are compounds contained by pine and eucalyptus oils. They exhibit some collecting properties and are very popular for copper concentrators.

(c) Aromatic alcohols

Cresylic acid is the most common aromatic frother. It is obtained by distillation of coal tar and contains essentially a mixture of cresols and xylenols. Its use is limited because of its toxicity.

3.1.1.2. Alkoxy-type frothers

These frothers tend to be somewhat more powerful and selective than the alcohol type. They find a wide range of applications in sulfide flotation in South Africa.

Table 1. Flotation frothers classification (Laskowski, 1998)

	Name	Formula	Solubility in H ₂ O
(1)	Aliphatic alcohols	R-OH	
	Methyl isobutyl carbinol (MIBC)	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \qquad \qquad \\ \text{CH}_3 \qquad \text{OH} \end{array}$	Low
	2-ethyl hexanol	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_2-\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{OH}$	Low
	diacetone alcohol	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \qquad \qquad \parallel \\ \text{OH} \qquad \text{O} \end{array}$	Very good
	2,2,4-trimethylpentanediol 1,3-monoisobutyrate (TEXANOL)	$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \qquad \qquad \text{O} \qquad \text{CH}_3 \\ \qquad \qquad \qquad \qquad \parallel \qquad \\ \text{CH}_3-\text{CH}-\underset{\text{OH}}{\text{CH}}-\text{C}-\text{CH}_2-\text{O}-\text{C}-\underset{\text{CH}_3}{\text{CH}} \\ \qquad \qquad \\ \qquad \qquad \text{CH}_3 \end{array}$	Insoluble
(2)	Cyclic alcohols		
	α -terpineol (Active constituent of pine oil)		Low
	Cyclohexanol	C ₆ H ₁₁ OH	Low
(3)	Aromatic alcohols		
	cresylic acid (Mixture of cresols and xylenols)		Low
(4)	Alkoxy-type frothers		
	1,1,3-triethoxybutane (TEB)	$\begin{array}{c} \text{O}-\text{C}_2\text{H}_5 \qquad \text{O}-\text{C}_2\text{H}_5 \\ \qquad \qquad \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH} \\ \qquad \qquad \\ \qquad \qquad \text{O}-\text{C}_2\text{H}_5 \end{array}$	Low
(5)	Polyglycol-type frothers	R(X)_nOH, R=H or C_nH_{2n+1}, X=EO, PO or BO	Very good or total
	DF 250	CH ₃ (PO) ₄ OH	Total
	DF1012	CH ₃ (PO) _{6.3} OH	32%
	Aerofroth 65 DF 400	H(PO) _{6.5} OH	Total
	DF-1263	CH ₃ (PO) ₄ (BO)OH	Very good

3.1.1.3. Polyglycol-type frothers

The third major class of frothers includes compounds manufactured by condensation of allylene oxides (e.g. ethylene oxide, propylene oxide or butylene oxide) with or without low molecular weight aliphatic alcohols. They range from completely miscible in water to partially soluble. They produce fine, fragile froths that are usually very selective and have no collecting action. Degree of selectivity tends to be inversely related to molecular weight. The products of Dow Froth, Cyanamid (Aerofroth), ICI Australia (Terric 400 series frothers), Huntsman (Unifroth 250), and Witco (Arosurf F-214 and F-215) are included in this group. (Laskowski, 2001)

3.2. Mechanism of action

Flotation requires fine bubbles in pulp to collect mineral particles and a stable enough froth to carry the collected solids with the loaded froth over the cell lip. Flotation froth is a three-phase system that contains liquid, air, and solid particles. The flotation froth stability is determined by foaming of the liquid phase and is also affected by solid particles, their particle size and surface properties.

The influence of frothers on flotation can be related to:

- (i) control of the bubble surface area flux and thus flotation kinetics by affecting bubble size;
- (ii) the effect on froth stability;
- (iii) some collecting properties;
- (iv) facilitation of particle to bubble attachment as postulated by the penetration theory.

Frothers control the bubble surface area flux and flotation kinetics by affecting bubble size. The flotation rate constant, k_c , is now rigorously used for the processes taking place in pulp only (collection zone) (Jameson et al., 1977).

$$k_c = \frac{1.5J_g P}{d_b} \quad (1)$$

The direct correlation of flotation rate to bubble size is poor. Gorain et al. (1997) showed that flotation rate correlates better with the superficial gas velocity. However, superficial gas velocity on its own cannot properly describe the flotation effects. Gorain et al. (1997) related the bubble surface area flux, S_b , to flotation rate constant and found a linear relationship regardless of impeller types. As the bubble surface area flux increases the flotation rate constant proportionally increases, too. This implies that there is a strong effect of bubble size on the flotation rate constant (equations 2 and 3).

The bubble surface area flux, S_b is defined (Finch and Dobby, 1990) as:

$$S_b = \frac{6J_g}{d_{32}} \quad (2)$$

where S_b = Bubble surface area flux ($\text{m}^2/\text{m}^2\text{s}$)

J_g = Superficial gas velocity (m/s)

d_{32} = Sauter mean bubble diameter (m).

This equation clearly shows that the bubble surface area flux depends on the superficial gas rate and the Sauter mean bubble diameter. Combining equations 1 and 2 gives a linear dependence of the flotation rate constant on bubble surface area flux.

$$k_c = \frac{1}{4} P S_b \quad (3)$$

where P is probability of collection.

Frothers are used in flotation to provide a large air-water interface of sufficient stability to ensure that a floated particle will not fall back into the flotation pulp before it can be removed (Lovell, 1982). In terms of froth stability, a successful frother should allow sufficient thinning of the liquid film between the colliding bubble and particle so that attachment can take place in the time frame of the collision and provide sufficient froth stability so that the weakly adhering or mechanically entrained particles of unwanted materials can escape with the draining liquid. (Klimpel and Hansen, 1988) As a result of the water drainage, the thick froth has low pulp water content in top layers and high upgrading degree. The upgrading in the froth is possible only if the froth is not too stable. If the froth phase is insufficiently stable, mineralized bubbles in the froth layer rupture prematurely and valuable particles drop back into the pulp. However, if the froth is too stable, nonselective entrainment of excessively large amounts of gangue particles reduce the product grade (Luttrell et al., 1991).

In summary, thin froth in the scavenger flotation promotes higher recovery and poorer selectivity (Kaya and Laplante, 1986). Therefore, in general, the froth is thick in cleaner cells and very thin in scavenger cells.

The overall flotation rate constant depends on the froth thickness as well (Laplante et al., 1989). To investigate the effect of froth depth on the flotation rate constant k , the flotation kinetics was studied as a function of froth depths in different flotation machines (Gorain et al., 1998). From these experiments, Gorain et al. (1998) concluded that the froth depth has a significant influence on the k - S_b relationship. Lower froth depth yielded the greater k value and as the froth depth increased, k values became smaller.

Another factor influencing the stability of froths is the size of the bubbles forming the froth. De Vries (1957) and Brown et al. (1953) found that the size of bubbles has a large effect on the overall stability of the froth. In general, small bubbles, resulting from increased frother concentration, produce a stable thick froth (Goodall and O'Connor, 1991).

Bubbles also affect the secondary upgrading processes in the froth phase. Bubble size is a major factor in determining the extent of entrainment in the froth phase. Larger bubbles increase entrainment and also subsequent drop back of particles from the froth. (Goodall and O'Connor, 1991). Rubinstein and Samygin (1998) noted that the entrainment of non-floating gangue increases from 49% to 85% as the bubble size increases in the froth phase. Goodall and O'Connor, (1991) also observed that the decrease in air rate and increase in frother concentration produced small bubbles and reduced entrainment.

Laskowski (1998) analyzed the effect of frothers on flotation in terms of HLB (Hydrophilic – lyophilic balance) numbers and molecular weight of frothers. At a given HLB number low molecular weight frothers tend to favor a higher grade, while frothers with higher molecular weights seem to promote recovery.

Richard et al. (1987) tested derivatives of hexanol and propylene oxide and ethylene oxide as coarse coal frothers. These frothers were found to be more effective in floating coarser coal particles than the existing commercial frothers; no explanation was, however, provided.

According to the theory of Schulman and Leja (1954), the frother primarily influences the kinetics of particle attachment to the bubble by interacting with collector molecules and facilitating thinning of the liquid layer between the particle and the bubble

when they contact each other. When the mineral particle attaches to the air bubble, as a result of the mutual penetration of the two interfacial films of surfactants (at the solid/liquid and at the gas/liquid interfaces), the particle-bubble aggregate is stabilized and is lifted to the surface of the flotation pulp (Schulman and Leja, 1954).

Rapid physical adsorption and diffusion of frother molecules at the air/water interface and their transfer to the solid/liquid interface facilitates attachment of particle to the bubble within the extremely short time of contact (Leja, 1957; Leja and Schulman, 1954).

From Gibbs's adsorption isotherm, the surface concentration of frother at the air/water interface can be calculated from surface tension measurements.

$$\Gamma = -\frac{1}{2.3RT} \bullet \frac{d\gamma}{d \log c} \quad (4)$$

where c is the concentration of frother, R is the gas constant, T is temperature in Kelvin degrees, Γ is the surface excess (adsorption), and γ is the surface tension.

3.3. Effect of bubble size on flotation.

The bubble size controls the probability of particle-bubble collisions and hence collection efficiency. This effect is manifested in the collection zone (pulp).

Smaller bubbles increase both collision and attachment efficiencies and therefore increase collection efficiency (Dobby and Finch, 1986). Yoon and Luttrell (1989) noted that the probability of collision of small bubbles to coal particles increases as a result of their lower rising velocity, increased bubble retention time in the pulp and favorable collision hydrodynamics. However, with a large decrease in bubble size, the buoyancy force may become insufficient for lifting the attached particles. Diaz-Penafiel and Dobby (1993) plotted collection efficiency versus the bubble size on a log-log scale for a particle

size range between 11.4 and 13 μm (Figure 2). This figure clearly shows the effect of bubble size on collection efficiency. The smaller the bubbles the larger the collection efficiency.

Fig. 2 Collection efficiency of silica versus bubble diameter for three sets of research results. (Diaz-Penafiel and Dobby, 1993)

Yoon and Luttrell (1989) showed that fine particles follow the streamlines around the very large bubbles due to their small inertial force and never collide with the bubbles in conventional flotation cell. Therefore, larger bubbles provide a low flotation rate and poor recovery of fine particles. Small bubbles are desirable for fine particle flotation since they increase particle-bubble collision probability as low collision rates are the main cause of the slow flotation rate of fine particles. Fine bubbles are thus far superior for the flotation of fine particles. This is accounted for in equations 2 and 3 with S_b increasing with decreasing d_{32} .

3.4. Effect of frothers on bubble size

One of the most important attributes of frothers in flotation processes is their ability to decrease the size of generated bubbles. As discussed in the previous section, smaller bubbles are advantageous for a number of reasons. Even trace amounts of surfactants change the bubble diameter in a flotation cell. Miller and Ye (1989) noticed that the mean bubble diameter dropped by almost 75% with an increase in surfactant concentration from 0 to 10^{-3} M. O'Connor et al. (1990) conducted measurements of bubble size in the presence of Dowfroth 250 and MIBC and found both reduce the size of the bubbles at very low frother concentrations. They believed that reduction of bubble size resulted from lowering of the surface tension by the frothers. Goodall and O'Connor (1991) confirmed that the bubble size decreases at increased frother concentration but at frother concentrations greater than 10 ppm the bubble size became constant. Tucker et al. (1994) measured the mean bubble size for five frothers at concentrations varying from 0 to 20 ppm. The same general trend for all the tested frothers was observed; the mean bubble size decreased with increasing frother dosage. However, the mean bubble size approached the same value around 20 ppm concentration for all the frothers. Among the four frothers tested by Tucker et al. (1994), the same bubble sizes were generated at lower frother concentrations in the sequence of DIBK<41G<MIBC<Dow 200. This finding implies that different frothers are characterized by different ability to reduce the bubble size. Both O'Connor et al. (1990) and Zhou et al. (1993) noticed that the ability of MIBC to reduce the bubble size is different from that of Dowfroth 250.

Numerous researchers, for instance Aldrich et al. (2000), hypothesized that the decrease in surface tension caused by frother was responsible for the reduction in bubble size. However, Sweet et al. (1997) found that the surface tension was not very sensitive

to frother concentrations used in flotation processes. Both bubble size and retention time were affected by the frother at concentrations over which the surface tension values were almost identical to those of distilled water (Figure 1). Sweet et al. (1997) concluded that bubble size is much more sensitive to a low surfactant concentration than surface tension and speculated that the bubble size measurements could be used for analytical purposes to test the presence of surface active substances at very low concentrations (Sweet et al., 1997).

3.5. Bubble size measurements

As discussed, bubble size has a significant effect on flotation performance. However, a lack of reliable and relatively simple methods of bubble size measurement has hindered further research in this area of flotation. The following experimental methods are now available to determine bubble size: (1) photographic technique, (2) dynamic bubble disengagement technique, (3) calculations using empirical or semi-empirical correlations, (4) estimation of bubble diameter from drift flux analysis, (5) estimation of bubble size using bubble population balance model, and (6) UCT bubble size meter.

3.5.1. Photographic method

Photographic techniques are commonly used to measure bubble size. Ahmed and Jameson (1985) determined bubble sizes photographically by drawing bubble-bearing liquid from the flotation vessel through a flat-sided cell of special design. The bubble swarm was drawn between two transparent plates 1 mm apart and photographed there. The photographs were analyzed manually. Standard statistical techniques were used to ensure that sufficient numbers of bubbles were counted to provide statistically significant

results. Vanderkruk et al.'s (1994) photographic cell contains two plates 4 mm apart. This enabled the magnification to be determined by measuring the distance between the magnified lines on the photographs and provided a calibration for the bubble measurements. The bubbles were counted manually while being magnified; the bubbles were measured and recalculated into the appropriate size fractions on a linear scale.

Due to the tedious and time consuming nature of the photographic method as described above, in most of the experiments only 300 bubbles were measured. Zhou et al. (1993) used photographic technique to determine bubble sizes and measured about 300 – 900 bubbles, except at very low gas flowrates and frother dosages; in this latter case fewer than 300 bubbles were measured. Lelinski et al. (1995) and Vanderkruk et al. (1994) measured 300 and 500 bubbles for each set of conditions.

Noting that counting a large number of bubbles in the photographic method is difficult, Lelinski et al. (1995) argued that just a few hundred bubble size determinations can be statistically sufficient. A count of 300 bubbles resulted in a distribution with the error for any particular size less than 8% with a 95% confidence limit. Reduction of this expected error to 5%, at the same level of confidence, would require counting of 2960 bubbles. In view of the other sources of error affecting such measurements, such small reduction in error hardly seems worth the effort.

Although the photographic technique is the most common and is quite reliable, the method is tedious, restricted to vessels with transparent walls and to a rather small number of counted bubbles. Therefore, in an operating column, it is almost impossible to determine the size of bubbles by the photographic technique, and other methods have to be employed.

3.5.2. Dynamic bubble disengagement technique

The dynamic bubble disengagement technique uses the dynamic gas hold-up in a gas-liquid reactor (Standish et al., 1991). In this method the volume fraction of gas in the reactor is measured after the flow of gas has been shut off. The rate of the decrease in the volume (height) of the aerated pulp provides a measure of the speed at which gas bubbles disengage from the reactor.

This technique employs five level height-indicating tubes of diameter 2.5 mm spaced at 5 mm intervals. When the air hold-up reaches a steady state the flow of air is stopped abruptly and the decrease of pulp level in the indicating tubes is filmed at 100 frames/s with a video camera. The rate of air bubble disengagement is determined from records of the distance traveled by bubbles in a given time.

The dynamic bubble-disengagement technique assumes that the gas bubbles are uniformly distributed throughout the gas-liquid reactor without any significant interactions between the bubbles in the steady state, and that the rising velocity of a bubble is a function only of its size.

Once the values of the operating variables, such as static gas hold-up and aerated pulp height are known the bubble size can be estimated from the equation. (Standish et al., 1991)

$$d_b = \epsilon_0 \frac{L_0(1 - \epsilon_0)[\epsilon_0 - \epsilon(t)]}{\epsilon_0 t K [1 - \epsilon(t)]} \quad (5)$$

where L_0 is the aerated pulp height, ϵ_0 is the static gas hold-up in the gas-liquid reactor, K is the constant, and d_b is the bubble size.

Standish et al. (1991) used photographic method for estimating the bubble sizes to evaluate the validity of the dynamic gas bubble-disengagement technique in clear water

(contained in a rectangular bubble column). They found a large discrepancy between the size of bubbles measured by this technique and those determined photographically. This discrepancy is caused by an overly simplistic description of the bubble movements in a reactor. However, this technique can be used as a first approximation.

3.5.3. Calculations using empirical or semi-empirical correlations

Sada et al. (1978) used an empirical correlation to estimate the bubble diameters produced from single hole sparger in a flotation column using equations 6 to 8 in a flotation column. If the bubble shape at the nozzle tip is a sphere and the drag force caused by the liquid flow may be approximated by the Newton drag force, the total force acting on the bubble at the nozzle tip is the sum of the buoyancy force and the drag force. The modified Froude number based on the bubble diameter can be derived from the total force equation as follows.

$$N_{Fr} = \frac{u^2}{gd_b + 0.33U^2} \quad (6)$$

where d_b is the initial diameter of bubble, u is the gas velocity through nozzle, U the superficial liquid velocity, and g the gravitational constant. Liquid velocity distribution was measured by taking photographs of streamline patterns in the column by means of aluminum powder suspended in water.

At gas velocities below 4 cm/s single bubbles were formed at the nozzle tip, but they coalesced at the nozzle tip at velocities above 4 cm/s. For the single bubble region, d/δ was plotted against N_{Fr} on log-log coordinates and correlated by

$$d/\delta = 1.55 N_{Fr}^{0.2} \quad (7)$$

where δ is the nozzle diameter.

In the region of coalescing bubbles the effects of the nozzle diameter and the gas flow rate were more pronounced than in the region of single bubbles. The bubble size in this region can be correlated by the following equation (Sada et al., 1978):

$$\frac{d}{\delta} = 2.5 N_{Fr}^{0.2} \left(\frac{\delta}{\delta^0} \right)^{0.1} - 3.5 \quad (8)$$

Masliyah (1979) used directly a particle hindered settling equation to estimate the bubble size. The lower bubble size measurement limit was approximately 0.2 mm and the upper bubble size limit was given by Reynolds number (Re) of 500 corresponding to a bubble size of approximately 2 mm. Above 2 mm, bubbles are no longer spherical. Yianatos et al. (1988) counted a minimum of 400-600 bubbles for each run using this method in a flotation column.

Bubbles and rigid spheres in water have virtually equivalent drag coefficients up to a bubble Re of approximately 500 (Perry and Green, 1984). Thus, for Re less than 500, an expression for hindered settling of spherical particles can be used to predict the bubble sizes.

$$U_{bs} = \frac{g \cdot d_b^2 \cdot F(\epsilon_L) [\rho_b - \rho_{susp}]}{18\mu_L [1 + 0.15 \text{Re}_b^{0.687}]}, \quad (9)$$

where

$$\text{Re}_b = \frac{d_b \cdot U_{bs} \cdot \rho_L \cdot \epsilon_L}{\mu_L} \quad (10)$$

where U_{bs} is slip velocity between bubbles and fluid or slurry, g is gravitational acceleration, d_b is bubble diameter, ϵ_L is fractional liquid holdup, and μ_L is liquid viscosity. Equation (9) can be simplified for a two-phase (gas-liquid) system, since $\rho_b \approx 0$, to

$$U_{bs} = \frac{g \cdot d_b^2 \cdot F(\epsilon_L) \cdot \epsilon_L \cdot (-\rho_L)}{18\mu_L[1 + 0.15\text{Re}_b^{0.687}]} \quad (11)$$

with the – sign indicating that the bubbles are rising.

In gas-liquid systems in which there is a net flow of both phases, the slip velocity, U_{bs} , is defined as the mean relative velocity,

$$U_{bs} = \frac{J_g}{\epsilon_g} \pm \frac{J_L}{(1 - \epsilon_g)}, \quad (12)$$

where J_g is superficial gas velocity, J_L is superficial liquid velocity, ϵ_g is fractional gas hold up, and + refers to countercurrent and – to co-current gas-liquid flow. All the parameters on the right-hand side are readily measured and consequently U_{bs} can be determined. Water manometers were used to measure the mean gas holdup ϵ_g , while J_g and J_L were measured by calibrated flow meters. Fractional gas holdup was calculated from the pressure drop measurements.

Bubble diameters are determined by repeated substitution of estimates of d_b until the calculated U_{bs} equals the measured U_{bs} .

Xu and Finch (1988) compared the photographic method to the hindered settling equation method and noticed the inaccuracy of the hindered settling equation method. There is an apparent tendency to undercalculate the sizes of small bubbles and overcalculate the large ones. They concluded that extending the bubble diameter estimation technique to mechanically agitated cells poses some problems.

3.5.4 Estimation of bubble diameter from the drift flux analysis

The drift flux approach uses gas hold up and bubble terminal rise velocity to estimate the bubble diameters in a flotation column (Dobby et al., 1988). This method is applicable to gas-slurry system. It requires measurement of gas and slurry flowrates, slurry density, and pressure drop in the lower portion of the column, i.e. gas holdup.

The bubble diameter in a bubble swarm in gas-slurry system is expressed by

$$d_b = \left[\frac{18\mu_f U_T}{g\Delta\rho} (1 + 0.15 \text{Re}_s^{0.687}) \right]^{1/2} \quad (13)$$

where

$$\text{Re}_s = \frac{d_b U_s \rho_f (1 - \varepsilon_g)}{\mu_f} \quad (14)$$

and U_T is obtained from

$$U_T = \frac{v_g}{\varepsilon_g (1 - \varepsilon_g)^m} - \frac{(v_g + v_f)}{(1 - \varepsilon_g)^m} \quad (15)$$

where d_b is the bubble diameter, μ_f is the viscosity of liquid, U_T is the terminal bubble rise velocity, g is the gravitational acceleration, $\Delta\rho$ is the density difference between two phase, U_s is the slip velocity between bubbles and liquid, ρ_f is the density of liquid, ε_g is the fractional gas hold up and both v_g and v_f are the superficial velocities (flowrate per unit area) and are positive upwards.

A primary estimate of the m value is used to initially calculate U_T . The final m value is subsequently determined through iterations of the entire calculation until an acceptable error is obtained (Dobby et al., 1988). Ityokumbul et al. (1995) used Dowfroth 250C, MIBC, and Triton X-100 frothers and showed that a single drift-flux relationship is not applicable for all frothers. In a bubble swarm, the bubble terminal rise velocity should be estimated using an appropriate drift flux relation which depends on the frother type.

The comparison of the photographic method and the drift-flux method showed good agreement (Dobby et al., 1988). Tavera et al. (2000) applied the drift flux analysis to estimate bubble size and the gas holdup in laboratory flotation columns using a conductivity probe. When the system contained no solids, the gas holdup could be accurately measured from the pressure difference. Image-analysis results and the drift-

flux analysis prediction were in good agreement, and therefore the drift flux technique is considered to be a reliable method to estimate the bubble sizes in two-phase systems.

3.5.5. Estimation of bubble size using bubble population balance model.

Sawyer et al. (1998) proposed a bubble population balance model for the prediction of Sauter mean bubble diameters in mechanical flotation cells. In the model, the flotation cell is divided into two separate, statistically homogeneous zones. These are the impeller zone and the bulk tank zone. Bubble breakage is assumed to happen only in the impeller zone because of the much higher rate of energy dissipation in this zone relative to the bulk zone, while bubble coalescence is assumed to take place in both zones. The population balance is solved by performing a bubble number balance in each zone. Because an analytical solution to the population balance equation is not possible due to its complexity, a numerical technique is required. The population balance is thus solved by transforming the population balance equation into a system of differential equations by discretizing the range of bubble volumes. In the Sawyer et al (1998) study, the volume range of bubbles was divided into 20 classes geometrically spaced from 0.2 mm to 5 mm, typical of the range of bubble sizes observed in industrial flotation cells. Initial values for the constants in the various balance functions are assumed, and a dynamic simulation of the bubble population with a variable time step is run using Microsoft Excel. A least squares technique is used to fit the simulation results to actual industrial data so that the constants in the various functions can be approximated.

3.5.6. The UCT bubble sizer

In search of a simple and more reliable method of bubble size determination, a team from the University of Cape Town developed a bubble sizer. The UCT bubble sizer

allows an accurate measurement of bubble sizes in flotation cells in both two phase (liquid/gas) and three systems (liquid/gas/solids systems) (Tucker et al., 1994).

O'Connor et al. (1990) gives a detailed description of the UCT bubble sizer. The sizing system consists of a capillary tube with a belled end passing between two pairs of photo-transistor-LED detectors mounted 5 mm apart. Bubbles are drawn up the capillary under vacuum. As the bubbles pass the detectors, changes in light intensity, caused by different refractive indices of air/liquid, are monitored. About 3000 bubbles are sized in each run in order to obtain an accurate bubble-size distribution. The bubbles are then collected in a gas burette so that the total volume of bubbles is known. At the end of a run the data are downloaded from the buffers of the data capture system to a micro-computer. A program is used to calculate the bubble volume from the velocity and length for each bubble. The bubble volumes are then normalized with respect to the total volume collected. This normalization is necessary because a thin film of water coats the inside of the capillary making the effective capillary diameter difficult to calculate. From these bubble volumes, a distribution of bubble diameters is obtained provided that there is no coalescence in the capillary.

Excellent reproducibilities in two phase (liquid/air) system have been reported by various authors. Bradshaw and O'Connor, (1996) conducted 50 runs to establish the reproducibility of the system and reported that it as excellent. They found that the average sauter mean diameter was 0.957 mm with a standard deviation of 0.021 mm. O'Connor et al. (1990) conducted numerous tests and proved that the reproducibility of the UCT bubble sizer was excellent. In the six repeated experiments for the two-phase system a mean bubble size of 2.822mm was recorded with a standard deviation of 0.015 mm.

The use of the UCT bubble size analyzer allows monitoring bubble size distribution and gas holdup in a pulp phase in two-phase systems. In three-phase frothing systems, the measurement accuracy of the equipment is limited by solid concentration. However, Tucker et al (1994) eliminated this problem with a bubble sampler that extracts bubbles from the slurry and transports them to a separate solids-free chamber where their sizes can be measured using the UCT bubble size analyzer. With the sampler fitted, Tucker et al. (1994) measured the average mean bubble size of 1.945 mm with a sample standard deviation of 0.023 mm.

Aldrich et al. (2000) combined the UCT bubble sizer with a machine vision system to monitor average bubble size in a pulp and in froth, bubble size distribution, froth stability and froth mobility, without being limited by the nature of the pulp or froth in a three phase (liquid/air/solid) system. At low solid concentration, they used both the bubble sizer and the machine vision system. At high solid concentrations, the machine vision system was used alone to analyze the whole frothing system. At high solid concentrations and low frother dosages, bubble size in the pulp phase differs from that in the froth phase. At higher frother dosages, however, the bubble size distributions in both the pulp and froth phases are very close.

3.6. Coalescence

The bubble coalescence phenomenon is very complex and its mechanism is not clearly understood. Bubbles tend to coalesce in pure liquids regardless of the liquid characteristics. However, in the presence of frothers, the coalescence of bubbles may be strongly retarded or prevented altogether. When two bubbles come in contact with each other, the liquid film between them thins and breaks, causing bubbles to coalesce

(Marrucci, 1969; Zieminski et al., 1967; Gourram-Badri et al., 1997). Sagert et al. (1976) proposed that the thinning of the interbubble layer of liquid occurs at first by drainage under gravitational forces and is then followed by movement of the liquid within the lamella (between the two air/liquid interfaces) by capillary pressures.

The rate of coalescence depends on the rate of drainage of the continuous phase between the bubbles (Zieminski et al., 1967). Leja (1982) pointed out that the most important factor in the formation of foam is the presence of a surfactant at the liquid/gas interface. Due to the uneven distribution of polar and nonpolar groups in frother molecules, frothers adsorb preferentially at the liquid/air interface. The adsorption of the frothers at the bubble interface and their molecular orientation affects the thickness of the film, viscosity, and the rate of drainage. The frother molecules adsorbed at the water/gas interface are responsible for the decrease in coalescence, primarily as their polar groups interact with water molecules, thereby increasing the amount of water bound to the surface of bubbles (Zieminski et al., 1967).

Since frother concentrations at the interface seem to affect the coalescence, the velocity of migration of such molecules to the interface is the determining factor for preventing coalescence. (Zieminski et al., 1967)

3.6.1. Surface-elasticity theory

Stability of the foam depends on the durability of liquid films between air bubbles. If the films easily break down, the foam is unstable and its volume is small. It has been postulated that surface elasticity is responsible for film stability (Kitchener and Cooper, 1959)

Gibbs showed that if a thin film of a dilute solution of a surface-active solute is subjected to local stretching, the surface tension of that part increases since the solute is

positively absorbed in the surface and any increase of surface area therefore leads to a decrease of average solute concentration within the film and increase of equilibrium surface tension. Therefore, the Gibbs elasticity of a thin film is defined as the ratio of the increase in film tension resulting from an infinitesimal increase in the area, and the relative increment of the area.

Under dynamic conditions the surface tension in a film is higher during extension and lower during compression than the equilibrium values (Sutherland, 1951). This is known as the Marangoni effect and operates on an expanding or contracting surface carrying an adsorbed layer and provides a restoring force which tends to protect a film against local thinning. To show such properties, the fluid must possess a special form of elasticity such that local thinning is rapidly opposed and counterbalanced by restoring forces generated during the initial displacements of the material. Pure liquids are completely lacking in the property of elasticity because their surface tension is independent of extension. (Kitchener and Cooper, 1959)

Andrew (1960) assumed that the entire resistance to the motion arises because slow diffusion of solute to the surface results in a higher than equilibrium surface tension of the film. Therefore the “solute diffusion times” associated with this model are more of the order of the stretching times.

Quantitative analyses of the surface adsorption and dynamic surface tension measurement of a bubble film has been scarce due to the lack of experimental methods. Recent dynamic surface tension measurements, (via maximum bubble pressure method), in combination with a derived adsorption model, shows promising results in quantitative evaluation of the relationship between dynamic adsorption parameters and foam stability (Comley et al., 2001)

Figure 3. Dependence of the retention time (rt) and the effective elasticity (E_{eff}) on number of carbon atoms in alkanol molecule (K. Malysa et al., 1992).

When a surface layer behaves as an insoluble monolayer the surface elasticity forces are at their highest and are called the Marangoni dilation modulus. (Malysa, 1992) The Marangoni dilational elasticity modulus represents the highest possible value of the surface elasticity forces for the given system. This value is obtained under the conditions that the equilibrium surface coverage is established at the surface at the moment when the dilation of the interface starts and that the disturbance is so rapid that the adsorption layer behaves as an insoluble monolayer (no diffusional exchange). Figure 3 shows the Maragoni dilational elasticity modulus and the rt (retention time) values were shown to depend strongly on the kind of surface-active substance and its concentration in a similar way as the effective elasticity. (Malysa, 1992)

3.6.2. Effect of surface viscosity

Plateau believed the surface viscosity is the chief factor in the development of foam lamellae (Kitchener and Cooper, 1959). It is generally conceded that there is a

strong correlation between foam stability and surface viscosity. The most important function of enhanced viscosity is to retard drainage of liquid from between the bubbles. It is clear that partial or complete immobilization of the outer surfaces of lamellae will have an increasingly strong effect in retarding flow. Consequently, high surface viscosity stabilizes the lamellae. The rate of coalescence of the bubbles decreases with decreasing bubble size and with increasing viscosity.

3.6.3. DLVO theory

According to Derjaguin (1937) very thin films owe their stability mainly to electrical repulsion between the ionic double layers formed by adsorption on both sides of the thin film.

However, this force needs only be considered when the thickness of the thin film is of the order of 0.05 microns (Harris, 1982). In the case of thicker films, surface elasticity or viscosity affect the kinetics of film drainage and determine their lifetime and stability (Malysa, 1992). Malysa (1998) found that the thinnest of α -terpineol foam lamellae, which were found in the top layers of column flotation cell, on average were 7 – 9 μm in thickness. Therefore, under normal flotation conditions, these shorter-range forces, i.e. electrical repulsion, can be neglected. (Harris, 1982)

3.6.4. Experimental data on the effect of frothers on coalescence

Sagert et al. (1976) determined experimentally the times for coalescence of two bubbles emerging from adjacent nozzles as a function of C_2 to C_6 n-alcohols concentration. The coalescence time was found to increase with the increase in alcohol concentration. The longer chain alcohols stabilize bubbles more efficiently. For the shorter chain alcohols, coalescence times were proportional to the alcohol concentration,

but for n-hexyl alcohol, coalescence times were proportional to the square of the alcohol concentration. n-amyl alcohol behaved in an intermediate manner.

Gourram-Badri et al. (1997) noticed that the two adjacent bubbles coalesce almost immediately in distilled water but when MIBC is added to this system, bubble coalescence decreases and two separate bubbles reach the surface. Goodall and O'Connor (1991) noticed that the frother concentration of greater than 10 ppm had a clear visual effect on the froth phase behavior reducing bubble coalescence and generally producing a more stable froth.

3.6.5. Bubble coalescence in flotation cell

Otake et al. (1977) studied wake coalescence model in a gas column with a stainless steel single nozzle. The coalescence process of two bubbles in a swarm follows three different stages. When two bubbles are brought close to about 3 to 4 times the bubble diameter (critical distance), the upper bubble begins to influence the lower bubble and the lower bubble approaches the upper one with vertical elongation. The following bubble is accelerated and enters the wake of the leading bubble. Then the two bubbles collide with each other and the thin film of liquid separating them is drained. Finally the liquid layer is ruptured and coalescence occurs. There is better chance of coalescence if the leading bubble is larger than the following one. Nevers and Wu, (1971) studied a wake-coalescence model in a flotation cell and found that the coalescence can be described reasonably well using this model.

Lee et al. (1987) and Prince and Blanch (1990) modeled bubble coalescence by considering bubble collisions due to turbulence, buoyancy, and laminar shear, and by analysis of the coalescence efficiency of collisions. The coalescence rate is intimately connected to the collision rate. In order to determine whether a given collision will result

in coalescence, it is necessary to determine the collision efficiency. Two bubbles will coalesce if they remain in contact for a period of time sufficient for the liquid film between them to thin to the critical value necessary for rupture. A primary cause of bubble collisions is the fluctuating turbulent velocity of the liquid phase. The increase in coalescence rates at higher gas throughputs is due to the dramatic increase in collision events.

Lee et al. (1987) observed that the bubble size affects both the coalescence time and the mean contact time. The larger the bubble size, the longer the coalescence time and the mean contact time. The bubble coalescence efficiency decreases with increasing coalescence time but it increases with increasing mean contact time. Thus, in the small bubble region where the bubble size has a stronger influence on the coalescence time than on the mean contact time, the bubble coalescence efficiency decreases with increasing bubble diameter. However, in the large bubble region the effect of bubble size on the mean contact time is more significant than that on the coalescence time. Therefore, the bubble coalescence efficiency will reach a minimum somewhere in the transition region before it begins to increase with bubble diameter in the large bubble region.

Aldrich and Feng (2000) noticed that the mean bubble diameter in the pulp phase is smaller than that in the froth phase at lower frother concentration due to bubble coalescence. The smaller bubbles coalesced into large bubbles as they moved up. At higher frother dosages, the size of bubbles in the pulp was similar to that in the froth.

CHAPTER 4

EXPERIMENTAL

4.1. Materials

4.1.1. Frothers

Experiments were performed using five different frothers: MIBC and four hexanol isomers/derivatives kindly provided by the Condea Vista Company.

MIBC:	Methyl Isobutyl Carbinol [(CH ₃) ₂ CHCH ₂ CH(OH)CH ₃] (MW: 102 g/mol)
Frother 1:	n-Hexanol [C ₆ H ₁₃ OH] (MW: 102 g/mol)
Frother 2:	Di ethoxy-mono propoxy hexanol [C ₆ H ₁₃ O H(EO) ₂ (PO)](MW: 253 g/mol)
Frother 3:	Di ethoxy hexanol [C ₆ H ₁₃ O H(EO) ₂] (MW: 194 g/mol)
Frother 4:	Mono propoxy-di ethoxy hexanol[C ₆ H ₁₃ O H(PO) (EO) ₂](MW: 268 g/mol)

4.1.2. Solutions

All the experiments were conducted at 21 ± 1 °C using distilled water from a Barnstead still/distillation unit.

For each of the five frothers tested, 0.1 percent stock solutions were prepared by adding 1g of each frother to 500 ml of distilled water in a 1 liter Pyrex volumetric flask. The flask was shaken vigorously for approximately 5 minutes, topped up to 1 liter mark and again vigorously shaken. A Mettler PC440 analytical balance with ± 0.002 g accuracy was used to weigh the frothers.

Two liters of the solution were used for the single -, three - hole bubble sizers and the tests in an Open-top Leeds flotation cell.

4.1.3. Spargers

Latex spargers.

A latex sheet was cut and mounted on the 10 cm diameter sparger unit with a hose clamp. Two holes were punctured using hypodermic syringe. The two holes were 4 cm apart to eliminate any possibility of coalescence so that they could be used as a single-hole sparger. Each hole was 2 cm from the center of the sparger.

Bronze spargers

Figure 4. Simplified bronze spargers.

Figure 5. Three-hole bronze sparger with coalescence funnel.

The bronze sparger was constructed from a 13 mm diameter bronze plate with either 0.1 mm or 0.15 mm drilled holes as shown in Figures 4a and 4b. The Plexiglas sparger casing was designed to allow easy exchange of different bronze plates.

Coalescence of bubbles was studied using the three-hole bronze sparger. The holes were separated 4 mm from each other. The experiment was conducted by placing a Kimax glass funnel on top of the sparger casing unit to force the bubbles to contact each other at the top of the funnel for a split second as shown in Figure 5.

4.2. UCT bubble size meter

The UCT bubble size meter with a 0.8 mm glass capillary was employed to measure the bubble size as described by Tucker et al. (1994). The general arrangement of the bubble generation tank and the UCT bubble sizer is shown in Figure 6.

The bubbles are drawn through the capillary detector under vacuum and collected in a gas burette. The total volume collected (corrected for ambient pressure) during the measurement cycle is recorded and entered into a PC at the end of the data collection. The program (BUBPRO) requires the total volume in order to determine the absolute size of the bubbles. Individual bubble sizes are calculated as a fraction of the total volume, proportional to the “length” pulse and inversely proportional to the “velocity” pulse.

A variable speed Master flex pump (Cole-Parmer Instrument Co.) was used to draw bubbles into the capillary detectors. A “damping pot” was used to eliminate the pulsing. Pulsing may have an undesirable effect on the sampling, making it difficult to read values of the gas burette.

The detector assembly incorporates both the optical detectors and the gas burette for measuring the total collected gas volume. The gas/liquid separation occurs in the

glass bulb immediately below the burette (“de-bubbler” unit). The bubbles are piped to this bulb via the flexible plastic capillary which is attached to the top of the glass capillary in which the optical detection occurs. The linear velocity in the glass capillary, when a gas bubble passes is in the order of 1 m/second. As the downward velocity of the water in the de-bubbler is only a few mm/second the bubbles rise directly into the gas burette. This de-bubbling process can be observed and it is a good indication that sampling is occurring and that the separation is effective. See Appendix C for more detailed UCT bubble size analyzer operation procedures.

The measurement assumes no bubble coalescence in the measuring capillary.

4.3. Methods

4.3.1. Bubble Size Measurements

The bubbles generated in either a single-hole or three-hole sparger passed through a coalescence funnel (Figure 5) before reporting to the UCT bubble size sampler. This fixture forced bubbles to collide with each other prior to collection in the sampler. In the experiments conducted in an Open Top Leeds Flotation Cell bubbles collide frequently with each other due to high intensity stirring, therefore, the coalescence funnel was not needed. Consequently, in both cases the measured bubble size results not only from the sparger dispersing efficiency, but also from the bubble coalescence.

The bubbles were generated through bronze spargers in a 3 liter Plexiglas tank using distilled water or aqueous solutions of different frothers. All experiments were conducted at $21 \pm 1^\circ \text{C}$. Approximately 3000 bubbles were sampled for each run and the measured mean bubble diameter is characterized by a very low standard deviation.

(Tables 3, 6) Three runs were carried out for each concentration of tested surfactant and the average of three runs is reported.

The size of a bubble forming at an orifice under equilibrium conditions can be calculated using thermodynamic data. To create conditions as close to equilibrium as possible, bubbles were generated at very low air flow rates of $2 \text{ cm}^3/\text{min}$ using a Bel-Art Rite flowmeter.

Figure 6: UCT bubble size measuring set-up

Rigid, bronze sparger was used for single and three hole sparger studies.

However, the bronze spargers produced very unpredictable and irregular flow of bubbles varying in size. To regulate the bubble size, it was decided to vibrate the rigid sparger system and in this way imitating latex sparger characteristics (see the discussion section for a full explanation).

The bubble generation tank was mounted on a Syntron Lapping-Polishing Machine and vibration was applied. As the frequency of the vibration increased stepwise, a small window of frequency was found in which the size of the generated bubbles became very uniform and consistent (within 5 %) over 5 runs of the bubble size measurements. This vibration frequency was thus set for the entire experiment.

In the experiments carried out in an open top Leeds flotation cell, the impeller speed was set at 1,000 rpm and the air flow rate was set at 5 L/min. The glass capillary sampler of the UCT bubble size meter was positioned 50 mm above the stator.

All bubble size measurements show quite broad bubble size distributions. Therefore, in this type of measurement it is important to decide on an appropriate measure of the change in bubble size that a certain surfactant causes. The most common became a calculation of the surface-volume mean diameter, also known as the Sauter diameter (Zieminski et al., 1967; Sweet et al., 1997) which was adopted in this study. The mean Sauter bubble diameters were calculated from the measured bubble sizes as follows:

$$d_s = \frac{6V}{A} = \frac{6 \sum \frac{1}{6} \pi d^3}{\sum \pi d^2} = \frac{\sum d^3}{\sum d^2} \quad (16)$$

A is the total area of the captured bubbles, (mm²)

V is the total volume of the captured bubbles, (mm^3)

d_s is the Sauter mean diameter, (mm)

Bubcap4.exe program is used to collect the data from the microprocessor. This data is then collated and analyzed by Bubpro.exe. The mean bubble diameter and other bubble statistics are given by this program (appendix B).

4.3.2. Sparger hole size determination

Following published data (Dobby and Finch, 1986, Diaz-Penafiel and Dobby, 1994), it was decided to work with bubbles of 1 to 2 mm in size, as they are most common for flotation systems. Using Eq. (20), the required size of the sparger opening was calculated to be within 0.1 – 0.15 mm, and drills of this size were used.

4.3.3. Dynamic Foamability Index

Figure 7. Determination of rt for MIBC frother

Since this methodology employs a two-phase system consisting of liquid and dispersed air, it has been decided to use the term foam instead of froth as put forward in the original publications by Malysa et al. (1978, 1981). The foamability measurement in

Malysa's procedure defines the retention time, rt , as the slope of the linear part of the dependence of the total gas volume contained in the system (solution + foam) on the gas flow rate as shown in Figure 7. Values of the retention time are claimed to be independent of the gas flow rate and geometry of the measuring column. Physically, rt is the average lifetime of a bubble in the whole system, *i.e.* in both solution and foam.

The dynamic foamability index (DFI) is defined as the limiting slope of rt vs. concentration as $c \rightarrow 0$.

$$DFI = \left(\frac{\partial rt}{\partial c} \right)_{c=0} \quad (17)$$

Graphical method of DFI determination was employed for this thesis as shown in Figure 8. Linear regression analysis was conducted to find the initial slope for each rt versus c curve and the slope was reported as the DFI value for each frother.

Figure 8. Retention time vs. Concentration

Alternatively, it is possible to fit an equation to the rt values versus c data in order to alleviate the need to find the initial slope graphically. The equation takes the form of an inverse exponential, which when expanded into a power series gives

$$rt - 2.4 = DFI \cdot c \quad (18)$$

where

$$DFI = rt_{\infty} \cdot k \quad (19)$$

The quantity 2.4 was given by Malysa as the value of rt for distilled water, rt_{∞} is the limiting rt value for $c \rightarrow \infty$, and k is a constant.

In the tests, the aqueous frother solutions were placed in the column (45 mm diameter, 92 cm height). Nitrogen¹ was pumped through the sintered glass disk initially at a flow rate of 100 cm³/min, and then was stepwise increased up to 2,000 cm³/min. After each change the resulting steady state volume (solution + foam) was recorded. The total volume was plotted versus flow rate to obtain the slope (retention time, Figure 7) using linear regression as already described (Sweet *et al.*, 1997).

4.3.4. Surface tension measurements

A Du Nouy Ring Tensiometer was used to measure the surface tension of aqueous solutions, with varying frother concentrations at 21 ± 1 °C (Appendix A). Correction factors were applied to calculate the value of the surface tension (Zuidema and Waters, 1941). The measured values without correction also corresponded well with the known values for distilled water and methanol solutions. The measurements involved preparation of a frother solution which was stirred in a 100 ml beaker for 5 minutes before the measurements.

¹ Nitrogen was used as it was available in the lab.

4.4. Results

4.4.1. Surface tension and bubble size measurements in brine

Both surface tension and bubble sizes were measured in saturated and 50% potash ore flotation brine (Appendix D). Unlike in the water, 6 mole/L of NaCl and KCl, foam height and retention time decreased as the concentration of the frothers increased. The experiments were outside the scope of this thesis and no further tests in brine were carried out.

4.4.2. Surface tension measurements

As Figure 9 shows, frothers 2 and 4 (containing propylene oxide groups) reduce the values of the surface tension significantly, whereas MIBC and n-hexanol are definitely less surface active. The surface tension values for frother 3 are situated somewhere between these two groups.

Figure 9. Effect of concentration on surface tension for tested frothers.

4.4.3. Dynamic foamability Index (DFI) measurements

Table 2. Dynamic foamability Index (DFI) measurements

Frothers	DFI (sec x L/mole)
MIBC	33,000
Frother 1	33,000
Frother 2	290,000
Frother 3	94,000
Frother 4	172,000

Frothers 2 and 4 produced the most stable and voluminous foam as shown in Table

2. With MIBC and Frother1, the volume of the foam was much lower. Frother 3 again yielded intermediate values. However, due to the very large fluctuations in foam height while measurements for DFI were being taken, reproducibility of the experiment can be poor.

4.4.4. Single hole sparger studies

4.4.4.1. Latex sparger study

Figure 10. Effect of frother concentration on bubble size using a latex sparger.

Frothers did not have any notable effect on bubble size over the tested concentration range when bubbles were generated from the single-hole latex sparger.

Figure 10 indicates that very uniform bubble sizes were obtained for each hole regardless of frother concentration (the holes were separated 4 cm from each other to eliminate any possibility of coalescence). The location of the holes, however, had a considerable effect on bubble size. When air is applied, the shape of the latex sparger changes and hence the holes become elongated. The degree of elongation depends on the location of the holes and a range of bubble sizes is generated. Although the holes were punctured using the same hypodermic syringe, 1.46 mm and 2.11 mm diameter bubbles were reported from hole 1 and hole 2, respectively.

4.4.4.2. Bronze sparger study

Figure 11. Effect of frother concentration on bubble size using a bronze single-hole sparger.

The tests carried out using the bronze sparger gave uniform and consistent bubble sizes provided that the sparger was vibrated (Figure 11).

The results shown in Figure 11 are consistent with equation (20). Since the surface tension measurements are constant over the tested concentration range the bubble size should be constant according to equation (20). Using this equation, the calculated

Sauter mean diameters of the bubbles generated from 0.1 mm and 0.15 mm spargers were 1.65 mm ($\sigma = 0.029$ mm) and 1.88 mm ($\sigma = 0.017$ mm), respectively. The average bubble sizes actually produced from the bronze spargers (figure 11) were in perfect agreement with the calculated sizes as shown in Table 3. In these experiments the bubble size did not change with frother concentration.

4.4.4.3. Three-hole sparger (0.1mm diameter) and Flotation cell studies

In the experiments with a three-hole sparger as well as in those carried out using a flotation cell, the measured size of the bubbles decreased with frother concentration (Figs. 12 and 13). In the case of frothers 2 and 4, very fine bubbles were obtained at very low frother concentrations.

Figure 12. Effect of frother concentration on bubble size using 0.1mm diameter 3-hole bronze sparger.

Apparently the degree of coalescence decreases with increasing frother concentration in such measurements. More powerful frothers (frothers 2 and 4) are characterized by greater ability to prevent bubble coalescence at lower concentrations.

Figure 13. Effect of frother concentration on bubble size measured in an Open-Top Leeds Flotation cell.

As the measurements of surface tension revealed, frothers 2 and 4 turned out to be more surface active than frother 3, hexanol and MIBC. The obvious difference between these two groups is the presence of a propylene oxide group in frothers 2 and 4.

As Figures 12 and 13 show, the Critical Coalescence Concentration (CCC) values were obtained by finding the intersections of the horizontal asymptote to the Sauter mean bubble diameter vs. frother concentration curve at higher concentrations with the slope of the line approximating the curve at lower concentrations.

4.5. Discussion

The flexible latex sheet single-hole sparger produced uniform size of bubbles as shown in Fig. 10 (Sauter mean diameters of 1.46 ± 0.029 mm and 2.11 ± 0.017 mm). However, depending on the location of the holes in the sparger, the size of the generated bubbles changed dramatically (1.46 mm vs. 2.11 mm). This suggests that the size of holes was not identical even though the holes were punctured using the same hypodermic syringe. Although methods of finding equivalent hole size were proposed (Rice and Howell, 1987), since the holes are not circular in the latex type spargers (Rice *et al.*, 1981), it is very difficult to determine the exact hole diameter. To overcome the uncertainty caused by the size of holes, rigid, bronze spargers were employed. While the hole diameter can easily be determined for such spargers, it turned out to be impossible to obtain a steady stream of bubbles at low flow rates. Rice and Lakhani (1983) noticed that at superficial gas velocities of less than $5 \text{ cm}^3/\text{sec}$, a rubber sparger produced a homogenous stream of bubbles as compared to the very unpredictable flow and size of bubbles when rigid spargers were employed. Since the only difference between the flexible latex sparger and the rigid bronze plate sparger is the ability of the latex sheet to oscillate and deform as gas passes through, it was decided to vibrate the rigid sparger system to mimic the latex sparger characteristics.

Prediction of bubble size for both rigid and flexible spargers is quite complicated. The analysis of the forces affecting the bubble includes buoyancy and gas flow momentum which are balanced by surface tension force, drag force and inertia (Geary and Rice, 1991). Rubinstein (1995) showed that for a bubble generation at bubble velocity $U_b = 0$, for bubbles $d_b > 0.2$ mm the detaching bubble diameter can be calculated from the following simplified equation.

$$d_b = \left(\frac{6d_c\gamma}{g(\rho_l - \rho_g)} \right)^{1/3} \quad (20)$$

Where d_b is the bubble diameter, γ is the surface tension of the liquid, d_c is the size of the capillary, ρ_l is the density of the liquid, and ρ_g is the density of gas.

As this equation shows, under certain conditions the bubble size depends only on inner capillary diameter (or sparger hole size) and surface tension of the solution.

Since the surface tension was practically constant throughout the range of tested frother concentrations (Figure 9), the size of generated bubbles was expected to be uniform for the same hole size spargers. As shown in Figure 10, the results are consistent with published equation 20.

Calculated diameters (from equation 20) of the bubbles generated from 0.1 mm and 0.15 mm spargers were 1.65 mm and 1.88 mm, respectively. The average bubble sizes actually produced from the bronze spargers were in perfect agreement with the calculated sizes as shown in Table 3 and Figure 11 and did not change with frother concentration.

If the three bubbles generated at the same time in a three-hole sparger are forced to collide in the coalescence funnel and are not stable then one large bubble can result. However, a wide spread of bubble sizes was obtained at lower frother concentrations indicating that three bubbles did not always coalesce into one at the top of the Kimax glass funnel. This wide spread of bubble size distribution is mainly caused by the inability to produce three bubbles at the same time from the three-hole bronze sparger. The spread was not found in Open-Top Leeds flotation experiments (appendix B). With increasing frother concentration the Sauter mean bubble diameter decreased and the

spread of the measured sizes also became narrower (Figure 14). Taking 1.65 mm (Table 3) as the average bubble diameter generated from the 0.10 mm three-hole sparger, three 1.65 mm bubbles when coalescing should give a larger bubble of 2.38 mm in diameter. This is again in a good agreement with the measured mean bubble diameters without any added frothers (Figure 12).

Figure 14. Bubble size distribution of 9,000 bubbles measured using 0.1 mm diameter 3-hole bronze sparger (Frother 1).

Table 3: Comparison of calculated (using Equation 20) vs. measured Sauter mean bubble diameters.

Capillary diameter (mm)	Calculated bubble diameter (mm)	Average measured Sauter mean bubble diameter $\pm$ st. dev.(mm)
0.10	1.65	1.65 ± 0.029
0.15	1.88	1.89 ± 0.017

Since the frothers do not affect the size of bubbles generated using a single hole sparger over the tested frother concentrations, the only possible mechanism that might affect bubble size when a multi hole sparger (or a flotation cell) is utilized would be the coalescence and/or breakage of bubbles. The measured bubble sizes were much smaller

than the critical size at which bubbles are prone to breakage (Prince and Blanch, 1990). Bubble breakage should therefore be ruled out as a possible mechanism for bubble size changes. This leaves bubble coalescence as the only possible mechanism responsible for bubble size changes in our multi-hole sparger and Open top Leeds flotation cell experiments.

It is commonly believed that the bubble size decreases with an increase in the frother concentration owing to a decrease in the surface tension. Such a conclusion can also be found in a very recent paper (Aldrich and Feng, 2000). As this thesis results demonstrate, at frother concentrations typical for the froth flotation systems, the bubble size in a flotation cell is not at all related to the surface tension. This confirms the validity of results obtained by Sweet et al. (1997) suggesting that there is a poor correlation between bubble size and surface tension.

Figure 1 compares the effect of concentration of two hexanol isomers on bubble size, retention time (foamability) and surface tension (Sweet et al., 1997). In order to facilitate comparisons the results were plotted in a normalized form. The term “normalization” is used to describe the ratio of the parameter of interest to its value measured at zero surfactant concentration.

As shown in Figure 1, the surface tension seems to be least sensitive to the surfactant concentration; both bubble size and retention time are affected by frother at the concentrations at which the surface tension values are practically identical to those of distilled water. Similar plots for other frothers give the same trend. Discussion of these results was hindered by the fact that the bubble size and foamability in this particular

project were measured with Cape Town tap water, while the surface tension data obtained using distilled water were quoted after other sources (Sweet et al., 1997).

Figure 15. Effect of MIBC on surface tension and bubble sizes generated from the 0.1mm single hole sparger and the Open-top Leeds flotation cell.

Figure 15 shows the effect of MIBC concentration in distilled water on bubble size and surface tension. This figure demonstrates beyond any doubt that bubble size in a flotation cell is not determined by a surface tension. It also reveals that bubble size is much more sensitive to the surfactant concentration than surface tension, and a bubble size measurements could be used for analytical purposes to test the presence of surface active substances at very low concentrations (as shown in Figure 15).

As Figures 10, 11, 12 and 13 reveal, in the experiments in which single-hole spargers were utilized (that is, under conditions in which bubbles could not collide with each other), there was no effect of frother concentration on bubble size. If the experiments were carried out using multi-hole spargers, or were carried out in a flotation cell, the size of bubbles was substantially larger at low frother concentrations. Xu and

Finch (1988) noticed that the gas hold-up became smaller (bubbles larger) without baffling between the spargers in a column flotation cell. The cause of this phenomenon was not however determined. It seems now that this effect was caused by the coalescence of bubbles. Without baffling, bubbles collide with each other as they are produced and coalescence occurs.

With increasing frother concentration, the degree of the bubble coalescence decreases and at a particular concentration (Critical Coalescence Concentration), the coalescence of the bubbles is completely prevented. The stronger frothers (those containing propylene oxide groups) reached the CCC point at a lower concentration. The values of the CCC seem to characterize the frothers very well; at concentrations

Figure 16. Effect of frother concentration on surface tension and CCC for tested frothers.

exceeding CCC, coalescence does not occur (Figures 12 and 13). Frothers 2 and 4 needed lower concentrations to reach the CCC values than MIBC, frothers 1 and 3. A very similar trend and the CCC values were observed in the Open Top Lead Flotation

Cell experiments (Figure 13). As shown in Figure 16, the CCC for all 5 frothers are reached while the surface tension values are practically identical to those of distilled water.

The smallest bubble size in a multi-hole sparger or flotation cell is achieved when coalescence does not occur, that is at the frother concentration exceeding CCC. The smallest bubble size, in other words, is the original size of the bubbles generated from spargers before any secondary process (such as coalescence) takes place. Since the size of generated bubbles and consistency of bubble size distribution are the two main factors used to compare different sparging systems (Rice *et al.*, 1981; Finch and Dobby, 1990), a true comparison can only be made when the secondary processes are eliminated. This happens only in solutions where frother concentration exceeds CCC.

Table 4: Comparison of CCC values obtained using a three-hole sparger and an open top Leeds flotation cell

Frothers	Three hole sparger CCC values (mol/l)	Open top flotation cell CCC values (mol/l)
MIBC	0.000077	0.000086
Frother 1	0.000077	0.000086
Frother 2	0.000017	0.000017
Frother 3	0.000031	0.000035
Frother 4	0.000017	0.000017

The three-hole sparger experiment, conducted in a controlled environment, provided CCC values that were identical to those obtained in an Open-Top Leeds Flotation Cell. This implies that the CCC values obtained for a given frother do not depend on the type of flotation cell employed in carrying out the experiments.

As seen from Table 4, the five tested frothers are characterized by unique CCC values. It is also possible to determine the CCC values from the data of Tucker *et al.* (1994) who measured the size of bubbles in a flotation cell using DIBK (di-isobutyl ketone), TEB (triethoxybutane), and MIBC frothers. Figure 17 shows the CCC values for

these three frothers. Tucker *et al.* (1994) and Goodall and O'Connor (1991) found that the size of bubbles did not change when MIBC concentration exceeded approximately 10 ppm (0.0001 mol/L). Although the current experiments were conducted in different flotation cells and under different conditions, the CCC values for MIBC are very similar.

Figure 17. Determination of CCC for Tucker et al.'s (1994) bubble size vs. frother concentration curves.

Figure 18 summarizes the effect of frothers on bubble size. At frother concentrations C lower than CCC, the bubble size is determined by coalescence. At frother concentrations that exceed CCC, bubble size is no longer determined by coalescence but depends on the sparger geometry and hydrodynamic conditions.

Fig. 18. Effect of frother concentration on bubble size (schematic).

Frother 2 in both Figures 12 and 13 shows a minimum on the bubble size vs. concentration curve around the CCC. As it is known, the presence of impurities in minute quantities causes the appearance of a minimum in the surface tension – concentration curve around the Critical Micelle Concentrations (CMC) (Leja, 1982). The existence of such a minimum has been employed as a very sensitive test for detecting the presence of an impurity-surfactant in a given surfactant sample. For purified surfactants the minimum in the γ – concentration curve disappears. It is possible that impurities also affect the bubble size in the conducted experiments. For frother 2, a minimum in the bubble sizes vs. concentration curve has been consistently observed (Figures 12 and 13). One can speculate that this is caused by the presence of some impurities in frother 2. Since the bubble size measurements are much more sensitive to low frother

concentrations than surface tension, the presence of such minima could possibly be used as a sensitive test for detecting the presence of impurities.

Figures 19 and 20 show the normalized relationships for 3-hole sparger and the Open Top Leeds Flotation experiments. As these Figures demonstrate, all the bubble size vs. frother concentration curves when plotted versus the normalized frother concentration (that is vs. C/CCC) converge on one single curve giving credence to the proposed explanation that rests principally on the coalescence as the main mechanism controlling the bubble size in foams. If coalescence determines the bubble size, then the measured CCC values should also correlate with the Dynamic Foamability Index.

Figure 19. Effect of normalized frother concentration on bubble size measured using 3-hole bronze sparger.

Figure 20. Effect of normalized frother concentration on bubble size measured in an Open-Top Leeds Flotation cell.

Figure 21. Relationship between DFI and Critical Coalescence Concentration for the tested frothers.

Table 5: DFI values for various commercial frothers using Cape Town tap water (Sweet et al., 1997)

Frothers	rt (s)	k (dm ³ /mol)	DFI (s•dm ³ /mol)
n-Butanol	20.5	65.3	1,000
2 -Butanol	12.7	65.0	800
t-Butanol	10.8	146.6	1,600
n-Pentanol	22.6	243.7	5,500
n-Hexanol	62.6	539.6	34,000
n-Heptanol	82.5	495.6	41,000
n-Octanol	87.3	908.5	79,000
n-Octanol	61.1	2,313.3	141,000
2-Ethyl-Hexanol	68.3	2,066.8	141,000
MIBC	55.0	672.2	37,000
a-Terpineol	27.1	5,093.9	138,000
Texanol	31.2	10,392.7	324,000
TEB	34.7	7,279.4	253,000
DowFroth 400	72.8	11,025.7	802,000
DIBK	21.5	3,589.6	77,000
n-Butanol*	20.8	61.0	1,000

* Test conducted in distilled water

Fig. 22. Effect of concentration of tested n-alcohols on the normalized Sauter mean bubble diameter. (Sweet et al., 1997)

Figure 21 shows the relation between CCC and DFI and demonstrates that the foamability of aqueous solutions measured under dynamic conditions is determined by bubble coalescence. The frothers characterized by lower CCC values give higher DFI values. The DFI values determined for various frothers using Cape Town tap water are shown in Table 5 (Sweet et al, 1997). It should thus be possible to predict CCC values for frothers used in these experiments.

Fig. 23. Relationship between DFI and $C_{0.6}$ (Sweet et al., 1997), dashed line, and DFI and CCC (from Fig. 7), continuous line.

Sweet et al. (1997) discussed their results in terms of an empirical coefficient that did not have any physical meaning, the $C_{0.6}$ concentration. This empirical coefficient was defined as the frother concentration at which the Sauter mean bubble diameter was reduced to 0.6 of its original value in water (at zero surfactant concentration). Figure 22 shows how the $C_{0.6}$ values were obtained from the experiments. As Figure 22 indicates,

the $C_{0.6}$ frother concentration is quite close to the critical coalescence concentration (CCC). Figure 23 provides an entirely different physical meaning for the correlations discussed by Sweet et al (1997). Only because the experimental $C_{0.6}$ values happen to be close to the CCC values, is the $DFI = f(CCC)$ plot (continuous bold line), which has a well defined physical meaning, not very different from the empirical relation $DFI = f(C_{0.6})$ obtained by Sweet et al. (1997) for two series of frothers (Figure 23).

4.6. Experimental Errors

4.6.1. Reproducibility of bubble size measurement

Numerous authors reported excellent reproducibilities of the UCT bubble size meter. O'Connor et al., (1990) carried out six repeat experiments for a two-phase (air/water) system and found a mean bubble size of 2.822 mm ($\sigma = 0.015$ mm). Since the standard deviation gives an indication of the distribution of bubble sizes, the low standard deviation of the repeat experiments proved that the reproducibility was excellent. Tucker et al., (1994) showed excellent reproducibility of the UCT bubble size meter as well. He found that an average mean bubble size was 1.945 mm with standard deviation of 0.023 mm.

The same UCT bubble size meter was employed in this study, and therefore the same degree of reproducibility was expected. Single hole bubble size measurements were carried out in 5 ppm of frother 1 solution to establish the accuracy of the results. In six repeat experiments for the 0.1 mm and 0.15 mm hole spargers, the mean bubble sizes produced were 1.659 ($\sigma = 0.0079$) and 1.878 ($\sigma = 0.0081$) mm. As shown in Tables 3 and 6 the standard deviations were very small in accordance with other reported data.

Table 6: Repeat experiments for 0.1 and 0.15 mm hole bubble size analyses.

	1mm hole bubble size	1.5 mm hole bubble size
Run 1	1.6694	1.8852
Run 2	1.6513	1.8756
Run 3	1.6519	1.8765
Run 4	1.6561	1.8649
Run 5	1.6681	1.8806
Run 6	1.6595	1.8873
Mean bubble size	1.6594	1.8784
Standard deviation	0.00785	0.00805

Figure 24. Effect of frother concentration on bubble size using a bronze single hole sparger for frother 1 with t-test at 95% confidence interval.

4.6.2. Possible experimental errors

In addition to the experimental error of the UCT bubble sizer (which was shown to be small) the overall error is also affected by:

- (i) weighing of frother using a Mettler PC 440 analytical balance with $\pm 0.002\text{g}$ accuracy. The error in preparing one liter of 0.1 % stock solution is $1\text{g} \pm 0.002\text{ g}$ or 0.2%.
- (ii) The volume reading of the meniscus when pipetting a given volume of the stock solution.
- (iii) Possible effect of temperature since the experiments were carried out

at $21 \pm 1^{\circ}\text{C}$. As shown in Figure 24, the combined effect of all possible errors is so small that the resulting 95% confidence intervals calculated by the t-test are very narrow.

The 95% confidence intervals shown for both holes of the bronze sparger along with Sauter mean bubble size values are far apart from each other indicating that the differences between the measured sizes of the bubbles generated for different holes are statistically significant. (See appendix E for a detailed explanation of the t-test)

CHAPTER 5

CONCLUSIONS

The bubble size in a flotation cell is not related to the surface tension at frother concentrations typical for froth flotation systems. The bubble size is determined by bubble coalescence at frother concentrations lower than the CCC. At frother concentrations higher than the CCC the bubble size is no longer determined by bubble coalescence but is determined by sparger geometry and hydrodynamic conditions.

The ability of frothers to prevent bubble coalescence is well characterized by the Critical Coalescence Concentration (CCC).

Foam stability measured under dynamic conditions is determined by bubble coalescence.

In the tests aiming at comparisons of different flotation spargers, frother solutions with concentrations higher than the CCC should be utilized.

CHAPTER 6

RECOMMENDATIONS

A new method has been developed to characterize flotation frothers. Bubble size measurements provide a sensitive technique to characterize flotation frothers and thus to study an important part of the flotation process. However, since this is a new method, it is recommended the following be further studied:

- More tests should be conducted using different flotation frothers to identify their unique CCCs.
- It is a common practice for the industry to use frother blends to optimize selectivity and recovery of valuable minerals. However, the industry does not have any means of quantifying the optimization of the frother blends. Finding CCC values for each frother blend will give guidance to their effect on bubble size and stability of foams.
- The bubble size measurements should be explored further as a very sensitive test for detecting impurities.
- The presence of the minimum on the bubble size concentration curve should be tested further. This could be done by studying different frother solutions with minute additions of another surfactant.

NOMENCLATURE

A	Total area of the capture bubbles, (mm ²)
c	Concentration of frother (mol/l)
CCC	Critical Coalescence Concentration, (mol/l)
d ₃₂	Sauter mean bubble diameter, (mm)
d _b	Bubble diameter, (mm)
d _c	Size of the capillary
DFI	Dynamic foamability index
d _s	Sauter mean diameter, (mm)
g	gravitational acceleration, (m/s ²)
HLB	Hydrophilic – lyophilic balance
J _g	Superficial gas velocity, (m/s)
J _L	Superficial liquid velocity
k	Constant
k _c	Flotation rate constant
L ₀	Aerated pulp height, (m)
MIBC	Methyl Isobutyl Carbinol
N _{Fr}	Modified Froude number
P	Probability of collection
R	Gas constant
Re	Reynolds number
rt	retention time, (s)
S _b	Bubble surface area flux, (m ² /m ² s)
T	Temperature, (K)
TEB	Triethoxybutane
u	Gas velocity through nozzle
U	Superficial liquid velocity
U _{bs}	Slip velocity between bubbles and fluid
U _s	Slip velocity between bubbles and liquid
U _T	Terminal bubble rise velocity
V	Total volume of the captured bubbles, (mm ³)
σ	Standard deviation

Greek Symbols

γ	Surface tension, (mN/m)
Γ	Adsorption
δ	Nozzle diameter
ε ₀	Static gas hold-up in the gas-liquid reactor
μ _f	Viscosity of liquid
μ _L	Liquid viscosity
ρ _f	Density of liquid, (g/cm ³)
v _f	Superficial velocity of liquid
v _g	Superficial velocity of gas
ε _g	Fractional gas hold up
ε _L	Fractional liquid holdup

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APPENDIX A

SURFACE TENSION MEASUREMENT

A.1 Du Nouy ring method

The static surface tension of the methanol solutions was measured by the Du Nouy ring method (Adamson, 1967). In this method a platinum wire ring is immersed in the liquid solution and the force necessary to lift and detach a film of the liquid is measured. The force of detachment W is described as:

$$W = 2\pi R \gamma + 2\pi(R+2r) \gamma + (\pi(R+2r)^2 - \pi R^2) 2\gamma \quad \text{and} \\ \gamma = W/2\pi (R + r)(1 + 2r)$$

The dimensions at the plane of breakage, R and r , are related to the dimensions of the ring, and the mass of the liquid lifted during the detachment (Figure A.1). The maximum weight W causing ring to separate is related to the surface tension through a correction factor F . The correction factor is calculated from the equation given below:

$$(F - a)^2 = (4b/\pi^2 \times 1/R^2) \times \gamma' / d_w + C$$

where

$$a = 0.7250$$

$$b = 0.00090705$$

$$c = 0.04534 - 1.679 (r/R)$$

$$d_w = \text{density of water}$$

$$\gamma' = \text{apparent surface tension}$$

$$\gamma = \gamma' \times F$$

Prior to the surface tension measurement, the calibration of the Tensiometer was performed using known weights. The weights were placed on the ring and the dial rotated to keep the index level. The results were graphed as the dial values versus apparent surface tension γ' by using the relationship

$$\gamma = Mg/2L$$

M is weight placed on ring, in grams

G is the gravity value cm/sec^2

L mean circumference of the ring

γ' apparent surface tension, dyne/cm, dial reading

For each measurement, 50 ml of prepared methanol solutions is poured in a clean sample container and placed carefully on the leveled platform of the Tensiometer. The platform is raised until the ring is immersed in the solution to a depth not exceeding 6 mm. Then the platform is lowered slowly, increasing the torque of the ring by keeping the pointer on the zero mark. Proceeding slowly with the adjustment, the dial reading at which the rupture of the solution film took place is recorded. The apparent value of the surface tension is read from the calibration curve.

a

b

**Figure A.1. Distention of surface film during surface tension measurement (a);
Condition of surface film at breaking point (b).**

APPENDIX B

BUBBLE SIZER STATISTICS

SUMMARY OF FILE

Typical Open top Leeds flotation cell test.
(15 ppm of frother 3 was used for this particular test)

Mean bubble volume -----	0.0008 (ml)
Standard deviation (volume) -----	0.0074 (ml)
Mean bubble diameter -----	0.8897 (mm)
Standard deviation (diameter) -----	0.4046 (mm)
Mean bubble surface area -----	3.0009 (mm ²)
Standard deviation area -----	6.5080 (mm ²)
Total bubble surface area -----	6616.9 (mm ²)
Number of velocity readings -----	1695
Number of period readings -----	2205
% Discrepancy in readings -----	23.13
Average Water Pulse Length -----	23.9181
Average Air Pulse Length -----	4.6096
The Bubble volume captured in the burette	1.80 (ml)

Figure B.1 . Typical bubble diameter distribution histogram for the Open top Leeds flotation cell. (15 ppm of frother 3 was used for this particular test.)

SUMMARY OF FILE
Typical Latex sparger test.
(5 ppm of Frother 2 was used for this particular test.)

Mean bubble volume -----	0.0018 (ml)
Standard deviation (volume) -----	0.0003 (ml)
Mean bubble diameter -----	1.4964 (mm)
Standard deviation (diameter) -----	0.0727 (mm)
Mean bubble surface area -----	7.0513 (mm ²)
Standard deviation area -----	0.6895 (mm ²)
Total bubble surface area -----	20392.4 (mm ²)
Number of velocity readings -----	2888
Number of period readings -----	2892
% Discrepancy in readings -----	0.14
Average Water Pulse Length -----	33.7070
Average Air Pulse Length -----	4.4694
The Bubble volume captured in the burette	5.11 (ml)

Figure B.2. Typical bubble diameter distribution histogram for the Latex sparger test. (5 ppm of frother 2 was used for this particular test.)

SUMMARY OF FILE
Typical 0.15 mm hole diameter bronze sparger test.
(Distilled water was used for this particular test.)

Mean bubble volume -----	0.0035 (ml)
Standard deviation (volume) -----	0.0003 (ml)
Mean bubble diameter -----	1.8852 (mm)
Standard deviation (diameter) -----	0.0475 (mm)
Mean bubble surface area -----	11.1725 (mm ²)
Standard deviation area -----	0.5506 (mm ²)
Total bubble surface area -----	26065.3 (mm ²)
Number of velocity readings -----	2331
Number of period readings -----	2333
% Discrepancy in readings -----	0.09
Average Water Pulse Length -----	119.5520
Average Air Pulse Length -----	9.2418
The Bubble volume captured in the burette	8.20 (ml)

Figure B.3. Typical bubble diameter distribution histogram for 0.15 mm hole diameter bronze sparger test. (Distilled water was used for this particular test.)

SUMMARY OF FILE
Typical three-0.1 mm hole diameter bronze sparger test.
(6 ppm of Frother 3 was used for this particular test.)

Mean bubble volume -----	0.0030 (ml)
Standard deviation (volume) -----	0.0015 (ml)
Mean bubble diameter -----	1.7420 (mm)
Standard deviation (diameter) -----	0.2543 (mm)
Mean bubble surface area -----	9.7358 (mm ²)
Standard deviation area -----	3.0063 (mm ²)
Total bubble surface area -----	21428.5 (mm ²)
Number of velocity readings -----	2195
Number of period readings -----	2201
% Discrepancy in readings -----	0.27
Average Water Pulse Length -----	173.6289
Average Air Pulse Length -----	8.3924
The Bubble volume captured in the burette	6.50 (ml)

Figure B.4. Typical bubble diameter distribution histogram for three-0.1 mm hole diameter bronze sparger test. (6 ppm of Frother 3 was used for this particular test.)

SUMMARY OF FILE
Typical 0.1 mm hole diameter bronze sparger test.
(10ppm of Frother 3 was used for this particular test.)

Mean bubble volume -----	0.0024 (ml)
Standard deviation (volume) -----	0.0004 (ml)
Mean bubble diameter -----	1.6581 (mm)
Standard deviation (diameter) -----	0.0845 (mm)
Mean bubble surface area -----	8.6594 (mm ²)
Standard deviation area -----	0.9160 (mm ²)
Total bubble surface area -----	20696.0 (mm ²)
Number of velocity readings -----	2388
Number of period readings -----	2390
% Discrepancy in readings -----	0.08
Average Water Pulse Length -----	129.0398
Average Air Pulse Length -----	8.6146
The Bubble volume captured in the burette	5.75 (ml)

Figure B.5. Typical bubble diameter distribution histogram for 0.1 mm hole diameter bronze sparger test. (10 ppm of Frother 3 was used for this particular test.)

APPENDIX C

BUBBLE SIZE ANALYZER MEASUREMENT PROCEDURE

Bubble sizer optical sensor has to be tested prior to a series of bubble size measurements using UCT bubble sizer analyzer.

The following summaries are as shown in the bubble size analyzer operating and service manual (1996).

Appendix C.1. Photo-detector unit: static adjustment.

1. Connect detector to the Photo-Detector (PD) unit and the PD unit to the main bubble sizer unit to the main bubble sizer unit.
2. Set the LED current potentiometers on the main unit to about 30% of maximum (approx. 15 mA).
3. Draw water into the capillary tube.
4. Adjust the "sensitivity" pots on the PD unit so that the Hi LED just turns on (on the edge between the OK LED and the Hi LED). This is not critical, it just indicated that the detector amplifier output is balanced in the middle of its range.
5. Blow the water out of the capillary tube.
6. PD Unit LEDs should switch to Lo.
7. Repeat steps 3 to 6 until reliable switching is achieved.
8. Above verifies correct operation of the optics.
9. Optics adjustments should be verified under dynamic conditions.

Appendix C.2. Zero and Gain adjustment procedures.

Once the photo-detectors have been setup, a bubble stream should be drawn into the capillary and the Zero and Gain pots trimmed so that detection of the bubbles by the threshold detectors occurs reliably.

ZERO adjustment

For each channel, set GAIN to mid range and adjust the ZERO pot so that both HI and LO LEDs flash on as bubbles are detected. Detection is indicated by the LED immediately to the left of the HI/LO LED indicators. Once the HI/LO LEDs are flashing symmetrically proceed to the gain adjust procedure.

GAIN adjustment

Back off the GAIN pot so that the HI amplitude LEDs are just on the edge of flashing. If only the LO amplitude LEDS are indicating the signal amplitude at the threshold detectors is 1 volt. This is the minimum amplitude required for reliable detection, a slightly higher amplitude, indicated by the HI LEDS is usually desirable.

Appendix C.3. Gas volume measurement.

The total volume of gas from all the collected bubbles must be entered into the data capture program at the end of each measurement cycle. This gas volume must be reported at ambient pressure. There are various techniques for equalizing the pressure in the burette prior to recording the volume. The following method for arriving at the correct volume was found to be most effective.

1. Set up the apparatus.
2. Run pump at the required operating speed (typically 30 to 40 ml/min).
3. Turn on air sparger to produce bubbles.
4. Allow burette to reach about half way mark.
5. Turn off air and record gas volume (Vol 1).
6. Turn off pump and vent the "damping pot".
7. Adjust level of water in damping pot to match the level in the burette.
8. Record the new volume in the burette (Vol 2).
9. $\text{Constant} = \text{Vol 2} / \text{Vol 1}$.
10. Repeat 3 – 5 times for accurate result.

During normal operation it is convenient to let the gas volume to reach a certain level, start the measurement, then record the final volume after sufficient bubbles have been detected. The correct volume will then be the difference in volumes multiplied by the correction constant.

Appendix C.4. Bubble size measurement procedure.

1. Ensure that all lines are flooded and no leaks occur when the pump is running.
2. Determine the pressure correction constant for calculating the gas volume at ambient.

3. Fill gas burette with water.
4. Reset MPU timing system by pressing start button.
5. Set Stop/Go switch on the detector system to the stop position.
6. Turn on air sparger to produce bubbles.
7. Verify bubble collection by observing "de-bubbler" and the LED indicators on the detector unit.
8. Switch Stop/Go switch to GO position when burette level reaches a set volume.
9. Record the burette level.
10. Sequence LEDs in the MPU timing unit will indicate "Measuring".
11. After sufficient bubbles have been collected press STOP button on the MPU timing unit. If the STOP button is not pressed the data transmission sequence will automatically commence when the data buffers are full. That is after about 3000 bubbles have been detected. Note that the WARNING LED comes on when the buffer is 75% full.
12. Record burette volume. Apply correction factor to the difference between start and end volumes to get total bubble volume at ambient pressure.
13. The data will then be transmitted to the PC.
14. Enter total bubble volume when prompted by the BUBCAPx program.

The above experimental procedure results in the creation of a data file for each measurement cycle. These file will have the extension BUB. These files must be facilitated by the BUBPRO (data processing) and BUBPLOT (graphics display and plotting) programs.

APPENDIX D

Effect of frothers on bubble size in concentrated electrolyte solution.

Figure D.2. Effect of frother concentration on surface tension measurements in brine solution.

Figure D.1. Effect of frothers on bubble size in saturated & 50% brine (Open top Leeds flotation cell test)

Table D.1. Effect of frothers on DFI values in electrolyte concentration.

Frothers	DFI Values (sec x liter/mole)
MIBC in saturated brine	-11,317
MIBC in 50% brine	-1,809
Frother 2 in saturated brine	-107,301
Frother 2 in 50% brine	-8,252

APPENDIX E

EXAMPLES OF FINDING t – CONFIDENCE INTERVALS

The standardized variable T has a t distribution with $n-1$ degree of freedom, and the area under the corresponding t density curve between $-t_{\alpha/2, n-1}$ and $t_{\alpha/2, n-1}$ is $1 - \alpha$ (area $\alpha/2$ lies in each tail)

Let $\bar{x}$ and s be the sample mean and sample standard deviation computed from the results of a random sample from a normal population with mean μ . Then a $100(1-\alpha)\%$ confidence interval for μ is

$$\left(\bar{x} - t_{\alpha/2, n-1} \cdot \frac{s}{\sqrt{n}}, \bar{x} + t_{\alpha/2, n-1} \cdot \frac{s}{\sqrt{n}} \right) \quad (1E)$$

• **0.1 mm hole bronze sparger (Frother 1)**

Concentration (ppm)	Sauter mean bubble diameter (mm)
0	1.698
2	1.642
4	1.673
6	1.654
8	1.662
10	1.655
15	1.632
Sample mean $\bar{X}$	1.659
Sample standard deviation S	0.021

For 95% confidence intervals:

Number of samples $n = 7$

$\alpha = (100\% - 95\%)/2$

$\alpha = 0.025$

$v = n - 1 = 6$

$t_{\alpha, v} = 2.447$ from Table E.1.

$\bar{X} - t_{\alpha/2, v} \cdot s / \sqrt{n} = 1.636$

$\bar{X} + t_{\alpha/2, v} \cdot s / \sqrt{n} = 1.683$

Confidence intervals: (1.636, 1.683)

• 0.15mm hole bronze sparger (Frother 1)

Concentration (ppm)	Sauter mean bubble diameter (mm)
0	1.868
2	1.871
4	1.878
6	1.895
8	1.888
10	1.912
15	1.903
Sample mean $\bar{X}$	1.888
Sample standard deviation S	0.016

For 95% confidence intervals:

Number of samples $n = 7$

$\alpha = (100\% - 95\%)/2$

$\alpha = 0.025$ See Table E.1

$\nu = n - 1 = 6$

$t_{\alpha, \nu} = 2.447$ from Table E.1.

$\bar{X} - t_{\alpha/2, \nu} \cdot s / \sqrt{n} = 1.870$

$\bar{X} + t_{\alpha/2, \nu} \cdot s / \sqrt{n} = 1.906$

Confidence interval: (1.870, 1.906)

Table E. 1 Critical values $t_{\alpha, \nu}$ for the t distribution

ν	α						
	.10	.05	.025	.01	.005	.001	.0005
1	3.078	6.314	12.706	31.821	63.657	318.31	636.62
2	1.886	2.920	4.303	6.965	9.925	22.326	31.598
3	1.638	2.353	3.182	4.541	5.841	10.213	12.924
4	1.533	2.132	2.776	3.747	4.604	7.173	8.610
5	1.476	2.015	2.571	3.365	4.032	5.893	6.869
6	1.440	1.943	2.447	3.143	3.707	5.208	5.959
7	1.415	1.895	2.365	2.998	3.499	4.785	5.408
8	1.397	1.860	2.306	2.896	3.355	4.501	5.041
9	1.383	1.833	2.262	2.821	3.250	4.297	4.781
10	1.372	1.812	2.228	2.764	3.169	4.144	4.587
11	1.363	1.796	2.201	2.718	3.106	4.025	4.437
12	1.356	1.782	2.179	2.681	3.055	3.930	4.318
13	1.350	1.771	2.160	2.650	3.012	3.852	4.221
14	1.345	1.761	2.145	2.624	2.977	3.787	4.140
15	1.341	1.753	2.131	2.602	2.947	3.733	4.073
16	1.337	1.746	2.120	2.583	2.921	3.686	4.015
17	1.333	1.740	2.110	2.567	2.898	3.646	3.965
18	1.330	1.734	2.101	2.552	2.878	3.610	3.922
19	1.328	1.729	2.093	2.539	2.861	3.579	3.883
20	1.325	1.725	2.086	2.528	2.845	3.552	3.850
21	1.323	1.721	2.080	2.518	2.831	3.527	3.819
22	1.321	1.717	2.074	2.508	2.819	3.505	3.792
23	1.319	1.714	2.069	2.500	2.807	3.485	3.767
24	1.318	1.711	2.064	2.492	2.797	3.467	3.745
25	1.316	1.708	2.060	2.485	2.787	3.450	3.725
26	1.315	1.706	2.056	2.479	2.779	3.435	3.707
27	1.314	1.703	2.052	2.473	2.771	3.421	3.690
28	1.313	1.701	2.048	2.467	2.763	3.408	3.674
29	1.311	1.699	2.045	2.462	2.756	3.396	3.659
30	1.310	1.697	2.042	2.457	2.750	3.385	3.646
40	1.303	1.684	2.021	2.423	2.704	3.307	3.551
60	1.296	1.671	2.000	2.390	2.660	3.232	3.460
120	1.289	1.658	1.980	2.358	2.617	3.160	3.373
∞	1.282	1.645	1.960	2.326	2.576	3.090	3.291

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