Characterizing Frothers by Their Bubble Size Control Properties

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In the name of God

To my parents and my dear husband

Abstract

Frothers are surface-active agents used in flotation to decrease bubble size and promote froth stability. The common frothers are alcohols and polyglycols. One means to classify frothers is by the extent of bubble size reduction. Bubble size measurement is labour-intensive and this thesis explores the use of gas holdup as a surrogate for bubble size.

Nine frothers with different chemical structures were tested in a bubble column equipped with instrumentation to measure bubble size and gas holdup. A correlation between frother structure and gas holdup is observed: for alcohols, gas holdup increases with hydrocarbon chain length and whether branched or straight chain does not seem to matter; and for polyglycols, gas holdup increases with number of propoxy groups. The ranking of the frother on the basis of gas holdup is the same as that given by other methods. The assumed unique relationship between gas holdup and bubble size is examined. For a given frother the relationship appears to hold. Evidence is presented that the continued increase in gas holdup at high frother concentration is correlated with a continued decrease in bubble size. When comparing frothers, however, it is shown that for equal gas holdup bubble size can be quite different. The effect is discussed in terms of bubble velocity in the swarm.

Résumé

Les moussants sont des agents tension-actifs utilisés en flottation afin de diminuer la taille des bulles et promouvoir la stabilité de l'écume. Les moussants communs sont des alcools ou des polyglycols. Une façon de classifier les moussants est par l'étendue de la réduction de la taille des bulles. La mesure de la taille des bulles est une tâche laborieuse et cette thèse explore l'utilisation de la teneur gazeuse comme alternative à la taille des bulles.

Neuf moussants ayant des structures chimiques différentes furent testés dans une colonne à bulles équipée pour les mesures de la taille des bulles et de la teneur gazeuse. Une correlation entre la structure du moussant et la teneur gazeuse est observée: pour les alcools, la teneur gazeuse augmente avec la longueur de la chaîne d'hydrocarbures qu'elle soit branchée ou non; et pour les polyglycols, la teneur gazeuse augmente avec le nombre de groupements d'oxide de propylene. Cet ordre des moussants selon leur teneur gazeuse est le même que celui observé par d'autres méthodes. La présumée relation unique entre la teneur gazeuse et la taille des bulles est examinée. Pour un moussant donné, la relation semble tenir. Il est prouvé que l'augmentation continue de la teneur gazeuse à des concentrations de moussant élevées est corrélée avec la diminution continue de la taille des bulles. En comparant les moussants, cependant, il est démontré que pour une teneur gazeuse égale la taille des bulles peut être très différente. L'effet est discuté en termes de la vitesse d'une population de bulles.

Contribution of Authors

This thesis was prepared in accordance with article C of the Guidelines Concerning Thesis Preparation of McGill University. The following are manuscripts written by the author that were used in preparation of this thesis. Manuscripts 1 and 2 make up Chapters 5 and 6, respectively.

1. **Fariba Azgomi, Cesar O. Gomez and James A. Finch**, "Characterizing Frothers using Gas Holdup", to be submitted.
2. **Fariba Azgomi, Cesar O. Gomez and James A. Finch**, "Correspondence of Gas Holdup and Bubble Size in Presence of Different Frothers", to be submitted.

All of the manuscripts presented above are co-authored by Prof. James A. Finch in his capacity as research supervisor. Dr. Cesar O. Gomez (Senior Research Associate in the Department of Mining, Metals and Materials Engineering, McGill University) is included as co-author recognizing his contribution in co-supervising the research. Beyond the contributions of the co-authors, the author performed all of the work presented in this dissertation.

Acknowledgements

I wish to express my sincerest appreciation and utmost gratitude to my supervisor, Prof. James A. Finch for his guidance, continuous encouragement, and valuable technical assistance and discussions. I particularly appreciate the relationship that has been established between us along the course of my study, and that will enrich my memories all my life.

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My parents, have been a source of inspiration all throughout my life and the true reason behind my achievements. They taught me the importance of a strong education and have always encouraged me to pursue my education to the highest levels. For that, I am eternally grateful.

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Chapter 1: Introduction

1.1: General Background

Mineral processing, otherwise known as mineral dressing, is the practice of concentrating valuable minerals from ore. The process involves two principal operations: comminution or size reduction to liberate minerals, followed by separation of valuable minerals from the valueless minerals or gangue.

Comminution is the "feed preparation" step, readying the minerals for separation. By size reduction particles are produced comprising a range in composition from free mineral (valuable and gangue) to the range of locked (mixed mineral) particle types. At a given level (degree) of liberation – mass fraction of mineral in free particle form – the minerals can be separated economically. Flotation, magnetic, and gravity methods are the major separation processes. Flotation is the most widely used. Flotation or froth flotation is a surface chemistry – based process to separate fine solids (typically < 200 μm), taking advantage of differences in the wettability of minerals. In operation, gas (typically air) bubbles are dispersed into a vessel (cell) containing solid particles suspended in an aqueous medium (i.e., forming a pulp or slurry). By addition of chemical reagents known as collectors, selected minerals are made hydrophobic and they adhere to the bubbles. The bubble-particle aggregates rise and form a froth phase, which is removed to recover the minerals. One type of a flotation cell or machine, a flotation column, is shown in Figure 1.1[1].

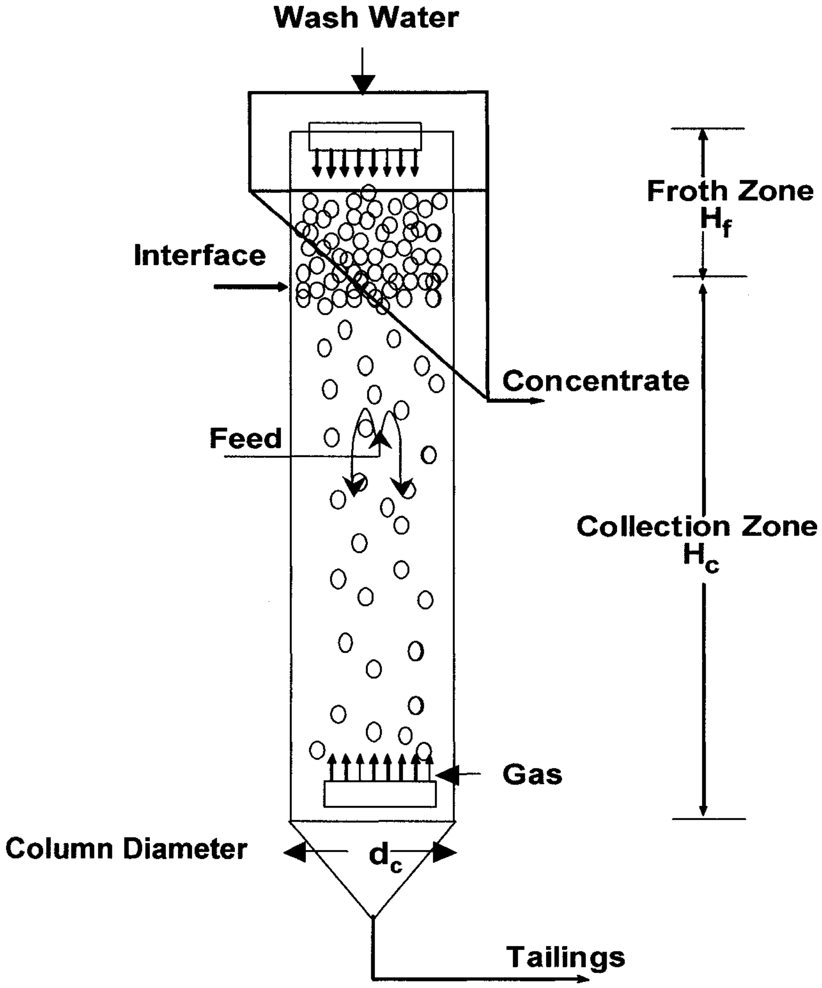

Figure 1.1: Schematic of flotation column, (adapted from Finch and Dobby[1])

Bubbles are generated by various means: passing air through a rotating impeller in the case of mechanical machines, various porous and jetting spargers in the case of flotation columns, and aspiration into a plunging slurry jet in the case of Jameson cells. Bubble size is an important variable in flotation, for example controlling the surface area over which solid particles and bubbles interact and contributing to system hydrodynamics, which affect process performance[2]. To be efficient, it is essential to produce a high population of small bubbles (0.5 – 2.5 mm, typically). Production of small bubbles is generally promoted by the addition of a surfactant called a frother, which acts to prevent bubble coalescence. This aspect of frother function is the subject of this thesis.

1.2: Frothers

Froth flotation commonly requires a range of reagents. Although it is arguable that the most important are collectors, which are used to render selected minerals hydrophobic, as the term froth flotation implies, the process is inseparable from the froth and hence frothers.

Frothers are surface-active agents (surfactants) used in flotation to decrease bubble size and promote froth stability. They have a heteropolar structure that causes them to adsorb at an air-water interface (i.e., bubble surface) to satisfy both their polar and nonpolar parts. This in turn stabilizes a water film on the bubble surface, which helps retard coalescence[3] (i.e., the coming together of two or more bubbles to form large bubbles). Pine-oil and cresylic acid were among the earliest frothers, but these have now mostly been replaced by synthetic alcohols and glycols[4].

The criteria for selecting frothers have changed over the years. In the past, the focus was mainly on cost, availability and being environmentally friendly. While still important, others factors related to performance, like bubble size and quality of froth produced, being increasingly considered. But there remains no accepted technique for the characterization of frothers. As a result, terms such as "powerful" or "selective," which have practical rather than scientific meaning are still commonly used to describe frothers.

Most characterization techniques appear to be based on froth properties[5,6,7,8]. Espinosa-Gomez et al.[9] did compare frothers on the base of bubble size reduction using gas holdup measurements. More recently Laskowski and coworkers[10,11,12,13] have developed a procedure based on the both the ability of frothers to reduce bubble size and increase foam stability. Comely et al.[14] characterized frothers using dynamic surface tension measurements. Their method addresses the mechanism driven by surface tension gradients by which frothers retard the loss of liquid at the gas/liquid interface to produce stable froths. Recognizing the importance of water transport by bubbles in flotation, Moyo[15] classified frothers based on water carrying rate. The method showed that the amount of water, transported as a layer on the bubble surface and as a trailing wake, was related to gas holdup and frother type. Finch et al.[16] showed that film thickness on bubble was dependent on frother type which offers another characterization possibility.

Even though these techniques have provided valuable insights into the role of frothers in flotation, what continues to be lacking is a full understanding of the mechanism(s) by which frothers act, and building from this, how to achieve the desired frother functions, bubble size reduction and froth stability.

This thesis examines primarily bubble size reduction. When bubble size decreases (e.g., with an increase in frother concentration) bubble rise velocity decreases and thus bubble retention time increases, which is reflected by an increase in gas holdup[17]. Gas holdup, therefore can be a surrogate for bubble size measurement and has the advantages of being simpler to measure and can be adapted to be continuous and on-line.

1.3: Objectives of Thesis

The overall objective of this Master's thesis is to develop a procedure to characterize frothers by their bubble size control properties as reflected in gas holdup. The specific research objectives are characterization of frothers using gas holdup as a surrogate for bubble size measurement; validation of a common claim that bubble coalescence is entirely prevented at frother concentrations exceeding the critical coalescence concentration (CCC)[18]; and testing the assumption that gas holdup, at a given gas rate, is uniquely dependent on bubble size regardless of frother type.

1.4: Structure of thesis

The thesis consists of the seven Chapters. Some are in the style of a manuscript for publication so inevitably some repetition with other chapters occurs.

Chapter 1 gives the general overview of flotation and frothers and introduces the objectives of this Master's work.

Chapters 2 and 3 are a review of so-called gas dispersion parameters, frother chemistry and, with specific emphasis, frother characterization techniques.

In Chapter 4, experimental procedures and measurement techniques are outlined.

Chapters 5 and 6 are presented as manuscripts. Chapter 5, **Characterizing Frothers Using Gas Holdup** by Azgomi F., Gomez C.O. and Finch J.A. explores a possible way to characterize (classify) frothers using gas holdup as a surrogate for bubble size measurement and represents a correlation between frother type and gas holdup.

Chapter 6, **Correspondence of Gas Holdup and Bubble Size in Presence of Different Frothers** by Azgomi F., Gomez C.O. and Finch J.A. investigates the effect of frother type on gas holdup and bubble size. It is shown that at equal gas holdup and gas rate, different frothers do not give the same bubble size.

Finally, Chapter 7 presents conclusions drawn from the work and explores further research possibilities.

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Chapter 2: Literature Review

Flotation at the fundamental level is a complex physicochemical process. There are many variables, chemical and physical, which can affect performance. This chapter reviews one class of variables, gas dispersion, which includes superficial gas velocity, bubble size distribution, gas holdup and bubble surface area flux. Specific emphasis is given to the effect of frother type and concentration on these variables.

In flotation, bubbles play the central role in separation of solid particles. The importance of bubble size in controlling flotation efficiency has been recognized since the early days[1,2,3,4]. A key factor controlling bubble size is the presence of frother[5]. Frothers appear to function by controlling (retarding) bubble coalescence[6]. This stabilizes a fine size bubble dispersion in the slurry (pulp) phase, which both increases collision rate with particles and enables a stable froth to form, which permits collected particles to overflow from the cell.

2.1: Gas Dispersion

In flotation the hydrodynamic variables that characterize gas dispersion in the pulp are superficial gas velocity (J_g) bubble size distribution (d_b), gas holdup (ε_g) and bubble surface area flux (S_b).

2.1.1: Superficial Gas Velocity

Superficial gas velocity, or simply gas rate (J_g, *cm/s*), is the volumetric flowrate (Q_g, cm^3/s) of air per cross sectional area (A, cm^2) of the cell,

$$J_g = \frac{Q_g}{A} \tag{2.1}$$

Typically, superficial gas velocity in flotation systems is 0.5 - 2.5 (*cm/s*)[7] depending on factors such as bubble size and slurry rheology.

2.1.2: Bubble Size

Bubble size distribution is a factor determining metallurgical response. By virtue of the mechanics of particle collision and attachment, bubbles must not be excessively large or small. When bubbles are too small, particles may have insufficient contact time to attach, or if attachment does occur, the bubble buoyancy may be too low for practical recovery. On the other hand, as bubble size increases the strength of the bubble streamline increases, making collision between particles and bubbles more difficult.

The Sauter mean diameter (d_{32}) is commonly considered the mean size relevant to flotation[8]. The size in flotation systems is ca. 0.5 – 2.5 mm[8]. Coalescence is one mechanism that reduces the air dispersion efficiency of a flotation system[9]. The bubble size distribution depends on the balance between coalescence and breakup[10]. The mean bubble size is influenced principally by gas rate, the presence of frother, the bubble generation device and operating pressure.

2.1.2.1: Effect of Superficial Gas Velocity on Bubble size

Several investigators report that the mean bubble size increases as gas rate is increased[2,8,11,12]. Figure 2.1, taken from Nesset et al.[13] presents bubble size (Sauter mean diameter, d_{32}) as a function of superficial gas velocity for a variety of cells (all forced air).

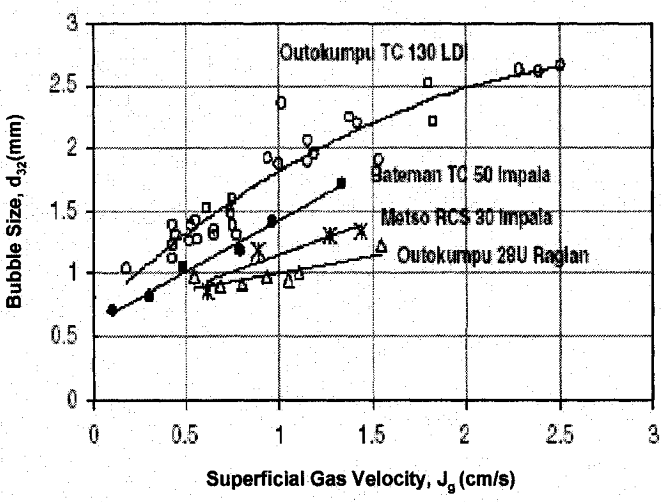


Figure 2.1: Cell Characterization: Sauter mean bubble size as a function of gas rate (after Nesset et al.[13])

Bubble diameter, d_b, for porous spargers has been empirically related to superficial gas velocity by[2],

$$d_b = \alpha J_g^{\beta} \tag{2.2}$$

where α and β are constants. For a variety of porous media, β is about 0.25 and α depends on frother type and dosage[2]. Nesset et al.[14] proposed a modification of the above relationship,

$$d_{32} = d_0 + CJ_g^{n} \tag{2.3}$$

where d_0 is the bubble diameter at J_g equal zero and C and n are parameters, as α and β in Equation 2.2, dependent on the bubble production mechanism, system chemistry and, possibly, slurry properties.

2.1.2.2: Effect of Frothers on Bubble Size

Frother type and concentration affect bubble size. For all frothers, an increase in frother concentration decreases bubble size up to a certain concentration above which further addition of frother has little effect[7]. Figure 2.2 illustrates this for the case of Dowfroth 250.

The action of frother is commonly attributed to control of coalescence[6]; decreasing coalescence with increasing frother concentration causes the decrease in bubble size. After a certain concentration, recently termed "Critical Coalescence Concentration" (CCC)[9], the argument is that coalescence is fully retarded and bubble size is constant. Different frothers have individual CCC values[9,15,16].

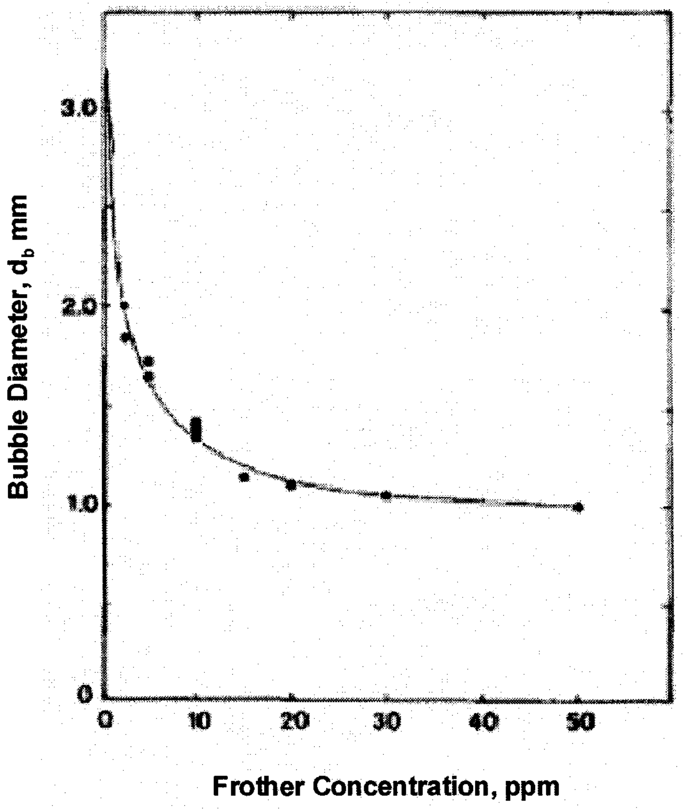


Figure 2.2: Effect frother (Dowfroth 250) concentration on bubble size, (adapted from Finch and Dobby[7])

A number of investigators have tried to link the frother's ability to reduce bubble size to surface tension. Lower surface tension values are usually associated with higher frother concentration that corresponds to smaller bubbles[17,18,19,20]. For a given family of frothers, e.g., alcohols, a relationship can be found. On the other hand, Aldrich and Feng[21] found that MIBC solutions with higher surface tension values than Dowfroth 200 solutions produced smaller bubbles. It was also noted that, over the concentration ranges used in flotation, surface tension hardly changes even though significant bubble size reduction is taking place. In the case of salts, above a certain concentration, coalescence is also retarded but solution surface tension increases[22]. These observations imply that prevention of coalescence is not related simply to the surface tension.

2.1.3: Gas Holdup

Gas holdup (or voidage) is a dimensionless parameter defined as the volume fraction of gas phase at any point in a cell. The average gas holdup in a total volume V_t is,

$$\varepsilon_g = \frac{V_g}{V_t}, \ \% \tag{2.4}$$

where V_g is the volume of gas. Likewise, it is possible to characterize the liquid and solid phase by their respective holdup values.

The gas holdup is one of the most important parameters used to characterize the hydrodynamic state of bubble column reactors[23,24]. It is a simple parameter to measure and useful as it combines the influence of both bubble size and gas rate. Gas holdup is dependent on several factors, including: gas rate, liquid properties (e.g., frother type and concentration), cell dimensions, operating temperature and pressure, gas distributor design and solid phase properties and concentration, to mention the most important. There are several techniques to measure gas holdup such as: pressure drop, electroconductivity, X-ray and γ-ray transmission, mean bubble residence time and optical fiber probes[23,25]. Three-dimensional maps of gas holdup can be generated using computer tomography.

2.1.3.1: Effect of Superficial Gas Velocity on Gas Holdup

Gas holdup depends directly on superficial gas velocity[26] and the relationship ε_g-J_g is often used to define the flow regime[27]. Figure 2.3 presents quantitatively the dependence of flow regime on gas holdup and superficial gas velocity in bubble columns. For columns in all manner of applications, gas holdup is found to first increase steadily with increasing superficial gas velocity in the bubbly flow regime, which is followed by a transition to an erratic response in the churn – turbulent regime [23,28,29,30,31].

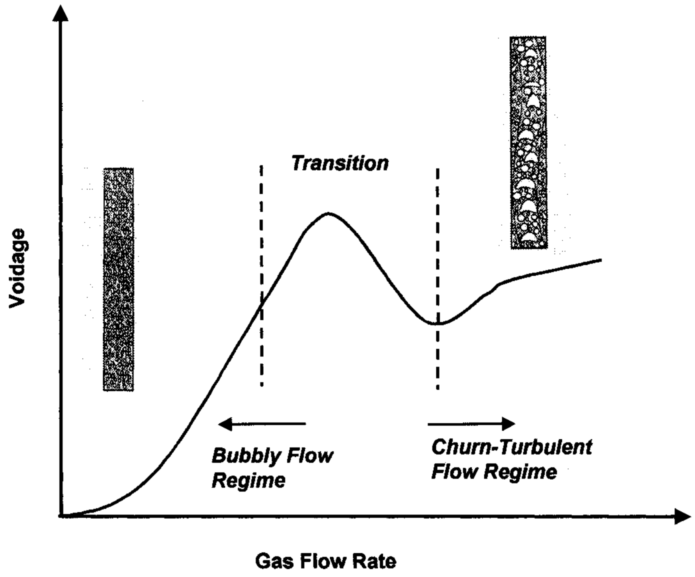


Figure 2.3: Flow regime for bubble column

Flotation operates best in the bubbly flow regime (both columns[14] and mechanical machines[32]). In this flow regime the relationship between gas holdup and superficial gas is often given in the form[33]:

$$\varepsilon_g = \chi J_g^a \tag{2.5}$$

where χ and a are empirical constants, and a is typically $0.7 \le a \le 1$[26], i.e., approximately linear.

2.1.3.2: Effect of Liquid Phase Properties on Gas Holdup

Liquid phase properties that impact bubble formation and/or coalescence will affect gas holdup. Addition of a small quantity of frother to water has a pronounced effect on reducing bubble size. Since smaller bubbles (≤ 2mm) rise more slowly, at a given gas rate this results in higher gas holdup. The effect of frother concentration is illustrated in Figure 2.4[4], where gas holdup increases significantly upon addition of Dowfroth 250 from 0 to 15 ppm.

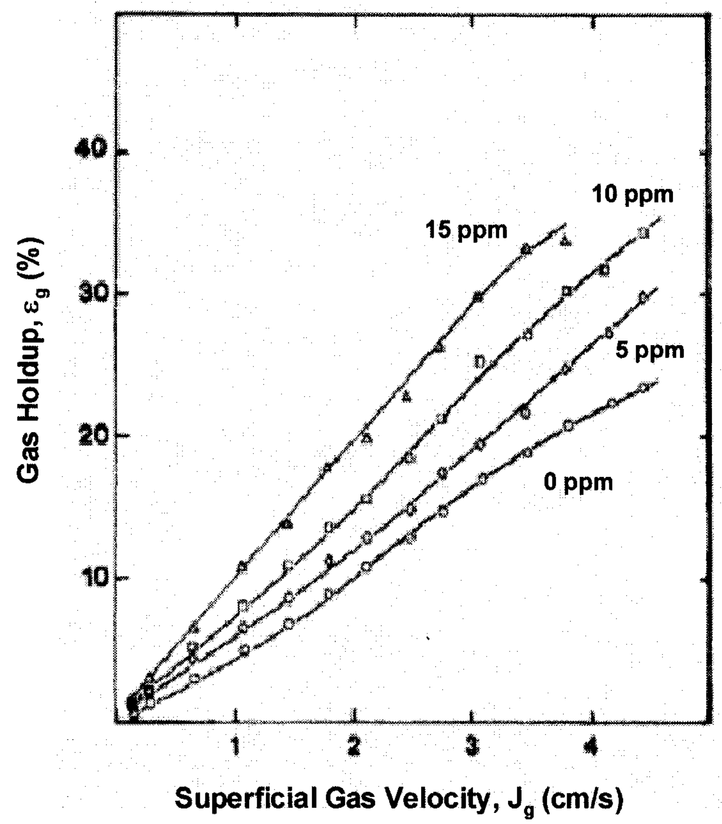


Figure 2.4: Effect of frother dosage on gas holdup and gas rate (adapted from Finch and Dobby[7])

Liquid properties produce a range of effects[31,34]. Ozturk et al.[35] measured the gas holdup in pure and mixed organic liquids and found that in several mixed cases the gas holdup was higher as compared to pure liquids with the same properties (surface tension, density, viscosity). Their findings were comparable of those of Bhaga et al.[36] who studied gas holdup in toluene/ethanol mixtures. They also concluded that the gas holdup was higher with high-density gases. Espinosa-Gomez et al.[6] investigated change in gas holdup upon adding fatty acid to 20 ppm frother (TEB, 1,1,3-triethoxybutane). They found that the gas holdup relative to that at zero fatty acid decreased by about 50% at fatty acid concentration 20 ppm and greater. They attributed this to a coalescence effect. Recently, Tang and Heindel[37] suggested that regular tap water, which is the most frequently used liquid in bubble columns, might cause significant reproducibility problems even in air–water two-phase studies as they observed time-dependent variations in gas holdup. This was related to water quality, column operation mode, sparger orientation and superficial gas and liquid velocities. They attributed this time-dependency to changes in concentration of volatile coalescence inhibiting species percent in tap water.

Veera et al.[38] investigated gas holdup in the presence of a foaming agent (n-butanol) and concluded that the effect of concentration on holdup profiles (gas holdup with height) depended upon the sparger design, column aspect ratio and superficial gas velocity. The authors observed that the gas holdup profiles became flatter at high foaming agent concentrations. Zhou et al.[39] found that for different frother systems, a higher gas holdup did not necessarily mean that a smaller bubble size was produced; that is, there appeared to be an effect of frother type on gas holdup in addition to its role in controlling bubble size.

Viscosity, among the physical properties of a liquid, can have on impact on gas holdup. It has been found that gas holdup decreases with increasing liquid viscosity[40,41,42]. Crabtree and Bridgwater[43] explained this behavior by suggesting that high viscosity promotes bubble coalescence, resulting in larger bubbles that have a higher rise velocity, which consequently lowers the gas holdup[44].

An effect of surface tension on gas holdup is occasionally reported[20,19,45] but this is indirect because of the corresponding formation of smaller gas bubbles due to coalescence inhibitation as discussed earlier.

2.1.3.3: Effect of Solid Particles on Gas Holdup

The effect of solid particle concentration and particle size on gas holdup has been investigated by a number of researchers[11,46,47,48,49,50]. Several concluded that an increase in solid concentration generally reduced the gas holdup, which is usually attributed to coalescence creating larger, faster rising bubbles. Gandhi et al.[50], also finding that as the solid content increased the gas hold-up decreased, attributed this to an increase in slurry viscosity preventing bubble break-up

Most of these studies do not relate to flotation conditions. Banisi et al.[51] studied the gas holdup in a flotation system (i.e., presence of frother) using calcite particles (74% > 53 μm) and again reported a decrease in gas holdup with increasing solid concentration, which did not appear to be related to a change in bubble size. They attributed the decrease in gas holdup to an increase in bubble rise velocity caused by wake stabilization, and a change in the radial holdup and flow profiles.

A common deficiency in these studies is the reliance on gas holdup measurements with few additional measurements such as bubble size. Combinations of measurements are required to resolve this coalescence/breakage controversy.

2.1.4: Surface Area Flux

Surface area flux (S_b), a derived gas dispersion parameter, is now commonly used in flotation to link the flotation rate with the hydrodynamic variables[12,52,53,54,55]. The flotation rate constant (k) has been correlated with surface area flux[56,57], and is usually expressed as (for the pulp zone):

$$\mathrm{k} = \mathrm{PS_b} \tag{2.6}$$

where P is the "flotability factor", which encompasses the contribution of particle size and hydrophobicity. Gas holdup can be correlated with the rate constant via the following relationship with S_b proposed by Finch et al.[58],

$$S_b = \frac{6 \cdot J_g}{d_b} = 5.5 \cdot \varepsilon_g \tag{2.7}$$

with S_b in s^{-1} and ε_g in %.

2.2: Frothers

Flotation frothers refer to those organic chemical substances that when dissolved in or dispersed in water, reduce bubble size and enable a froth to form that remains stable long enough to discharge from the flotation cell and then breaks down. Frother molecules are heteropolar, i.e., consist of two groups, polar and non-polar. The non-polar group is a hydrocarbon chain, containing preferably at least six carbon atoms, which can either be straight, branched or cyclic[59]. It is believed that the hydrocarbon chain must not be too long since the resulting molecule is not soluble (or possibly dispersible) enough to be a frothing agent. The polar group could be a hydroxyl (OH), carbonyl (-C=O-), ester (-COOR-), carboxyl (-COOH), amine (-NH_2), nitrile (-CN), phosphate (=PO_4), or sulphate (=SO_4)[16,60].

At the moment of bubble generation, frother molecules adsorb on the bubble surface with the hydrocarbon chain on the airside and the polar group on the waterside where it hydrogen bonds with water molecules. This orientation is illustrated in Figure 2.5 for methyl isobutyl carbinol (MIBC)[61].

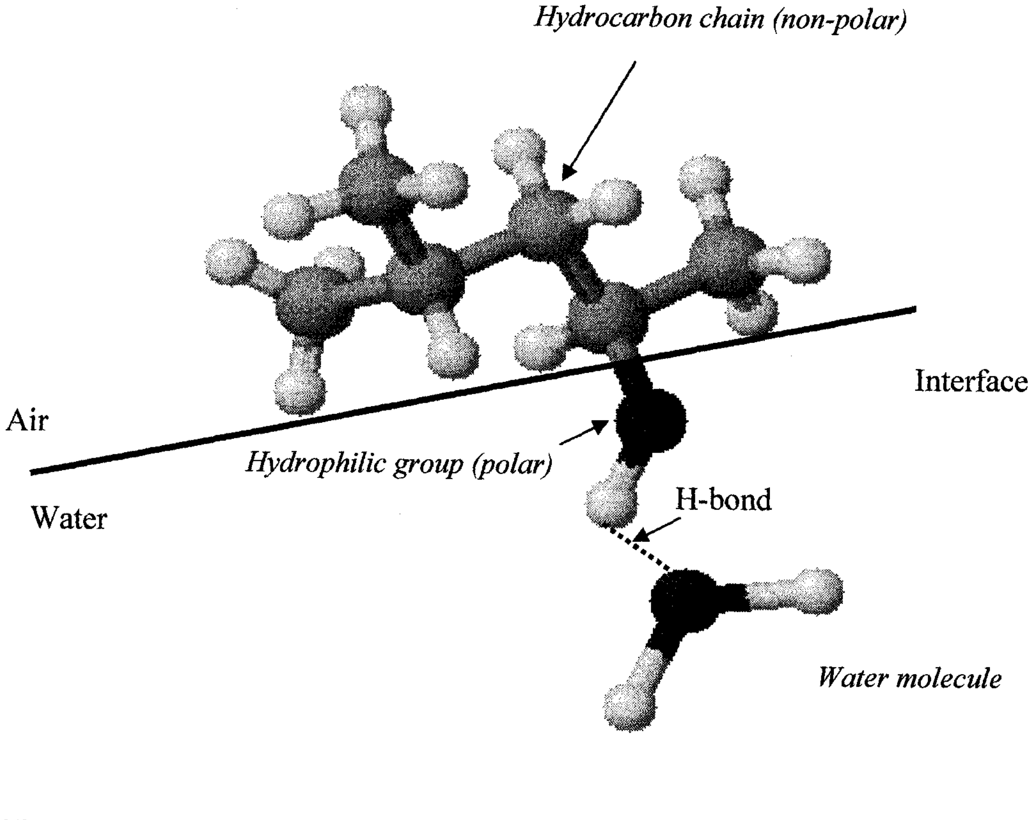


Figure 2.5: Typical structure and orientation (MIBC) after adsorption at bubble surface

According to Gibbs, those solutes that reduce surface tension adsorb in the surface layer. Gibbs' adsorption model can be expressed as follows[60]:

$$\Gamma = -\frac{C}{RT} \times \frac{d\sigma}{dC} \qquad (2.8)$$

where,

Γ: The excess concentration of molecules adsorbed at the interface

C: Concentration of solute molecules in the bulk of the solution

σ: Surface tension

R: Gas constant

T: Absolute temperature

$\frac{d\sigma}{dC}$: The surface activity of a surfactant

In addition to lowering surface tension, frothers also prevent coalescence. Several mechanisms have been proposed[62]. One is that the hydrogen bonding with water molecules forms a stabilized (bound) water film around the bubble, Figure 2.6. This film resists drainage and thus retards coalescence[63].

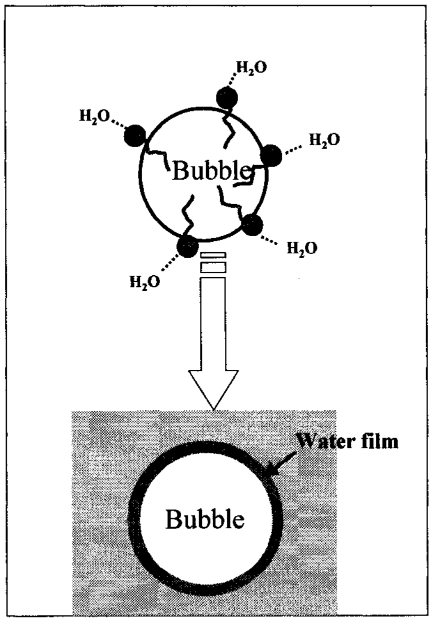


Figure 2.6: A bubble surface with a bound water layer

Frother type and concentration probably affect the bound water film thickness. Gelinas et al.[63] measured the film thickness on an air bubble blown in solutions of two industrial frothers, MIBC and Dowfroth 250, using inferferometry. They found that Dowfroth 250 gave a thicker water film than MIBC. The difference was attributed to the molecular structure of the frothers, which influences the way they hydrogen bond with and order (stabilize) water molecules.

The second mechanism relates to surface tension-driven phenomena. Upon drainage of the intervening water layer, prompted for example by bubble collision, a drag force on the bubble surface is induced causing the surface to flow. This reduces the local frother concentration on the surface, which means the local surface tension increases. Hence a surface tension gradient is established which opposes the motion of the surface (Gibbs elasticity effect). The gradient promotes motion in the surface towards the higher surface tension region which then promotes a flow in the adjoining water layer which furthers counters the flow out of water (the Marangoni effect). Together these two effects oppose film drainage and retard coalescence[62].

The same forces that prevent coalescence and maintain a fine bubble dispersion in the pulp zone also promote formation of a stable froth. In flotation systems, particles attached to a bubble evidently enhance froth stability. In fact without solids froth rarely forms at the frother dosages used in practice. The particles can be considered as physically blocking water drainage, which can be modeled as an increase in effective viscosity of the inter - bubble film.

According to the Leja-Schulman penetration theory[64,65], frothers at the bubble surface interact with collector molecules adsorbed on the solid particles during collision and attachment. The extent to which this attribute of frothers is important remains an open question[16].

2.2.2: General Specifications of Frothers

Frothers must have certain practical features, such as[60,66]:

I. Creation of a froth that is sufficiently stable but not tough, so that it facilitates pumping and further processing and collapses readily once outside the cell

II. Production of a froth that allows further separation of valuable minerals from gangue through drainage of water
III. Having a low sensitivity to pH changes, collectors and dissolved salt content of flotation pulp
IV. Being cheap, available for large-scale use and environmentally friendly
V. Being easily dispersed but not necessarily readily soluble in aqueous medium

2.2.3: Frother Chemistry and Classification

There are three main groups of reagents employed by the mineral industry as frothers: alcohols, alkoxy type and polyglycol type (i.e., polyglycols and polyglycol ethers). Table 2.1 summarizes some properties of common frothers[67].

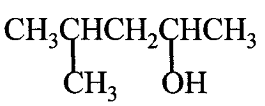
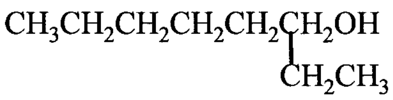
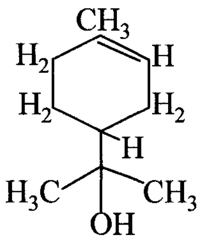
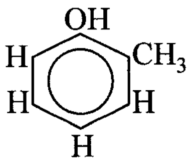
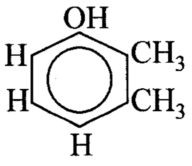
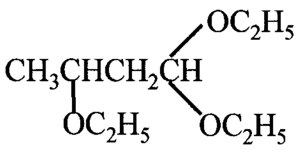
2.2.3.1: Alcohols

There are 3 subgroups in the alcohol class: linear aliphatic, cyclic and aromatic. As commercial products they may also contain a variety of other compounds formed during their manufacture. The linear aliphatic include both linear and branched forms that have a chain length 5 to 8 carbon atoms. Cyclic and aromatic alcohols are much less soluble in water than linear alcohols and are less sensitive to pH. The alcohol frothers tend to produce a froth, which is relatively shallow, carries little water (i.e., is dry), entrains less gangue slimes (i.e., is selective), and is less stable and persistent[68].

2.2.3.2: Polyglycols

Polyglycols divide into two groups: polypropylene or polyethylene glycols and their ethers. They are readily soluble in water so can be diluted to any given strength. Besides their particular structure, molecular weight plays a significant role in their performance. The glycol frothers tend to produce a froth which is comparatively thick, carries more water (i.e., is wet), entrains more gangue slimes (i.e., is less selective) and is relatively stable and persistent with, again, low sensitivity to pH changes[68]. This character of polyglycols is considered an advantage when recovering coarse particles[66].

Table 2.1: Classification of flotation frothers

Frother Name	**Formula**	**Solubility in Water**
Aliphatic Alcohols	R^*OH	
Methyl isobutyl carbinol (MIBC)	 $CH_3\underset{CH_3}{C}HCH_2\underset{OH}{C}HCH_3$	Low
2-Ethyl hexanol	 $CH_3CH_2CH_2CH_2CH_2\underset{CH_2CH_3}{C}H_2OH$	Low
Cyclic Alcohols		
α-Terpineol ($C_{10}H_{17}OH$)		Low
Aromatic Alcohols		
Cresylic acid (mixture of cresols and xylenols)	 o-Cresol  2,3-Xylenol	Low
Alkoxy paraffins		
1,1,3-Triethoxybutane	 $CH_3\underset{OC_2H_5}{C}HCH_2\overset{OC_2H_5}{\underset{OC_2H_5}{C}}H$	Low
Polyglycol-type	$R'^{\dagger}\,(X)^{\ddagger}_nOH$	
Dowfroth 250	$CH_3(PO)^{\S}_4OH$	Total
Dowfroth 1012	$CH_3(PO)_{6.3}OH$	Total
Aerofroth 65 (Dowfroth 400)	$CH_3(PO)_{6.5}OH$	Total

---

[*] $R= C_nH_{2n+1}$

[†] R'=H or C_nH_{2n+1}

[‡] X=EO, PO or BO

[§] EO= C_2H_4O, PO=C_3H_6O and BO= C_4H_8O

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Chapter 3: Frother Characterization Techniques

Flotation frothers have periodically been the focus of attention over the years. These studies have led to a number of procedures to characterize frothers, which are summarized in this chapter.

3.1: Dynamic and Static Foam[**] Tests

Two types of foam stability test are generally used, dynamic and static. In dynamic tests, air is constantly supplied and foam grows until steady state is reached where rate of formation is in equilibrium with rate of decay (bubble bursting). In a static test the rate of foam formation is zero: once the foam is formed, it is allowed to collapse without further supply of gas or agitation[1].

3.1.1: Dynamic Tests

Bikerman proposed the original dynamic test[2,3]. He defined a unit of foaminess (Σ), as the average lifetime of a bubble in foam. The idea was to propose Σ as a physical property of a frother solution just like its density and viscosity. Measurements were carried out in a cylinder. Air was dispersed through a sparger and the foam was allowed to grow until equilibrium was reached. Foam height or volume was then measured. The dynamic foam stability (Σ) was expressed as:

$$\Sigma = \frac{V_f}{Q_g} = \frac{H_{\max} \times A}{Q_g} \tag{3.1}$$

where, V_f is the foam volume, Q_g the gas volumetric flowrate and H_{max} and A are the total foam height and the cross-sectional area of the vessel, respectively. It was found that Σ was independent of the gas flowrate, the shape of container and the average pore size of sparger.

[**] The word 'foam' is employed when no solids are present; when solid particles are included the term froth is generally used.

Sun[4] designed a frother-meter specially to measure the foaming characteristics of pine oils and other frothing reagents. He defined a foamability index (FI) as the ratio of foam volume produced to the volume of foam produced from a chosen standard solution of n-hexyl-alcohol. He also defined a stability index (SI) as the ratio of the persistence (time for foam to collapse) of the frother under test to the standard frother.

Malysa et al.[5,6] studied the surface rheology and foamability of n-octanoic acid and n-octanol solutions. They determined the Marangoni surface elasticity by using the pulsing bubble method and quantified foamability in terms of the retention time (*rt*) values. The retention time was determined under steady-state conditions based on the total gas volume contained in both the foam and the solution, hence determining the average time necessary for unit gas volume to pass through the system. Graphically, *rt* is the slope of the linear section of the dependence of the total gas volume contained in the system, V_g, on the gas flow rate, Q_g,

$$rt = \frac{\Delta V_g}{\Delta Q_g} \tag{3.2}$$

They found that retention time values increased more rapidly at low than at high concentration and also determined *rt* to be independent of the gas flowrate and the dimensions of the measuring equipment. The "Dynamic Foamability Index" (*DFI*), defined as the limiting slope of the *rt* dependence on concentration (c) for $c \to 0$, was proposed as the parameter to compare frothers and their action under conditions of identical foamability.

$$DFI = \left(\frac{\partial rt}{\partial c} \right)_{c=0} \tag{3.3}$$

Malysa et al.[7] related foamability (*rt*) to surface elasticity of a bubble film. The bubble was made to oscillate with known amplitude and frequency immediately after formation. It was found that the effective surface elasticity (E_{eff}) and *rt* varied in a similar manner with the chain length of n-alcohols. Both E_{eff} and *rt* showed dependences on carbon chain length with the maximum observed for C_6 - C_8 and then rapidly decreased for n-nonanol and n-decanol. The magnitude of these maxima depended mainly on the solute concentration.

Sweet et al.[8] characterized different frothers using the *DFI* and $C_{0.6}$, the concentration at which the Sauter mean diameter is reduced to 0.6 times that in water, Figure 3.1. They determined that normal alcohols behaved differently from branched chain alcohols. For n-alcohols the correlation is given by:

$$\frac{C_{0.6}}{0.059} = DFI^{a_1} \tag{3.4}$$

and for branched chain alcohols:

$$\frac{C_{0.6}}{65.91} = DFI^{a_2} \tag{3.5}$$

where a_1 and a_2 are constant and equal to 0.64 and 1.16, respectively.

Comely et al.[9] characterized frothers using dynamic (time dependent) surface tension measurements (determined by the maximum bubble pressure technique). Figure 3.2 shows the results for a series of alcohols. The technique was refined to facilitate measurement at high bubble rates, an important criterion with respect to the analysis of small, fast adsorbing molecules at low concentration such as flotation frothers. They developed an adsorption model, which was used to interpret the behaviour of frothers with respect to bubble size in flotation.

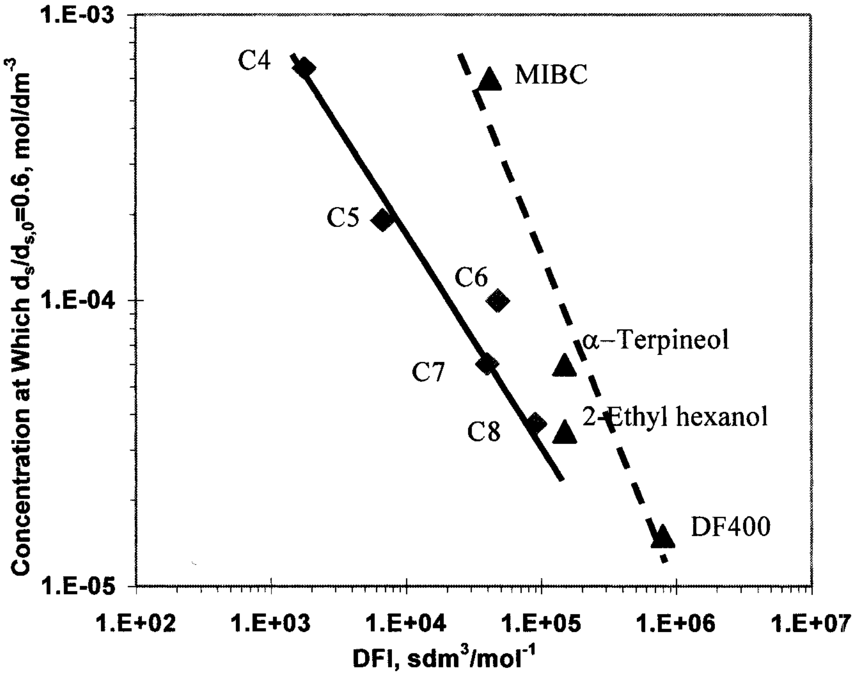

Figure 3.1: Relationship between the concentration at which the Sauter mean bubble diameter is reduced to 0.6 times that in water and DFI (adapted from Sweet et al.[8])

Although in two-phase systems several techniques have been used to measure foam stability, transfer to three-phase systems might not be straightforward since the presence of solids also affects the stability of foam[10]. In this regard, some work has been carried out to investigate the effect of solids upon the stability of froths[11].

Barbian et al.[12,13] developed a dynamic stability test for mineral flotation froths, that could be used in both laboratory and industrial scale conditions. They also tried to relate the unit of foaminess to flotation performance. Froth growth was monitored with time and the following relationship was found,

$$H_f = H_{\max}(1 - e^{t/\tau}) \tag{3.6}$$

where H_{max} is the total froth height, H_f is the froth height at time t and τ is the characteristic average bubble lifetime (i.e., Σ). They found that the equilibrium height and the dynamic stability factor depended significantly upon both the airflow rate and the frother concentration.

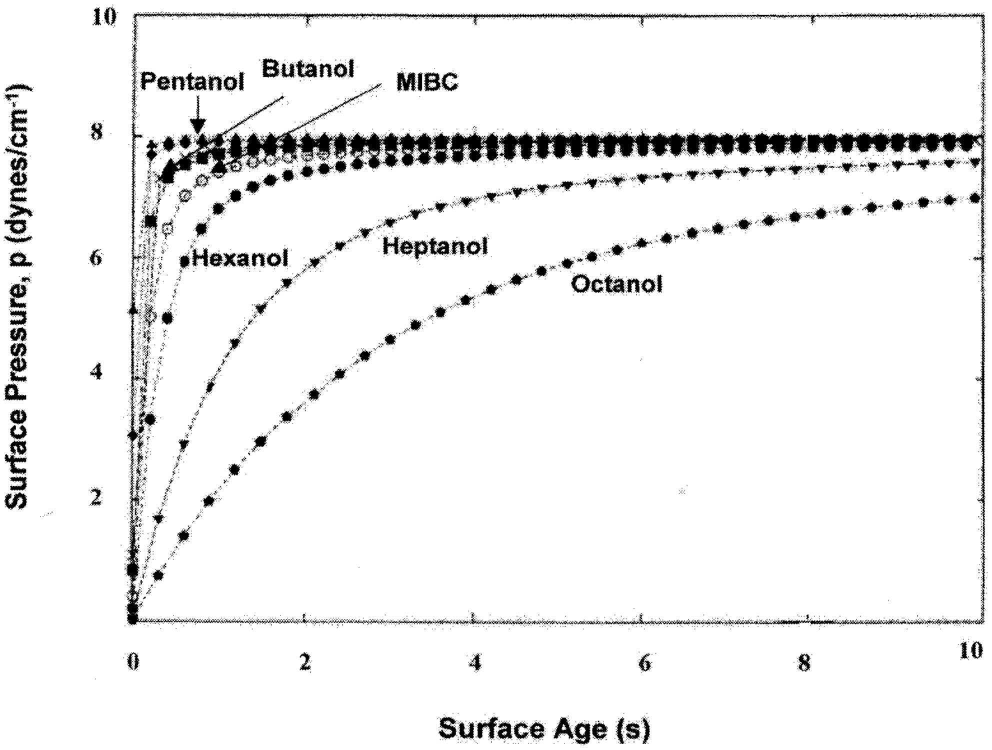

Figure 3.2: The effect of frother type on dynamic surface pressure for an equilibrium surface pressure of 8 dyne/cm^{-1} [9]

3.1.2: Static Tests

Iglesias et al.[14] modified Bikerman's technique by switching off gas once the dynamic equilibrium height was reached. The decay of foam volume was measured with time; a parameter $t_{1/2}$ was defined as the time for the foam to decay to half the original height (for constant cross sectional area). This parameter was used to characterize the persistence of the foam produced from a solution of known concentration.

Xu et al.[15] proposed a new method of evaluating froth stability and foamability. Their argument was based on the fact that when frothers were compared at the same concentration they would produce different froth heights and hence different froth stabilities (different $t_{1/2}$). Foam heights were plotted against $t_{1/2}$ and a good linear correlation was obtained for different frothers. It was found that alcohols (MIBC, n-heptanol, n-octanol and 2-octanol) had the same slope, which showed that they had almost the same foam stability.

3.2: Bubble Size Properties

Gourram-Badri et al.[11] studied the coalescence of bubbles in the pulp zone of flotation cells. They carried out experiments at laboratory scale under similar conditions to those found in industrial flotation machines to study the coalescence of two mineralized bubbles and the role that flotation frother (MIBC) plays in flotation selectivity. They developed a method to quantify the ability of MIBC to reduce bubble coalescence and to determine the effect of solids on the foaminess of the reagent. They determined the foaminess of MIBC by measuring the total froth height, including the solution and the froth zone, as a function of time. They found that the total froth height increased with time and after 2 min it reached a steady-state value that varied with frother concentration. These findings were similar to those previously reported by Johansson and Pugh[10]. They found that the total foam height depends on the presence of particles in the froth, being lower with particles. This difference in height increases as the MIBC concentration increases. Also, it was found that more hydrophobic particles did not produce a stable steady-state height.

Cho and Laskowski[16,17] studied the effect of flotation frothers on bubble size and its implications for foam stability. Following the procedure previously introduced by Malysa et al.[6], they performed experiments to measure the dynamic foamability index in a two-phase system using different frothers and spargers. They found a) that the bubble size is not affected by variations in the frother concentration if bubbles cannot collide with each other, and b) when the frother concentration reaches a certain concentration, tagged the critical coalescence concentration (CCC), bubble coalescence is totally prevented. They correlated the CCC values and the dynamic foamability index, and proposed that both are determined by bubble coalescence.

A correlation between dynamic surface tension and bubble size can be seen by comparing Figure 3.3, the bubble size data from Sweet et al.[8], and Figure 3.2.

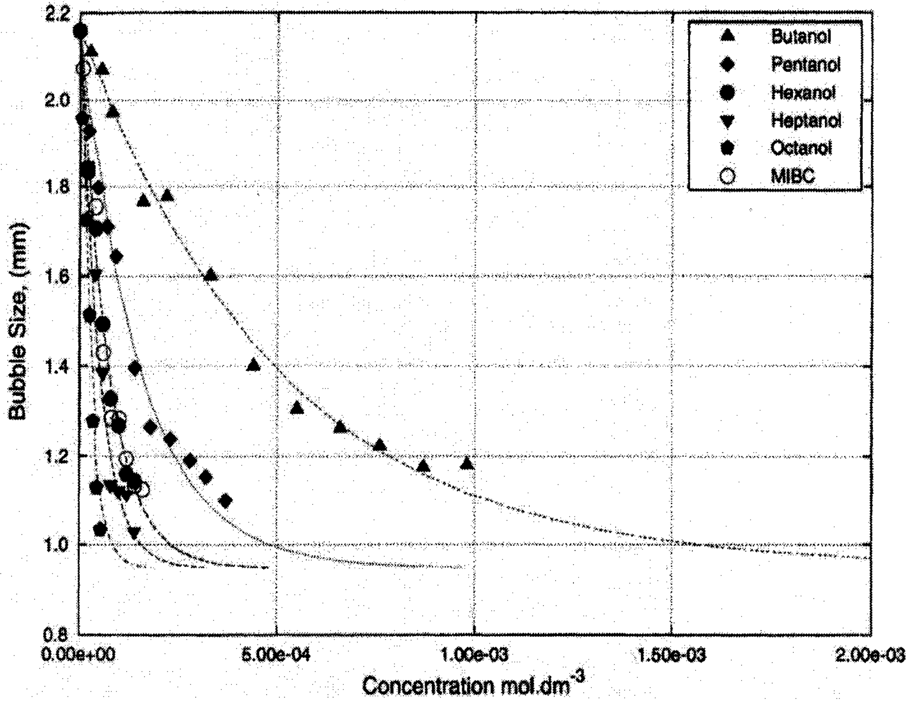

Figure 3.3: Sauter mean bubble diameter as a function of frother type and bulk concentration (after Sweet et al.[8])

Laskowski et al.[18] investigated a series of polyoxypropylene alkyl ethers (DF 200, DF250 and DF1012). They found a relationship between the number of propoxy (PO, OC_3H_6) groups in the $CH_3(OC_3O_6)_nOH$ and the CCC value, and the values of the dynamic foamability index, Figure 3.4. It was also found that blending frothers at a molar ratio could be based on the corresponding CCC values of individual frothers. Laskowski[19] suggested that frothers characterized by low CCC and high DFI values have properties of strong frothers, while those with high CCC and low DFI values are more selective.

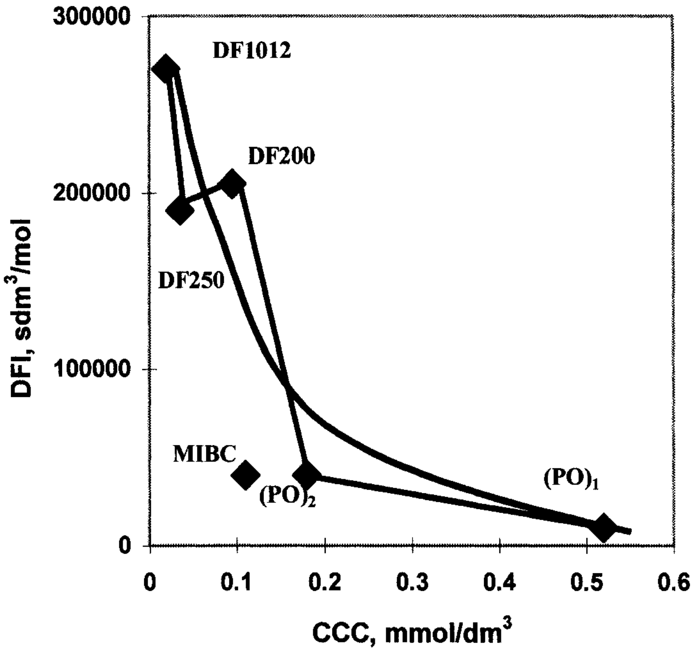

Figure 3.4: Relationship between CCC and DFI values for a series of polyoxpropylene alkyl ethers (adapted from Laskowski et al.[18])

3.3: Water Carrying Rate

In flotation, the amount of water reporting to the concentrate is closely related to the recovery of gangue particles by entrainment, which is detrimental to the float product grade[20]. Water is transported both as a film on the bubble surface and as a tailing wake, Figure 3.5 Bubble size[21], gas rate[22], froth depth[22] and frother type[23] influence the amount of water to overflow.

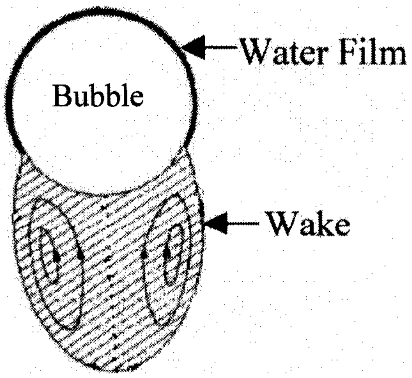

Figure 3.5: Schematic of bubble carrying water

Moyo[24] suggested a method to characterize frothers based on water carrying rate by using gas holdup as the correlating variable, which combines a bubble size and gas rate effect on water transport. It was found that the common frothers could be grouped into four classes or families based on the gas holdup (ε_g) - water carrying rate (J_{wo}) relationship, Figure 3.6.

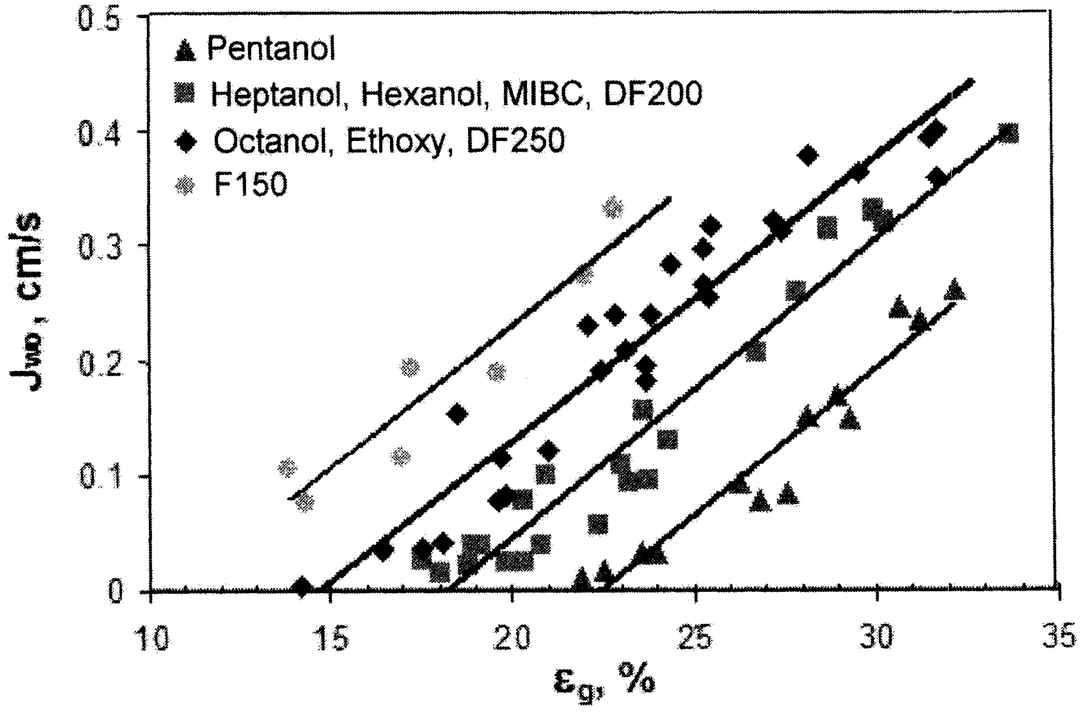

Figure 3.6: Classification of frothers based on water carrying rate[24]

Other researchers have used water recovery as a measure of frother performance. Melo et al.[25] studied how frother type affected froth structure and water recovery in two and three-phase (coal flotation) systems. Rahal et al.[26] worked on several (chemically unidentified) frothers and found that the relationship between entrainment recovery and water recovery was independent of frother type and concentration.

3.4: References

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Chapter 4: Experimental Procedures

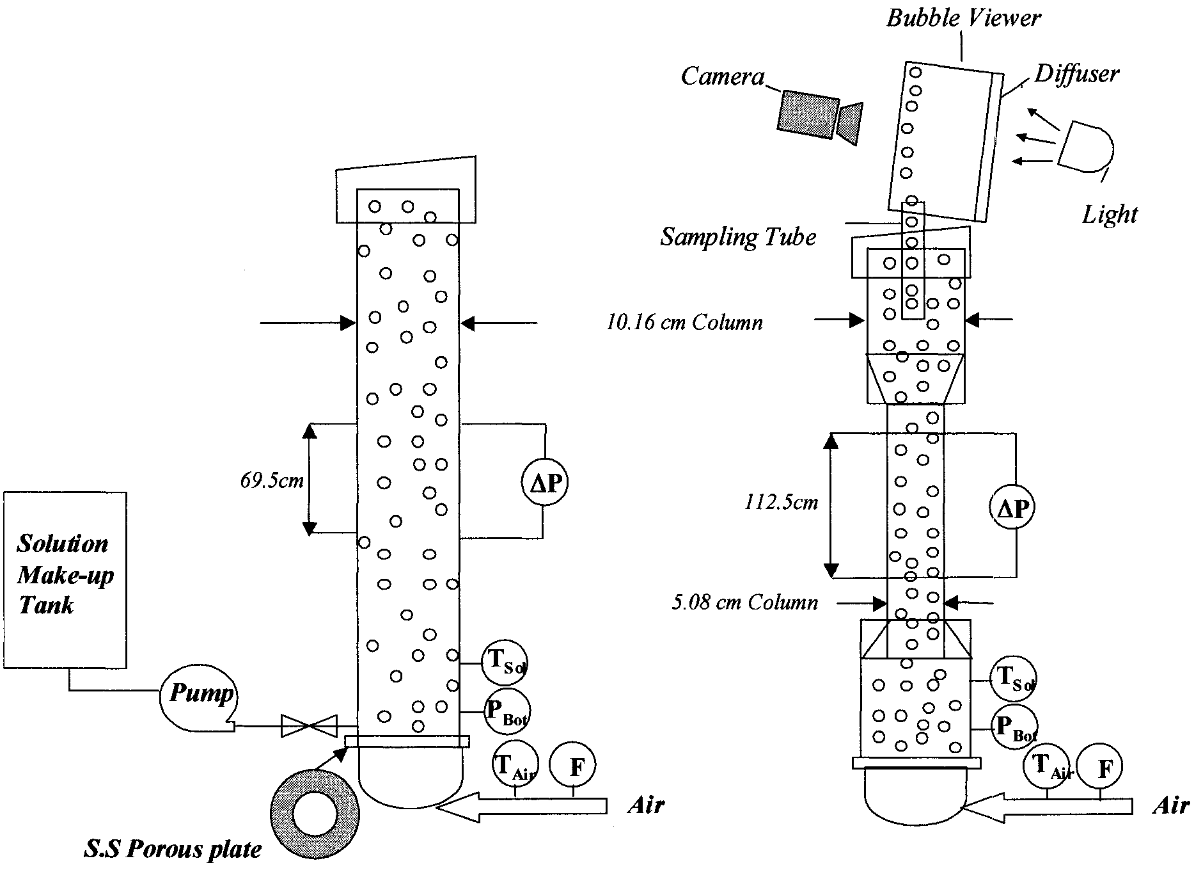
To characterize frothers by their bubble size control properties, a bubble column is used equipped with instrumentation to measure bubble size, gas holdup and superficial gas velocity. In this chapter a description of the column is given along with the instrumentation and measurement techniques.

4.1: Bubble Column

4.1.1: Basic Apparatus

Figure 4.1(a) shows the basic set-up: a 238 cm × 10.16 cm diameter Plexiglas column. The column was operated batch, the feed solution being introduced using a pump (Cole Palmer model 7520-25). The bubble generator was a porous, stainless steel plate sparger[††] that covered the base. A pressure transmitter (P_{Bot}) was placed 11.5 cm above the sparger to monitor the total head in the column. A calibrated mass flow meter[‡‡] (F) was used to control the gas flow rate. Temperature sensors (Thermopar type K) monitored input air (T_{air}) and solution temperature (T_{sol}) in the column. All the tests were carried out at temperature range of 20 ± 3 °C. Average of temperature between T_{air} and T_{sol} and P_{Bot} was used to correct the air mass flow meter reading to the conditions of the test. A visual basic program was developed to convert air mass flowrate to volumetric flowrate[1]. A differential pressure transmitter (ΔP) (Bailey model PTSDDD) was located between 67 cm and 136.5 cm above the sparger to determine gas holdup. All the instruments were connected to an interface and signal conditioner, Opto 22. Readings were carried out under steady state conditions and outputs were monitored every second through a software package, Intellution IFix, installed in a PC. Data were stored and processed using an in-house historical data extraction program.

[††] See Appendix A for characterization of a set of plate spargers.
[‡‡] Calibration curves are presented in Appendix B.



(a) **(b)**

Figure 4.1: Experimental set-up: (a) basic; and (b) modified

4.1.2: Modified Apparatus

To limit the number of bubbles entering the bubble viewer and thus improve reliability of bubble size measurement by reducing bubble clustering, most bubble size measurements were carried out in a modified set-up, Figure 4.1(b). The column was divided into three sections: base section, 56 cm × 10.16 cm, mid section 142 cm × 5.08 cm, and top section 81 cm × 10.16 cm. Gas holdup was measured in the mid section and bubble images were taken from the top section.

4.2: Measurements

4.2.1: Gas Holdup

When the system contains no solids (as here), gas holdup can be accurately estimated from the pressure difference, using Equation 4.1[2],

$$\varepsilon_g = \frac{\Delta P}{L} \times 100 \tag{4.1}$$

4.2.2: Bubble Size

The McGill bubble size analyser[3,4] or "bubble viewer" was used (Figure 4.2). The bubble viewer consists of a sampling tube attached to a viewing chamber with a window inclined 15° from the vertical (in this case). The viewing chamber (31.7 × 22.1 × 13.0 cm) is made of PVC with two facing glass windows. To operate, the sampling tube is closed (note the globe valve) and the assembly filled with water of similar temperature and chemistry (e.g., the same frother and concentration) as present in the bulk (to preserve the bubble environment and prevent bubble coalescence). The sample tube is immersed to the desired location below the froth and is opened. Bubbles rise into the sampling tube by buoyancy and enter the viewing chamber where they spread into a single plane after contact with the inclined window. Due to diffused (note the 'filter') backlighting, bubbles cast shadows, which are digitally imaged as the bubbles slide up the window.

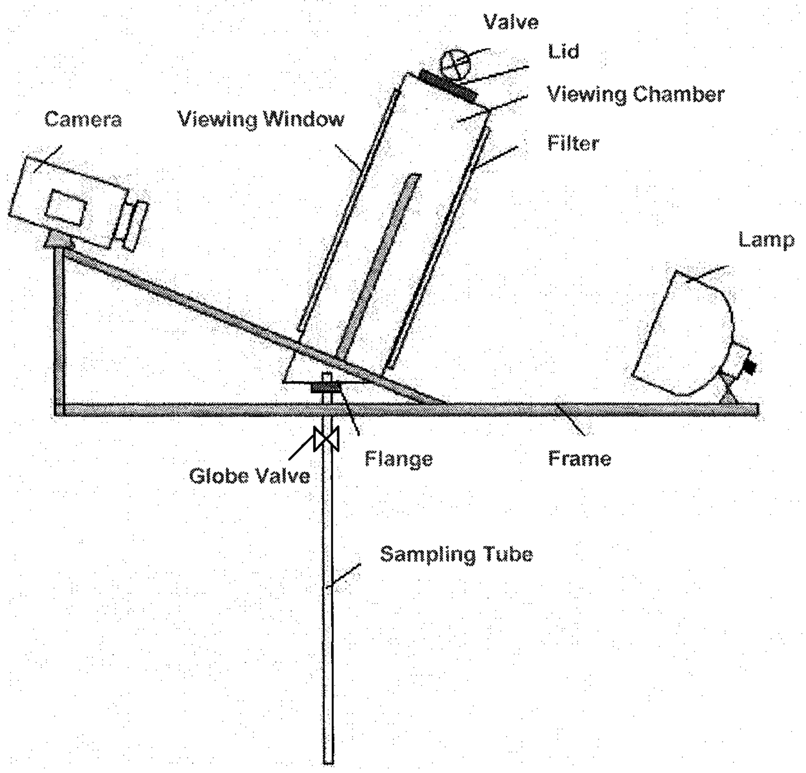


Figure 4.2: McGill bubble viewer[4]

All data presented in this thesis were collected using a digital CCD camera, and the PVC plastic sampling tube used had an inner diameter of 2.54 cm and length of 78 cm, with a globe valve. Typically 3000 bubbles were processed for a given experiment. Images were captured and analyzed using Empix Northern Eclipse v6.0 and in-house Empix BSD (bubble size distribution) processor software. Timing between frames was selected to avoid repeat counting of the same bubble. Bubble size distributions, as presented in this thesis, are generated as a number distribution and represented by two means, the number mean (d_{10}) and Sauter mean (d_{32}), calculated as follows:

$$d_{10} = \frac{\sum_{i=1}^{i=n} d_i}{\sum_{i=1}^{i=n} n_i} \tag{4.2}$$

$$d_{32} = \frac{\sum_{i=1}^{i=n} d_i^3}{\sum_{i=1}^{i=n} d_i^2} \tag{4.3}$$

where,

d_i: Equivalent spherical bubble diameter. For each bubble, the maximum and minimum axes are computed by software and d_i is obtained from: $d_b = \sqrt[3]{d_{\max}{}^2 d_{\min}}$, where d_{max} and d_{min} are the maximum and minimum diameters, respectively.

n: Total number of bubbles

4.2.3: Disengagement Technique

To help detect fine bubbles, at the end of some bubble size measurement tests the gas was switched off, i.e., a disengagement technique was used. The bubble images were recorded with time, and the time for bubbles to exit (disengage) the column was determined as a function of frother dosage; the longer the disengagement time the greater the fine bubble population. Images were captured each second to remove any duplication of bubbles in a sequence of frames. The disengagement time was determined by adapting the image analysis software to indicate when a frame is free of bubbles.

4.3: Frother Types

Table 4.1 gives a summary of the frothers examined. Frothers were used as supplied. Solutions (w/w) were made using Montreal tap water. Between each test, the column was emptied and carefully cleaned.

Table 4.1: Summary of frother properties, suppliers and cost

Frother	Structure	Molecular Weight g/g.mol.	Density g /cm^3	Solubility in water	Supplier	Cost (US$/lb)[§§]
3 Methyl-1-butanol	Aliphatic alcohol	88.15	0.809	Moderate	Sigma Aldrich	0.55
1-Pentanol	Aliphatic alcohol	88.15	0.815	Moderate	Sigma Aldrich	0.7
MIBC	Aliphatic alcohol	102.18	0.802	Low	Sigma Aldrich	0.9
1-Hexanol	Aliphatic alcohol	102.18	0.814	Low	Sigma Aldrich	0.9
1-Heptanol	Aliphatic alcohol	116.20	0.822	Slightly low	Sigma Aldrich	0.9
1-Octanol	Aliphatic alcohol	130.22	0.827	Slightly low	Sigma Aldrich	0.85
Dowfroth 250	Polyglycol ether	264.35	0.98	Very good	The Dow chemical company, USA	0.7
Dowfroth 200	Polyglycol ether	206.29	0.97	Very good	Flottec, USA	0.8
F150	Polyglycol	425	1.01	Very good	Flottec, USA	1.1

4.4: References

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Chapter 5: Characterizing Frothers Using Gas Holdup

5.1: Abstract

A possible way to characterize (classify) frothers using gas holdup as a surrogate for bubble size was explored. Nine industrial frothers with different chemical structures were selected and tested in a bubble column equipped with instrumentation to measure gas holdup and superficial gas velocity. A correlation between frother type and gas holdup was observed: for alcohols, gas holdup increased with hydrocarbon chain length and the effect was the same whether branched or straight chained; for polyglycols, gas holdup increased with number of propoxy groups. A ranking using gas holdup gave the same result as other frother characterization techniques.

5.2: Introduction

The importance of bubble size in controlling flotation efficiency has been recognized since the early days[1,2,3,4]. Flotation or froth flotation commonly requires a range of reagents. Frothers are surface-active agents (surfactants) used in flotation to decrease bubble size and promote froth stability.

Flotation frothers refer to those organic chemical agents that when dissolved or dispersed in water help produce small bubbles and form a froth. Frother molecules are heteropolar, i.e., consist of two groups, polar and non-polar. The non-polar group is a hydrocarbon chain, containing preferably at least six carbon atoms, which can either be straight, branched or cyclic[5]. It is believed that the hydrocarbon chain must not be too long since the resulting molecule is not soluble enough to be a frothing agent. Their heteropolar structure causes them to adsorb at an air-water interface (i.e., bubble surface) to satisfy both their polar and non-polar parts. This in turn stabilizes a water film on the bubble surface, which helps retard coalescence (i.e., the coming together of two or more bubbles to form larger bubbles)[6]. Pine-oil and cresylic acid were among the earliest frothers, but these have now been mostly replaced by synthetic alcohols and glycols.

The criteria for selecting frothers are changing. In the past, focus was mainly on cost, availability and being environmentally friendly. These factors remain important but other parameters related to performance, notably the bubble size produced and the quality of froth generated, are increasingly considered. However, there remains no accepted technique for the characterization of frothers. As a result, terms such as "powerful" or "selective," which have practical rather than scientific meaning are still commonly used to describe the performance of frothers. To select frothers for industrial applications empirical tests involving trial-and-error batch flotation tests are generally conducted.

Most characterizing techniques appear to be based on froth properties[7,8,9,10,11]. Two types of tests are generally used, dynamic and static. In dynamic tests, air is supplied continuously and foam is allowed to grow until steady state is reached where the rate of formation is in equilibrium with rate of decay (bubble bursting). In static tests the rate of foam formation is zero: once the foam is formed, it is allowed to collapse without further gas input or agitation.

There have been other measures. Espinosa- Gomez et al.[12] compared frothers on the basis of bubble size reduction using gas holdup measurements. More recently Laskowski and coworkers [13,14,15,16] have developed a procedure based on both the ability of frothers to reduce bubble size and increase foam stability. Comely et al.[17] characterized frothers using dynamic surface tension measurements. Recognizing the importance of water transport by bubbles in flotation, Moyo[18] classified frothers based on water carrying rate. The method showed that the amount of water, transported as a layer on the bubble surface and as a trailing wake, was related to frother type and gas holdup.

Even though these techniques have provided valuable insights into the role of frothers in flotation, what continues to be lacking is a full understanding of the mechanism(s) by which frothers act, and building from this, how to achieve the desired frother functions, bubble size reduction and froth stability.

It is well known that when bubble size decreases (e.g., with an increase in frother concentration) bubble rise velocity decreases and thus bubble retention time increases, which is reflected by an increase in gas holdup[19,20]. Gas holdup, therefore can be a surrogate for bubble size measurement and has the advantages of being simpler to measure and can be adapted to be continuous and on-line[12]. Based on these observations, in this work a possible way to characterize (classify) frothers using gas holdup was explored.

5.3: Experimental

5.3.1: Apparatus

Figure 5.1 shows the set-up: a 238 cm × 10.16 cm diameter Plexiglas column. The column was operated batch, the feed solution being introduced using a pump (Cole Palmer model 7520-25). The bubble generator was a porous, stainless steel plate sparger that covered the base. A pressure transmitter (P_{Bot}) was placed 11.5 cm above the sparger to monitor the total head in the column. A calibrated mass flow meter (F) was used to control the gas flow rate. Temperature sensors (Thermopar type K) monitored input air (T_{air}) and solution temperature (T_{sol}) in the column. All the tests were carried out over the temperature range 20 ± 3 °C. The average of the temperature between T_{air} and T_{sol} and P_{Bot} was used to correct the air mass flow meter reading to the conditions of the test. A Visual Basic program was developed to convert air mass flowrate to volumetric flowrate. A differential pressure transmitter (ΔP) (Bailey model PTSDDD) was located between 67 cm and 136.5 cm above the sparger to determine gas holdup. All of the above-mentioned instruments were connected to an interface and signal conditioner, Opto 22. Readings were carried out under steady state conditions and outputs were monitored every second through a software package, Intellution IFix, installed in a PC. Data were stored and processed using an in-house historical data extraction program.

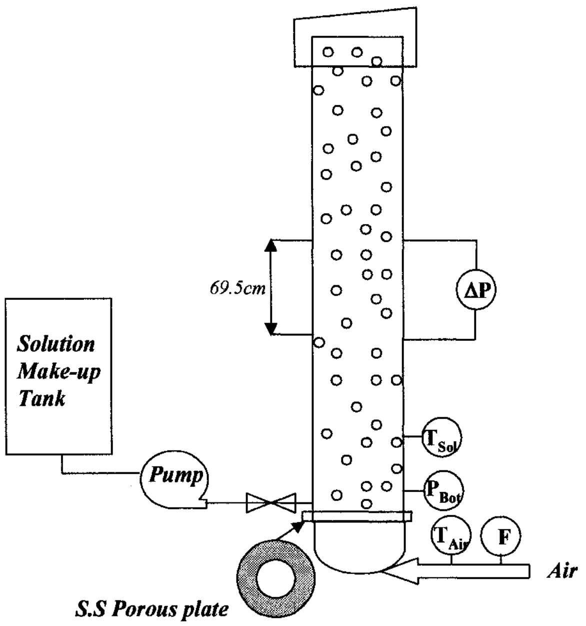


Figure 5.1: Experimental set-up

5.3.2: Frother Types

Table 5.1 is a summary of the frothers examined. Frothers were used as supplied. Solutions (w/w) were made using Montreal tap water; between each test, the column was emptied and carefully cleaned.

5.3.3: Gas Dispersion Parameters

Superficial gas velocity, or simply gas rate (J_g, *cm/s*) is the volumetric flowrate (Q_g, cm^3/s) of air per cross sectional area (A, cm^2) of the column.

$$J_g = \frac{Q_g}{A} \tag{5.1}$$

Gas holdup (ε_g) (or voidage) is a dimensionless parameter defined as the volume fraction of gas phase occupied at any point in a cell, usually expressed as a

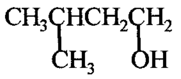
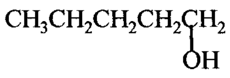
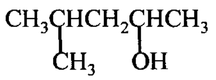
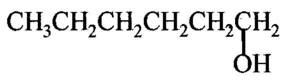
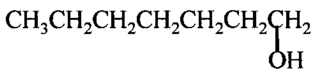
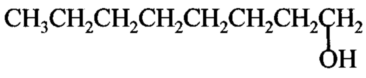
$$\%.\varepsilon_g = \frac{V_g}{V_t} \tag{5.2}$$

where V_g and V_t are volume fraction of gas phase and total volume, respectively.

When the system contains no solids, gas holdup (ε_g) can be accurately measured from the pressure difference, using Equation 5.3[20],

$$\varepsilon_g = \frac{\Delta P}{L} \times 100 \tag{5.3}$$

Table 5.1: Summary of frother properties, suppliers and cost

Frother	**Structure**	**Formula**	**Molecular Weight g/gmol**	**Supplier**	**Cost[***] (US$/lb)**
3 Methyl-1-butanol	Aliphatic alcohol	 $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2\underset{\underset{OH}{\vert}}{C}H_2$	88.15	Sigma Aldrich	0.55
1-Pentanol	Aliphatic alcohol	 $CH_3CH_2CH_2CH_2\underset{\underset{OH}{\vert}}{C}H_2$	88.15	Sigma Aldrich	0.7
MIBC[†††]	Aliphatic alcohol	 $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2\underset{\underset{OH}{\vert}}{C}HCH_3$	102.18	Sigma Aldrich	0.9
1-Hexanol	Aliphatic alcohol	 $CH_3CH_2CH_2CH_2CH_2\underset{\underset{OH}{\vert}}{C}H_2$	102.18	Sigma Aldrich	0.9
1-Heptanol	Aliphatic alcohol	 $CH_3CH_2CH_2CH_2CH_2CH_2\underset{\underset{OH}{\vert}}{C}H_2$	116.20	Sigma Aldrich	0.9
1-Octanol	Aliphatic alcohol	 $CH_3CH_2CH_2CH_2CH_2CH_2CH_2\underset{\underset{OH}{\vert}}{C}H_2$	130.22	Sigma Aldrich	0.85
Dowfroth 250	Polyglycol ether	$CH_3(PO)^{‡‡‡}{}_4OH$	264.35	The Dow chemical company, USA	0.7
Dowfroth 200	Polyglycol ether	$CH_3(PO)_3OH$	206.29	Flottec, USA	0.8
F150	Polyglycol	$H(PO)_7OH$	425	Flottec, USA	1.1

[***] Costs for bulk supplied by, Frank Cappuccitti, Flottec, USA, June 2005
[†††] Methyl isobutyl carbinol
[‡‡‡] PO = C_3H_6O

5.4: Results and Discussion

5.4.1: Reproducibility

A vital requirement of any experiment is reproducibility. Repeat tests were conducted at two J_g (J_g = 0.85 cm/s and J_g = 1.3 cm/s) and 6 different MIBC concentrations. These were full repeats, including making fresh solution. Table 5.2 shows the conditions for each test.

Table 5.2: The reproducibility test results

Frother Concentration (mmol/L)	Run 1 J_g= 0.85 cm/s	Run 2 J_g= 0.85 cm/s	Run 3 J_g= 1.3 cm/s	Run 4 J_g= 1.3 cm/s	Run 5 J_g= 1.3 cm/s
	ε_g (%)	ε_g (%)	ε_g (%)	ε_g (%)	ε_g (%)
0	4.87	4.23	6.15	6.90	6.70
0.05 ± 0.002	6.30	5.79	9.29	9.26	9.23
0.10 ± 0.002	12.30	11.12	15.78	16.37	16.14
0.15 ± 0.002	13.95	12.28	18.44	18.04	18.53
0.25 ± 0.002	15.66	13.24	21.49	20.12	21.27
0.40 ± 0.002	16.77	14.55	23.76	21.97	--

Sample standard deviation (s) was calculated by the following:

$$s = \sqrt{\frac{\sum_{i=1}^{N}\left(x_i - \bar{x}\right)^2}{N-1}} \tag{5.4}$$

where x_i , $\bar{x}$ and N are the individual measurements, the average and number of measurements, respectively.

When several small sets have the same sources of indeterminate error (i.e., the same type of measurement but different mean) the standard deviations of the individual data sets may be pooled to more accurately determine the standard deviation of the analysis method.

Pooled standard deviation (s_{pooled}) was calculated by the following:

$$s = \sqrt{\frac{\sum_{i=1}^{N_1}\left(x_i - \bar{x}_1\right)^2 + \sum_{j=1}^{N_2}\left(x_j - \bar{x}_2\right)^2}{N_1 + N_2 - 1}} \qquad (5.5)$$

Therefore the pooled standard deviation is equal to 0.36%. This shows a high precision, sufficient to discriminate the variables tested.

5.4.2: Selecting Test Conditions

Gas holdup is influenced by gas rate and, in this case, sparger porosity. Apart from the need to produce a sensitive response in gas holdup, the choice of gas rate and porosity is arbitrary, but these two parameters need to be set prior to comparing frother types. The frother MIBC was used to determine a gas rate and porosity.

Figure 5.2 shows the effect of gas rate (J_g) at a fixed porosity (5 μm nominal pore size). As expected, gas holdup increases with J_g. A J_g = 0.85 cm/s was selected. Figure 5.3 shows the effect of porosity. Again as expected, while pore size (nominal) decreases, i.e., bubble size generated decreases, gas holdup increases. A porosity of 10 μm was selected. Although giving a more sensitive response, it was felt prudent to avoid the 5 μm sparger as this was more prone to plugging (the air line was not filtered).

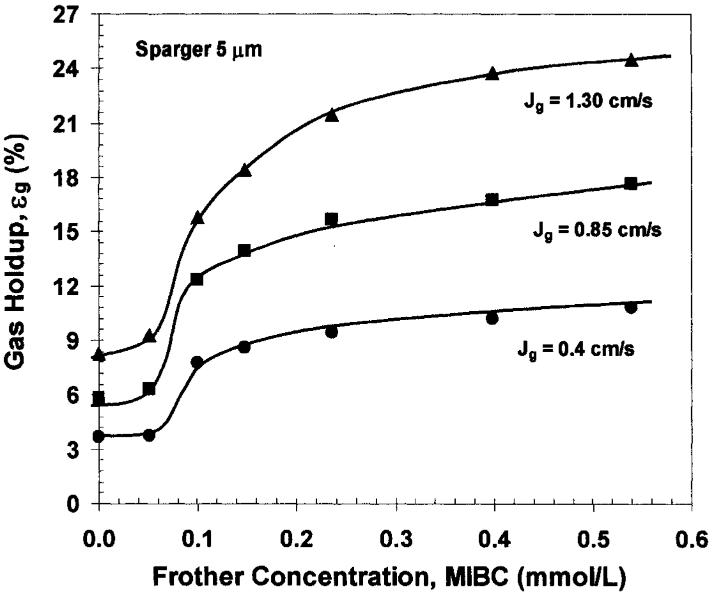


Figure 5.2: Gas holdup as a function of frother concentration: effect of gas rate

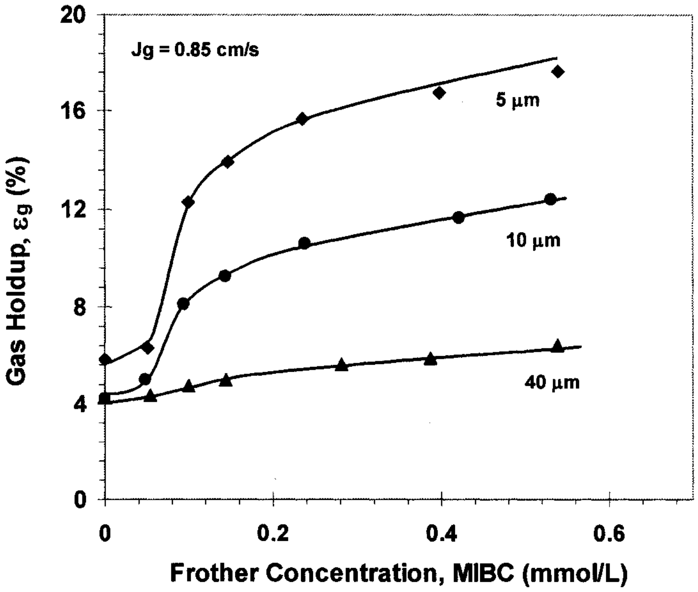


Figure 5.3: Gas holdup as a function of frother concentration: effect of sparger porosity

5.4.3: Frother Classification

Figure 5.4 presents gas holdup as a function of concentration of branched and straight chain alcohols. It is observed that gas holdup increases with the length of hydrocarbon chain. It was also found that MIBC, a branched 6 carbon chain alcohol, demonstrated similar behavior to 1-Hexanol its straight chain analogue and likewise for 1-Pentanol and 3-Methyl-1-butanol (both 5 carbons). This suggests that for alcohols, whether branched or straight chained does not seem to matter. Sweet et al.[13] suggested that the frothers with branched chain (e.g., MIBC vs. 1-Hexanol) produced a different bubble size-concentration relationship. This seems at odds with what is found here (given the same gas holdup means the same bubble size).

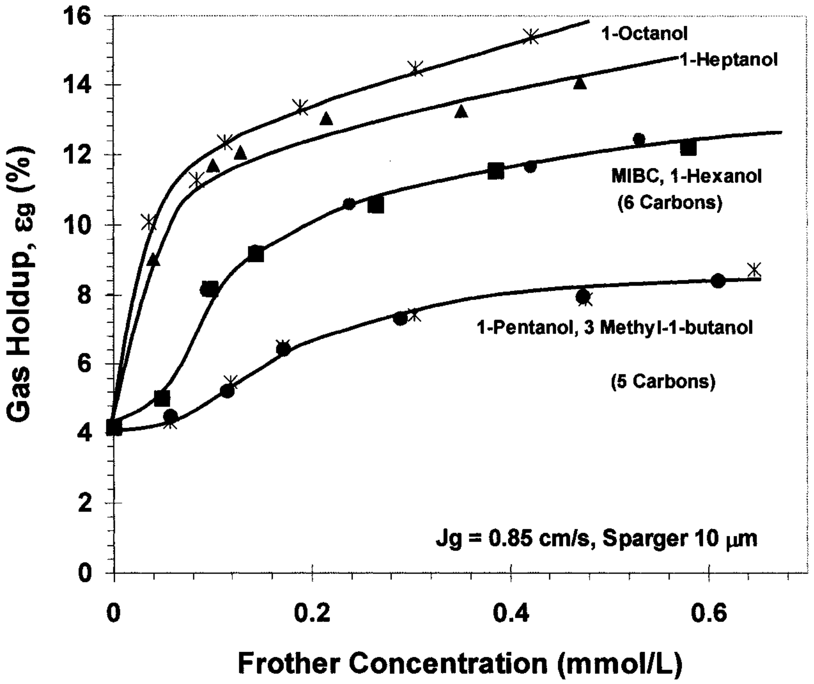


Figure 5.4: Gas holdup as a function of frother concentration: comparison of alcohols

Figure 5.5 shows a comparison of polyglycol-type frothers. The results indicate that with increasing number of propoxy (PO) groups in the frother molecule, gas holdup increases for a given frother dosage.

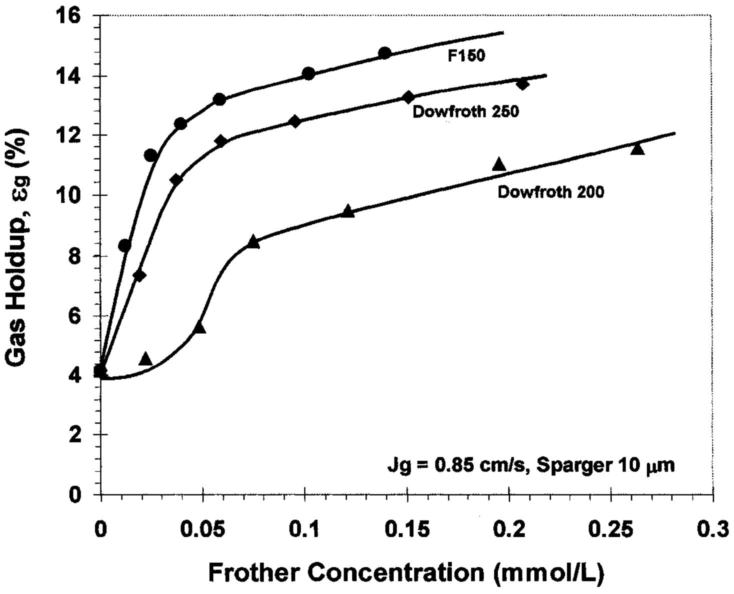


Figure 5.5: Gas holdup as a function of frother concentration: comparison of polyglycols

Figure 5.6 shows the results for all frothers tested. There are clear differences in gas holdup among the frothers. The order (ranking) is from the least effect (on increasing gas holdup) by 5 carbon alcohols to greatest effect by F150. The order is essentially the same as that given in terms of bubble size[13,16], dynamic foamability index (DFI)[13,16] and water carrying rate[18] as Table 5.3 demonstrates. The correspondence with bubble size is expected (it was the basis for using gas holdup). The similarity to DFI ranking is probably because as part of that determination the increase in solution volume upon introducing gas is measured; this measure contains the effect of gas holdup (it there is no foam buildup the increase in volume is entirely due to the gas holdup). As for water carrying rate, Moyo[18] used the relationship with gas holdup as the means of dividing the frothers into classes. The current findings support that gas holdup is related to frother type.

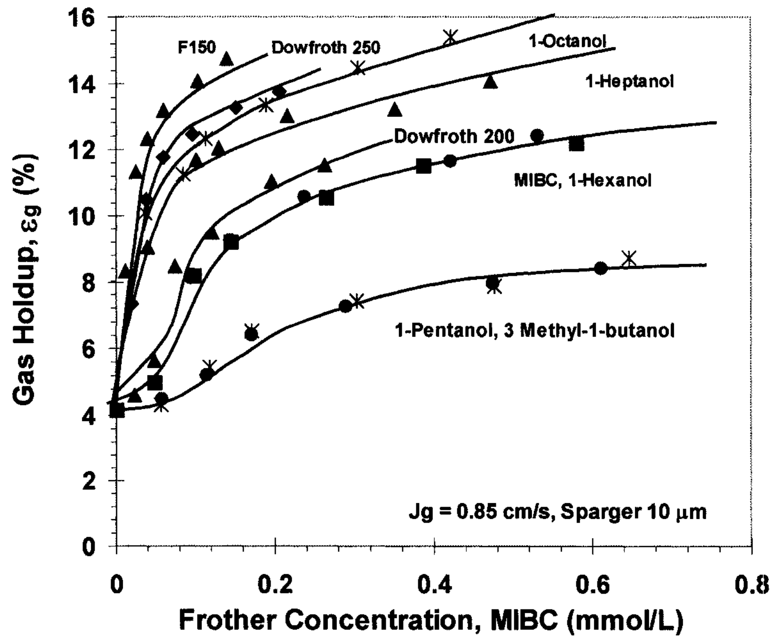


Figure 5.6: Gas holdup as a function of frother concentration: comparison of all frothers tested

Table 5.3: Summary of frother rankings

Gas Holdup	Bubble Size[13,16]	Dynamic Foamability Index (DFI)[13,16]	Water Carrying Rate[18]
3 Methyl-1-butanol / 1-Pentanol	1-Butanol	1-Butanol	-
	1-Pentanol	1-Pentanol	1-Pentanol
MIBC / 1-Hexanol	MIBC	MIBC	MIBC
	1-Hexanol	1-Hexanol	1-Hexanol
Dowfroth 200	Dowfroth 200	Dowfroth 200	Dowfroth 200
1-Heptanol	1-Heptanol	1-Heptanol	1-Heptanol
1-Octanol	1-Octanol	1-Octanol	1-Octanol
Dowfroth 250	Dowfroth 250	Dowfroth 250	Dowfroth 250
F150	-	-	F150

The comparison is strictly on a technical performance level, knowing the bulk costs (Table 5.1) the comparison can be turned into performance (gas holdup increase) versus cost (Figure 5.7). The cost basis is $ per cubic meter of solution. (This correctly stresses that frother functions on a volume of water, not per tonne of dry solids, which is the common dosage metric.) The ranking does not alter much (the cost differential is not large.) It does now imply (Figure 5.7) that 1-octanol is the most effective.

5.4.4: Some Features of the Gas Holdup – Frother Concentration Relationship

The expectation with increasing frother dosage is an increasing gas holdup reflecting the decrease in bubble size till the CCC (critical coalescence concentration) is reached when gas holdup (and bubble size) becomes constant. The results (Figure 5.6) generally agree with this trend but there are features that emerge needing commentary.

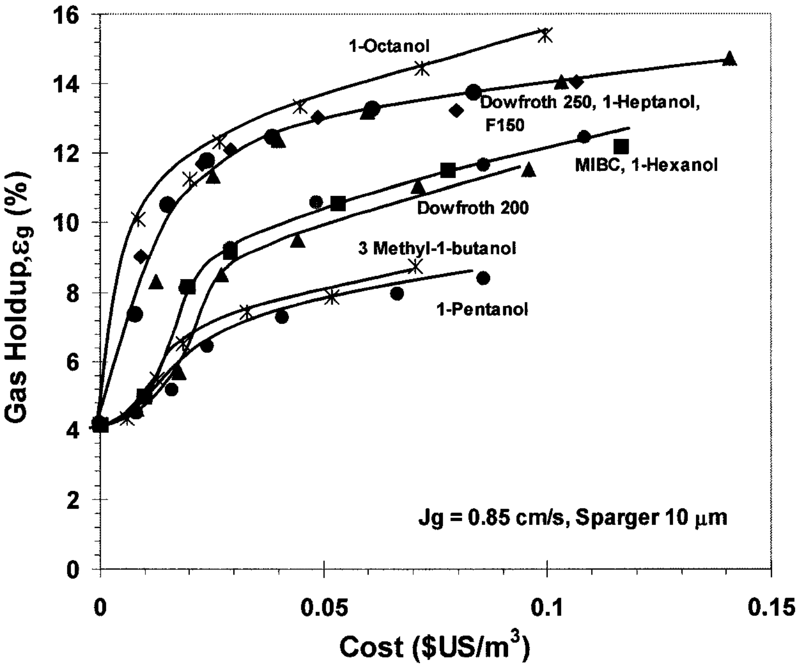


Figure 5.7: Gas holdup as a function of cost: practical comparison of all frothers tested

The first feature is evident for the less effective frothers (i.e., those that increase gas holdup the least): there is a region of low concentration where little increase in gas holdup occurs. This is either because bubble size is not decreasing or the decrease is not sufficient to reduce bubble rise velocity. It is likely the latter taking terminal velocity for a single bubble as a guide; this requires a bubble size less than 1.5 – 2 mm[19] before velocity becomes a function of bubble size.

At higher concentration, for all frothers the second feature is evident: the gas holdup continues to increase steadily, apparently not reaching a maximum. This means either that the bubble size continues to decrease with increasing frother dosage or there is some unanticipated phenomenon causing the velocity of the bubble in the swarm to decrease.

To help answer, bubble size measurements are required. Initial measurement attempts were thwarted in the basic set-up as the bubble population in some situations was too numerous for clear discrimination between bubbles.

The next chapter shows how the apparatus was modified to solve this problem. The bubble size information is then used to probe the two features described. The data were also interrogated to answer whether at equal gas holdup the bubble size was the same regardless of frother type. This is the expected situation, as, for example, use of drift flux analysis to estimate bubble size assumes[21,22]. However, at least one reference challenging this is known[23]. Given the assumed correlation between gas holdup and bubble size applied in this Chapter this needs assessing.

5.5: Conclusions

A possible way to characterize frothers using gas holdup was explored. A correlation between frother type and gas holdup was observed: for alcohols gas holdup increases with hydrocarbon chain length and is independent of whether the chain is branched or not; for polyglycols, gas holdup increases with number of propoxy (PO) groups.

A ranking of frothers based on gas holdup was identical to that given by more elaborate techniques. The gas holdup – concentration trends are more or less as anticipated from the relative impact of the frothers on bubble size but some unexpected features are noted.

5.6: Acknowledgments

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SGS Lakefield Research. Assistance of Mr. Claudio Acuna in developing software is also gratefully acknowledged.

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Chapter 6: Correspondence of Gas Holdup and Bubble Size in Presence of Different Frothers

6.1: Abstract

Chapter 5 has shown that frothers can be classified (ranked) according to gas holdup. The argument in using gas holdup is a correspondence with bubble size. This is examined in this chapter. With MIBC as an example, the two regions identified in Chapter 5 are examined: I, low concentration where gas holdup varied little, and II, high concentration where a steady, continuous increase in gas holdup occurred. By adapting the test apparatus, bubble size data are obtained which contribute to an explanation. Another test is to examine whether the bubble size is the same at equal gas holdup regardless of frother type. This is shown not to be the case, for example F150 producing significantly larger bubbles than 1-Pentanol. This is not predicted, drift flux analysis for example, assumes a unique relationship among bubble size, gas holdup and gas rate. Possible explanations are discussed.

6.2: Introduction

In Chapter 5 it was shown that the gas holdup – concentration relationship was dependent on frother type. This permitted a ranking of frothers, which corresponded to those reported using other measures. Thus it was shown that the simple measure of gas holdup could be used to characterize frothers.

This use of gas holdup was predicated on its relationship with bubble size: as bubble size decreases, gas holdup increases. In Chapter 5, the relationship was assumed but not tested and there were some intriguing results that raised some question regarding the relationship that required further exploration. One was the insensitivity of gas holdup at low concentration with the 'lower ranked' frothers; another was the steady increase in gas holdup at higher concentration, evident for all frothers. In this chapter those two observations are examined.

An additional point, which was also raised was whether the bubble size at equal gas holdup (and gas rate) is the same regardless of frother type. This is the common consumption, for example in applying drift flux analysis to estimate bubble size.[1]

To address these points the set-up had to be modified as at high population of small bubbles there was significant bubble clustering which the current software cannot discriminate (clusters are eliminated) leading to poor counting statistics (as well as possible biasing as clusters may not contain a random sample of individual bubbles).

The modified apparatus is described. It is tested to make sure the results are the same as in the 'basic' set-up. Using MIBC as an example, the low and high concentration region effects are probed. And, bubble size data at equivalent gas holdup (6% and 8%) are compared across a suite of frothers.

6.3: Experimental

6.3.1: Apparatus

The basic and modified test rigs are shown in Figure 6.1 (a) and (b), respectively. The basic set-up is as described in Chapter 5.

The modification was designed to reduce the number of bubbles entering the bubble viewer and thus improve reliability of bubble size measurement. The same column was divided into three sections: base section (as before), 56 cm × 10.16 cm, mid section (new) 142 cm × 5.08 cm, and top section (as before), 81 cm × 10.16 cm. Gas holdup was measured in the mid section and bubble images were taken from the top section, where they had spread and thus the number sampled and entering the viewing chamber is reduced. The angle connecting the two end sections to the mid section was shallow (7°) to limit bubble collision and possible coalescence in the transition. It will be verified that the gas holdup - gas rate relationship measured in the mid section is the same as in the basic set-up (i.e., the source of the original data in Chapter 5). All the measurement devices and instruments are the same as in the basic set-up. In this Chapter just the bubble size measurement is described.

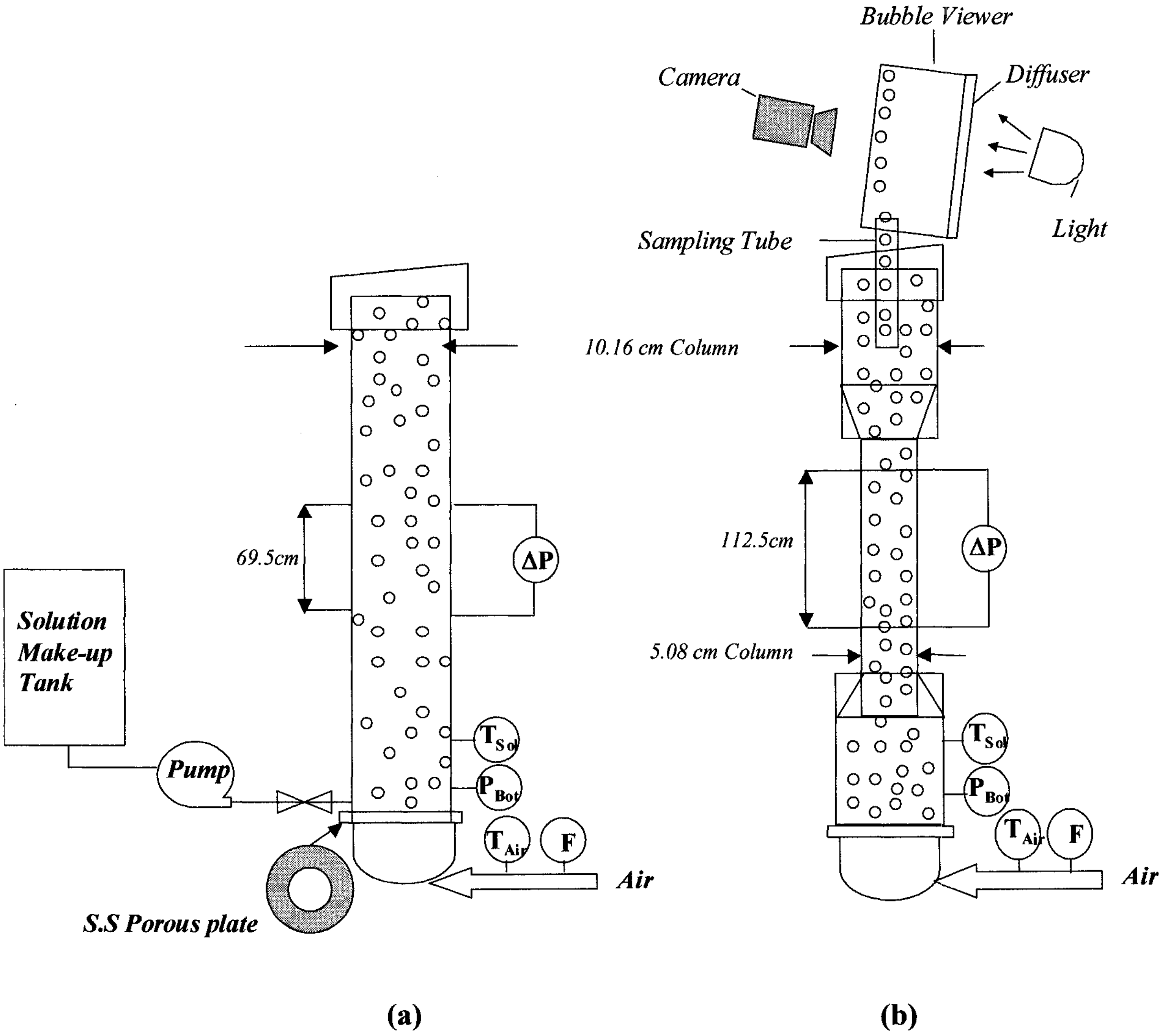


Figure 6.1: Experimental set-up: (a) basic; and (b) modified

6.3.2: Bubble Size

The McGill bubble size analyser[2,3] or "bubble viewer" was used (Figure 6.2). The bubble viewer consists of a sampling tube attached to a viewing chamber with a window inclined 15° from the vertical (in this case). The PVC plastic sampling tube used had an inner diameter of 2.54 cm and 78 cm length, with a globe valve. The viewing chamber (31.7 × 22.1 × 13.0 cm) is made of PVC with two facing glass windows. To operate, the sample tube is closed with the valve and the assembly filled with water of similar temperature and chemistry (i.e., the same frother type and concentration) as present in the bulk (to preserve the bubble environment and prevent bubble coalescence). The sample tube is immersed to the desired location below the froth and the valve opened. Bubbles rise into the sampling tube by buoyancy and enter the viewing chamber where they spread into a single plane after contact with the inclined window. The sloped window is a unique feature of the McGill bubble viewer that reduces bubble overlap and provides an unambiguous focal plane. Using diffused (note the 'filter') backlighting, bubbles cast shadows, which are digitally imaged as the bubbles slide up the window.

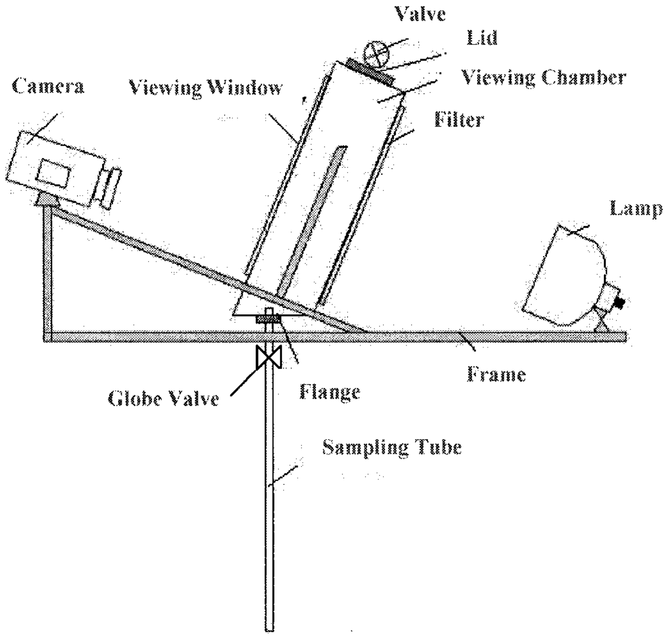


Figure 6.2: McGill bubble viewer[3]

Images were collected using a digital CCD camera. The time between frames was selected to avoid duplicate bubble counting. Typically 3000 plus bubbles were processed for a given experiment. Images were captured and analyzed using Empix Northern Eclipse v6.0 and in-house Empix BSD processor software. Bubble size distributions are generated as a number frequency distribution and represented by two means, the number mean (d_{10}) and Sauter mean (d_{32}) calculated as follows:

$$d_{10} = \frac{\sum_{i=1}^{i=n} d_i}{\sum_{i=1}^{i=n} n_i} \tag{6.1}$$

$$d_{32} = \frac{\sum_{i=1}^{i=n} d_i^3}{\sum_{i=1}^{i=n} d_i^2} \tag{6.2}$$

where,

d_i: Equivalent spherical bubble diameter. For each bubble, the maximum and minimum axes are computed by software and d_i is obtained from: $d_b = \sqrt[3]{d_{\max}{}^2 d_{\min}}$, where d_{max} and d_{min} are the maximum and minimum diameters, respectively.

n: Total number of bubbles

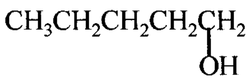
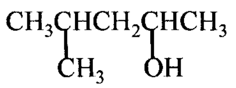
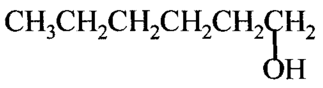
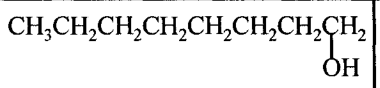
6.3.3: Disengagement Technique

To help detect fine bubbles at the high frother concentration conditions, at the end of a test the gas was switched off and the bubble images were recorded over time till the bubbles all had exited the column. This is known as a 'disengagement' technique and the time to exit is the disengagement time (the longer the time the greater the fine bubble population). The procedure was repeated for a range in frother (MIBC) concentration. Images were captured each second to remove any duplication of bubbles in a sequence of frames. The disengagement time was determined by adapting the image analysis software to indicate when a frame is free of bubbles.

6.3.4: Comparison of ε_g/d_b for the Frother Types

Table 6.1 is a summary of the frothers examined, chosen to give a wide range of gas holdup - frother concentration (Figure 5.6). The experimental conditions were as in Chapter 5. A gas holdup was selected that was attained by all frother types at the selected conditions (J_g and sparger porosity) used in Chapter 5 in order to compare d_b.

Table 6.1: Summary of frother properties and suppliers

Frother	**Structure**	**Formula**	**Molecular Weight g/gmol**	**Supplier**
1-Pentanol	Aliphatic alcohol	 $CH_3CH_2CH_2CH_2\underset{OH}{C}H_2$	88.15	Sigma Aldrich
MIBC[§§§]	Aliphatic alcohol	 $CH_3\underset{CH_3}{C}HCH_2\underset{OH}{C}HCH_3$	102.18	Sigma Aldrich
1-Hexanol	Aliphatic alcohol	 $CH_3CH_2CH_2CH_2CH_2\underset{OH}{C}H_2$	102.18	Sigma Aldrich
1-Octanol	Aliphatic alcohol	 $CH_3CH_2CH_2CH_2CH_2CH_2CH_2\underset{OH}{C}H_2$	130.22	Sigma Aldrich
F150	Polyglycol	H(PO)[****]$_7$OH	425	Flottec, USA

6.4: Results and Discussion

6.4.1: Reproducibility

Three full repeat tests for bubble size determination were conducted at 0.1 mmol/L MIBC in the modified set-up (Table 6.2).

Table 6.2: The reproducibility test results

Frother Concentration (mmol/L)	Run 1		Run 2		Run 3	
	d_{10} (mm)	d_{32} (mm)	d_{10} (mm)	d_{32} (mm)	d_{10} (mm)	d_{32} (mm)
0.10 ± 0.002	0.841	0.962	0.851	0.973	0.874	0.994

Sample standard deviation (*s*) was calculated by the following:

[§§§] Methyl isobutyl carbinol

[****] PO = C_3H_6O

$$s = \sqrt{\frac{\sum_{i=1}^{N}\left(x_i - \bar{x}\right)^2}{N-1}} \qquad (6.3)$$

where x_i , $\bar{x}$ and N are individual measurements, the average and number of measurements, respectively.

The standard deviation for d_{10} and d_{32} are 0.01 mm and 0.009 mm, respectively. As with gas holdup this shows a high precision is achieved

6.4.2: Comparing Basic and Modified Set-ups

Modifying the set-up was driven by a need to improve bubble image processing by spreading the bubbles more. To ensure this has not altered the basic set-up results, it is necessary to establish that the gas holdup – gas rate relationship in the mid-section is equal to that in the basic set-up (otherwise the bubble size measurement will not have the correspondence required).

Figure 6.3 shows the ε_g-J_g relationships for the modified and basic design do agree. That is the sloped connections do not disturb the hydrodynamics or promote bubble coalescence / breakage (this was evident visually also). Thus the bubble sizes measured in the top section will correspond to those in the mid-section (and thus to those in the basic design).

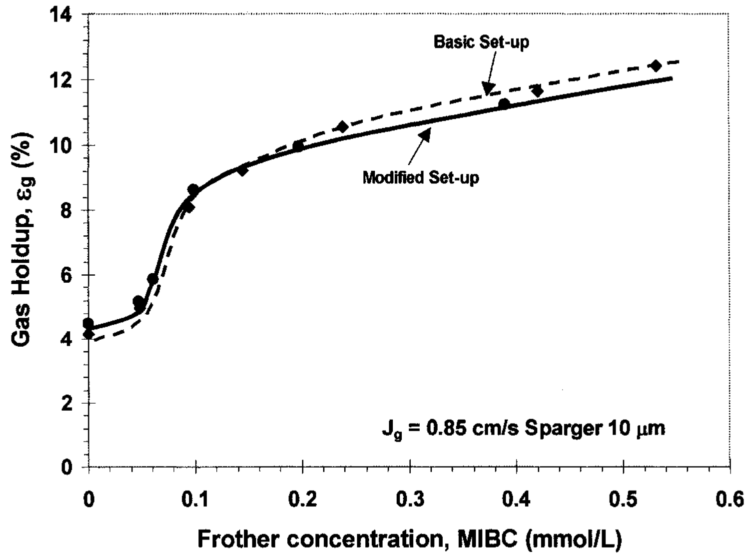
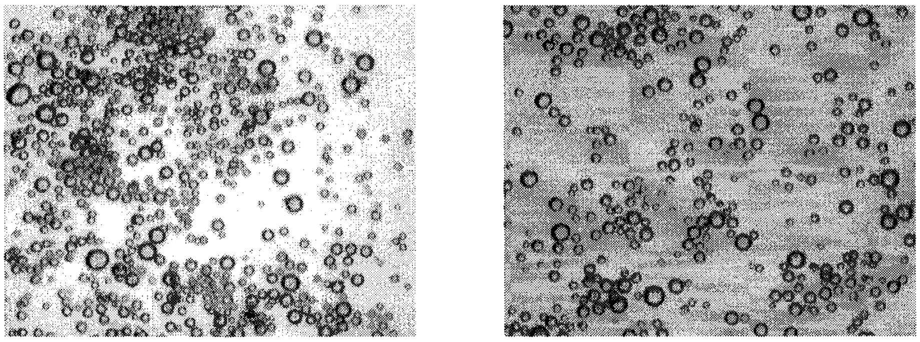


Figure 6.3: The $\varepsilon_g - J_g$ relationship for modified and basic set-up

The advantage of the modified design in improved image quality is evident in Figure 6.4: image (a) was obtained is using the basic set-up, image (b) using the modified set-up at the same ε_g / J_g point. A comparison of the mean size results (see below images) shows the measurements are within the precision of the analysis procedure.



d_{10} = 0.877 mm d_{32} = 1.020 mm

(a)

d_{10} = 0.863 mm d_{32} = 1.021 mm

(b)

Figure 6.4: Comparing images for basic (a) and modified (b) set-up 0.2 mmol/L MIBC

6.4.3: The Low and High Frother Concentration Regions

The frother selected was MIBC as it showed the two ε_g regions (low and high concentration) that were to be explored (Figures 5.2 and 5.6). The gas holdup and bubble size versus concentration relationships determined in the modified set-up are shown in Figure 6.5.

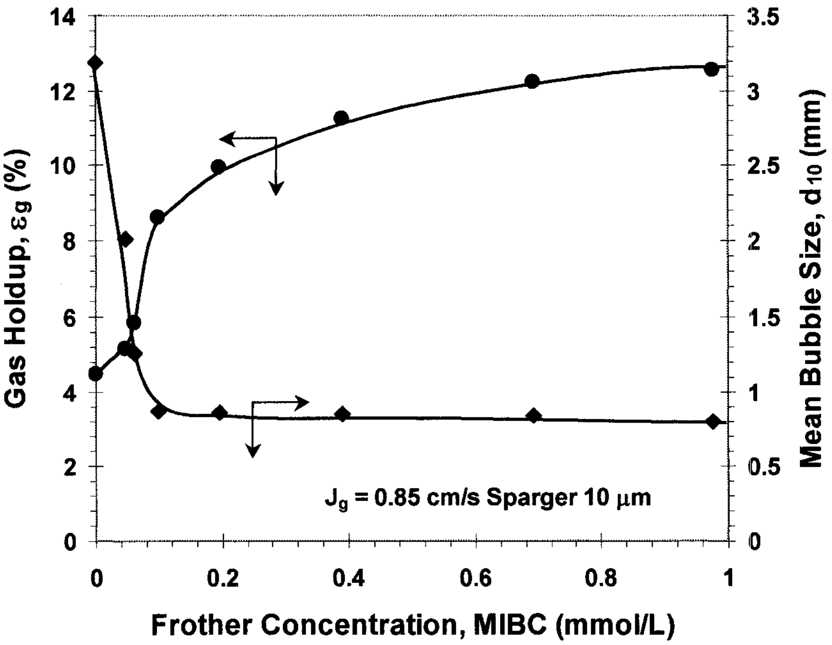


Figure 6.5: Gas holdup and bubble size vs. frother concentration (MIBC)

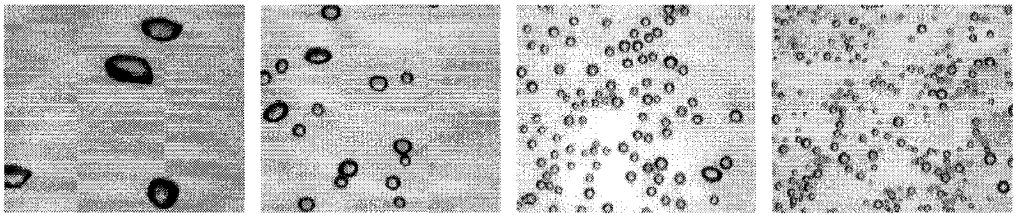
I) Low Concentration region

Although not as definitive, as was seen in Figures 5.2 and 5.6, Figure 6.5 shows that gas holdup was less influenced by frother (MIBC) dosage initially, up to ca. 0.08 mmol/L, than beyond.

The bubble size corresponding to the start of the more rapid increase in gas holdup is about 1.5 mm. From the relationship between bubble size and terminal velocity[4], it is known that terminal velocity is essentially constant for $d_b > 1.5$ mm (up to ca. 10 mm) and decreases (as a power function) for bubbles $d_b < 1.5$ mm. It is postulated that the region of limited gas holdup response is related to the bubble size being greater than ca. 1.5 mm where the velocity is insensitive to size. The bubble size clearly is decreasing in this low concentration region but remains > 1.5 mm till the concentration reaches ca. 0.08 mmol/L.

II) High concentration region

Figure 6.5 clearly shows the steady, continuous increase in gas holdup at higher concentration noted in Figures 5.2 and 5.6. This was 'unexpected' in the sense that the concentration is above the reported CCC (ca. 0.083 mmol/L[7]) and bubble size is expected to be constant and therefore so is velocity, retention time and gas holdup in consequence. Figure 6.6 does hint at a constant Sauter mean (d_{32}) bubble size above ca. 0.1 mmol/L (see the mean sizes recorded below each image), similar to that noted by various authors[5,6,7]. The d_{10} data, however, do show a consistent decrease as concentration increases. The d_{10} is more sensitive to fine bubbles than the d_{32} thus this does suggest that the fineness of the bubble population is increasing. The question is whether the small increase in fineness detected in d_{10} can account for the increase in gas holdup. One approach to answering is to apply drift flux analysis[8,1]: does the predicted size of bubble from ε_g (at the given J_g) decrease at the same rate with concentration as the d_{10}?

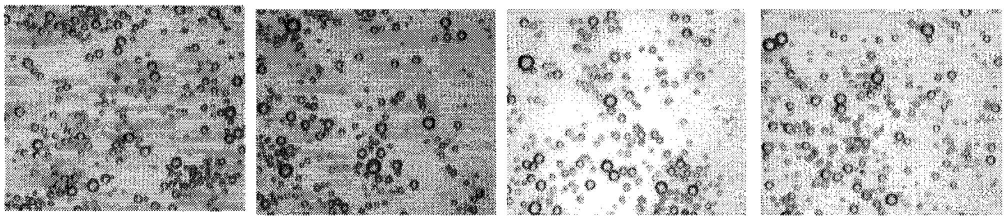


0 mmol/L $d_{10}=3.195$ $d_{32}=4.281$

0.05 mmol/L $d_{10}=2.031$ $d_{32}=2.155$

0.065 mmol/L $d_{10}=1.262$ $d_{32}=1.351$

0.1 mmol/L $d_{10}=0.874$ $d_{32}=0.994$



0.2 mmol/L $d_{10}=0.863$ $d_{32}=1.021$

0.4 mmol/L $d_{10}=0.854$ $d_{32}=1.035$

0.7 mmol/L $d_{10}=0.838$ $d_{32}=1.001$

1 mmol/L $d_{10}=0.802$ $d_{32}=1.040$

* Note: d_{10}, d_{32} in mm

Figure 6.6: Bubble images and corresponding mean diameters as a function of MIBC concentration

Table 6.3 shows the result: the rate of decrease in d_{10} and in predicted d_b are in reasonable agreement. Also included in the Table is % -1 mm from the distribution and this is steadily increasing. (The apparently anomalous high % -1 mm with zero MIBC is commonly seen when sparging into water alone and appears to result from a coalescence induced bubble break-up phenomenon[9] which adding frother prevents.)

It is tentatively concluded that the increase in gas holdup is related to the small but consistent increase in bubble fineness with increasing frother dosage.

This conclusion was tested using the disengagement technique. The gas was shut off and bubble size tracked with time. The result for two concentrations, 0.1 and 1 mmol/L, are shown in Figure 6.7. The bubble size decreases with time as the coarser, faster moving bubbles disengage first, and it takes longer for disengagement to complete at the higher concentration compared to the lower but the final, minimum size in the population is essentially unchanged (ca. 0.38 mm).

Table 6.3: Various bubble size measurements and estimation from drift flux model

MIBC mmol/L	**ε_g %**	**% -1 mm**	**d_{32}, mm Measured**	**d_{10}, mm Measured**	**d_b, mm Predicted (Drift Flux Model)**
0.000	4.47	8.1	4.28	3.20	2.28
0.050	5.17	0.8	2.16	2.01	1.94
0.065	5.85	12.7	1.35	1.26	1.69
0.100	8.62	72.2	0.99	0.87	1.13
0.200	9.94	73.4	1.02	0.86	0.99
0.400	11.23	76.5	1.03	0.85	0.89
0.700	12.26	80.3	1.00	0.84	0.82
1.000	12.54	80.7	1.04	0.80	0.81

The disengagement time was determined for a range of concentration and is plotted in Figure 6.8. The trend (dashed line) is clearly to an increasing disengagement time. The fact it takes longer to disengage at higher concentration means a lower swarm velocity and higher retention time, which corresponds to the increase in gas holdup.

A reasonable explanation is that the longer time indicates more fine bubbles (although not finer bubbles), which simultaneously hinder the swarm bubble rise velocity and decrease the mean size d_{10}.

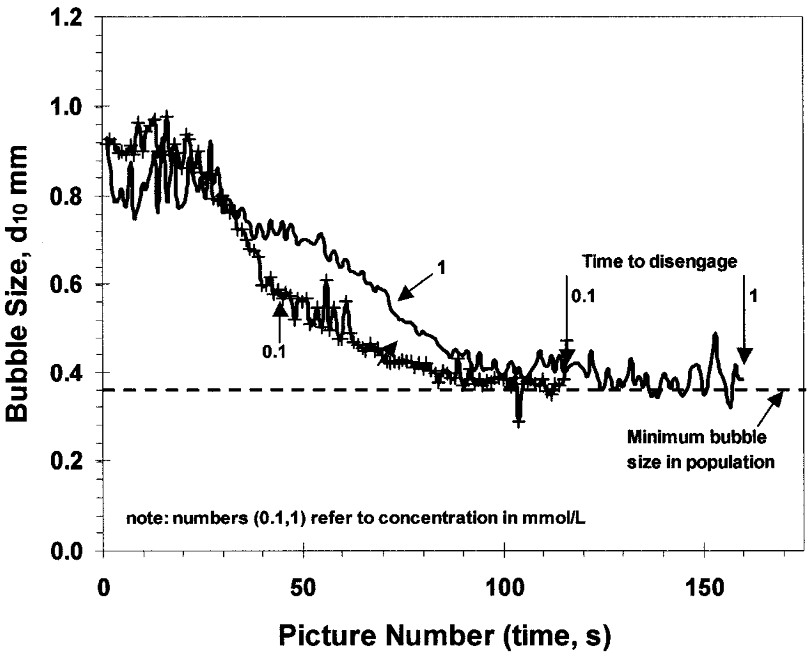


Figure 6.7: Disengagement test: bubble size as a function of time after gas is shut off

Combining the evidence directly from bubble sizing and indirectly from the disengagement result, the conclusion is that the continued increase in gas holdup with concentration does indicate a bubble population becoming finer.

This means that bubble size continues to decrease above the CCC. This appears to be a conclusion also recently drawn by others[10]. This does not invalidate CCC as a useful 'aid to thought'. By the time the frother concentration reaches CCC it is possible the bulk of coalescence has been prevented and at higher concentrations the effects are residual (although it is possible a different mechanism, directly influencing bubble production perhaps driven by surface tension, also comes into play.) From a practical point of view, plants would rarely choose to operate above the CCC so it retains the notion of a practical upper limit, such that concentration relative to CCC becomes a potentional guide to where the plant is operating. A dimensionless concentration by making it relative to the CCC may be useful to compare operations and parts of the same operation. This places some emphasis on a rigorous CCC estimation routine.

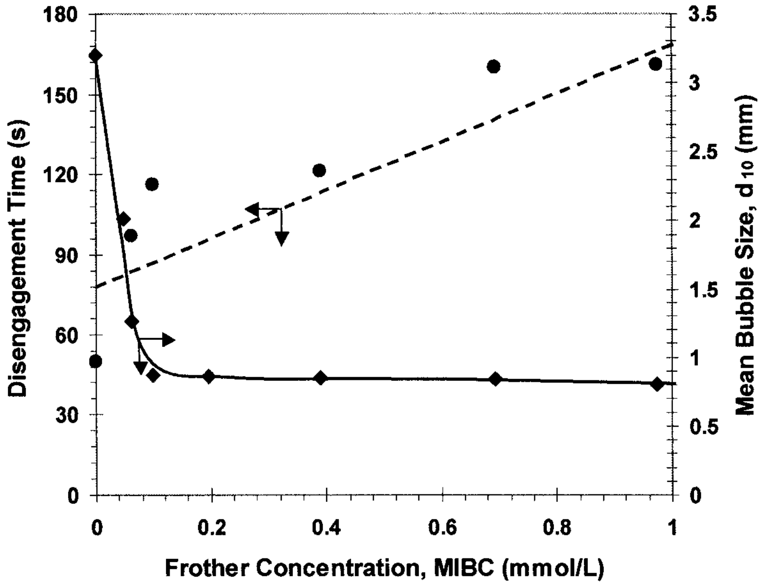
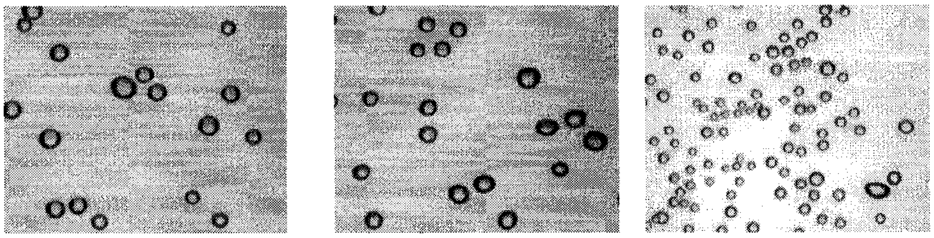


Figure 6.8: Disengagement time as a function of frother concentration

6.4.4: Bubble Size Measurement at Equal Gas Holdup

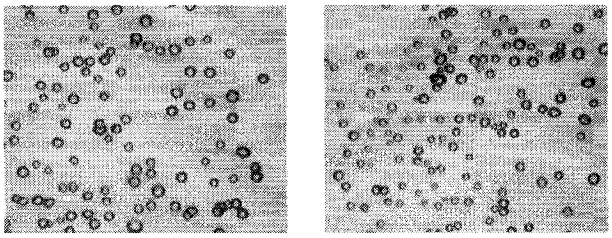
The common assumption is that there is a unique $d_b/J_g/\varepsilon_g$ relationship, i.e., it is independent of how the relationship is achieved, i.e., frother type. This is now tested. Figure 6.9 and Figure 6.10 show bubble size measurements for the selected frothers at gas holdup equal to 6% and 8%, respectively. The Figures reveal an unexpected finding: for equal gas holdup, the different frothers did not give the same bubble size. Since gas holdup is a function of bubble velocity, the results imply, for example, that the F150 bubbles move slower than expected for their size and/or the 1-Pentanol bubbles move faster than expected for their size.



0.002 mmol/L F150
d_{10} = 2.159 d_{32} = 2.328

0.014 mmol/L Octanol
d_{10} = 2.074 d_{32} = 2.153

0.065 mmol/L MIBC
d_{10} = 1.262 d_{32} = 1.351

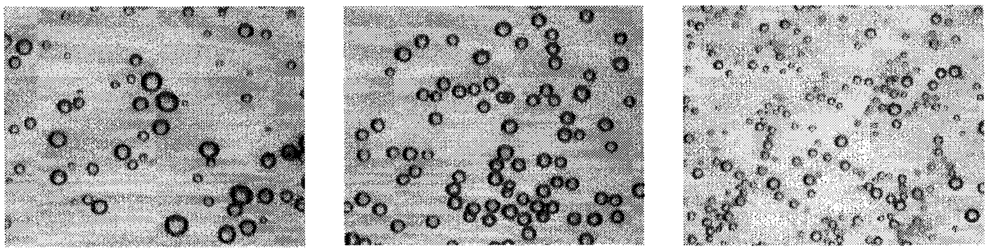


0.065 mmol/L Hexanol
d_{10} = 1.211 d_{32} = 1.286

0.15 mmol/L Pentanol
d_{10} = 1.088 d_{32} = 1.215

* Note: d_{10}, d_{32} in mm

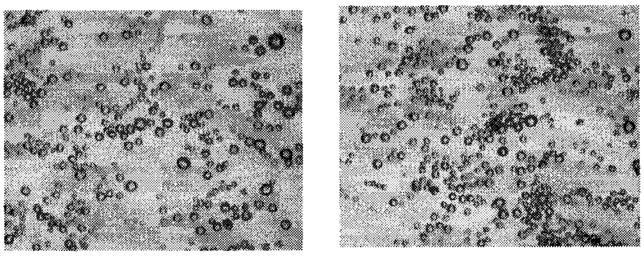
Figure 6.9: Bubble size measurements at equal gas holdup for different frothers: ε_g = 6%



0.004 mmol/L F150
d_{10} = 1.382 d_{32} = 1.665

0.016 mmol/L Octanol
d_{10} = 1.559 d_{32} = 1.605

0.1 mmol/L MIBC
d_{10} = 0.864 d_{32} = 0.998



0.1 mmol/L Hexanol
d_{10} = 0.784 d_{32} = 0.902

0.5 mmol/L Pentanol
d_{10} = 0.746 d_{32} = 0.853

* Note: d_{10}, d_{32} in mm

Figure 6.10: Bubble size measurements at equal gas holdup for different frothers: ε_g = 8%

The phenomenon may be related to differences in the amount of water carried in the bubble film and/or wake. Finch et al.[11] measured the water film layer thickness on bubbles blown in air using interferometry and reported a bound water thickness of less than 160 nm for 1-Pentanol and ca. 1000 nm for F150. Could the different film thickness act as an added mass and slow the F150 bubble rise? This effect should show as a decrease in the terminal velocity of single bubbles. Sam et al.[12] measured the terminal velocity of single bubbles in different frother systems and found the terminal velocity was weakly dependent on frother type. This[12] and other evidence[13] does not support such a drastic effect of frother type on terminal velocity. It may be that bubble velocity in the swarm is affected. Zhou et al.[14] found that for different frother systems, a higher gas holdup did not necessarily mean that a smaller bubble size was produced; that is, there appeared to be an effect of frother type on gas holdup independent of bubble size.

6.5: Conclusions

Measurements of bubble size versus concentration were used to help interpret the gas holdup vs. concentration relationship reported in Chapter 5. The relatively slow increase in gas holdup at low concentration (region I) appears to result from bubble being greater than ca. 1.5 mm where bubble velocity is insensitive to size. The continued increase in gas holdup at high concentration (region II) appears to result from a continued (if slow) decrease in bubble size. This is supported by several observation: the increase in % -1 mm bubbles; a decrease in number mean (d_{10}) (which is sensitive to the fine bubble population); correspondence between d_{10} and d_b derived from drift flux analysis; and, an increase in disengagement time with frother concentration.

The assumed unique relationship among gas holdup bubble size and gas rate is challenged by the present findings. Comparing at equal gas holdup the bubble size was dependent on the frother type; for example, F150 showed nearly twice the d_{10} compared to 1-Pentanol.

6.6: Acknowledgments

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Chapter 7: Conclusions and Recommendations

7.1: Conclusions

The following conclusions were reached:

A possible way to characterize frothers using gas holdup was explored. A correlation between frother type and gas holdup was observed: for alcohols gas holdup increases with hydrocarbon chain length and is independent of whether the chain is branched or not; for polyglycols, gas holdup increases with number of propoxy (PO) groups.

A ranking of frothers based on gas holdup was identical to that given by more elaborate techniques.

Measurements of bubble size versus concentration were used to help interpret the gas holdup vs. concentration relationship. The relatively slow increase in gas holdup at low concentration (region I) appears to result from bubbles being greater than ca. 1.5 mm where bubble velocity is insensitive to size. The continued increase in gas holdup at high concentration (region II) appears to result from a continued (if slow) decrease in bubble size. This is supported by the following evidence: the increase in % -1 mm bubbles; a decrease in number mean (d_{10}) (which is sensitive to the fine bubble population); correspondence between d_{10} and d_b derived from drift flux analysis; and, an increase in disengagement time with frother concentration.

The assumed unique relationship among gas holdup bubble size and gas rate is challenged by the present findings. Comparing at equal gas holdup the different frothers gave a different bubble size; for example, F150 showed nearly twice the d_{10} compared to 1-Pentanol.

7.2: Future Work

To further understand frother properties the following recommendations are made:

Since gas holdup is a function of gas velocity, it is worth studying the effect of frother type on bubble rise velocity in the swarm. A re-check of the effect of frother type on terminal velocity of a single bubble is also suggested. It is possible frother chemistry affects velocity by influencing the motion (zig-zag vs. straight) of a bubble. It is recommended to conduct experiments to study bubble motion.

It is suggested to conduct a study to investigate effect of solids on frother properties, to identify solid types that alter gas holdup and / or bubble size.

Test quality of water. It will be interesting to further investigate how the quality of water influences gas dispersion parameters, e.g., the role of dissolved salts, as in concentrator-recycle water compared to 'tap' water.

Appendix A: Characterization of a Set of Porous Stainless Steel Plate Spargers

A.1: Definitions

Permeability is a property of a porous medium and is a measure of the capacity of a medium to transmit fluids. The particular numerical value of the permeability is constant and independent of the fluid used in the measurement. Applying Darcy's theory to the present case, the pressure drop across a sparger is directly proportional to the volume rate of flow of fluid passing through and inversely proportional to the viscosity of the fluid.[1] A porous medium has permeability of one Darcy when a single-phase fluid of one centipoise viscosity passes through a cross-sectional area of one square centimeter at a rate of one cubic centimeter per second under a pressure of one atmosphere.

A.2: Characterization of Porous Medium

Spargers can be characterized according to their permeability by applying Darcy's law[2], which can be represented as:

$$J_i = -\frac{K_i}{\mu_i}\left[\frac{dP}{ds} - \rho g \frac{dZ}{ds}\right] \tag{A.1}$$

where,

J_i: Volume Flux across a unit of the porous medium in unit of time, m/s

K_i: Permeability of the medium, m^2

μ_i: Viscosity of the fluid, kg/m.s

$\frac{dP}{dS}$: Pressure gradient along S at the point to which J_i refers

S: Direction of the flow

ρ_i: Density of the fluid, kg/m^3

g: Gravity acceleration, m/s^2

Z: Vertical coordination directed downward

In the case of a porous plate with vertical flow (Figure A.1) of compressible fluids (gas), Darcy's law represents a linear relationship between flowrate and pressure drop. A plot of pressure drop as a function of flowrate on a log-log scale should give a line with slope equal one.

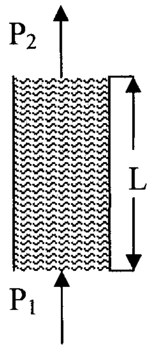


Figure A.1: Vertical flow

$$K = \frac{\mu \times Q_{ave.} \times L}{A \times \Delta P} \tag{A.2}$$

$$\log \Delta P = \log Q_{ave} + \log(\frac{\mu L}{Ak}) \tag{A.3}$$

where,

Q_{ave}: Gas flowrate at the medium average pressure, m^3/s

L: Thickness of the medium, m

A: Area of medium, m^2

ΔP: Pressure drop across the medium, atm

The difference between the permeability of a porous medium to liquid and to gas is due to the phenomenon known as "slip". Based on theoretical and experimental work of Klinkenberg[1], there is a relationship between the permeability of a porous medium to gases and liquids, represented as follow:

$$K_L = \frac{K_g}{1 + \frac{b}{P_m}} \tag{A.4}$$

where :

K_L: Permeability of the medium to a single liquid phase completely filling the pores of the medium

K_g: Permeability of the medium to a gas completely filling the pores of the medium

B: Klinkenberg's constant for a given gas and for a given porous medium

P_m: Algebraic sparger mean spargers, $(P_1+P_2)/2$

According to Equation A.4 a plot of K_g vs. $1/P_m$ should also result in a straight line with an intercept of K_L and a slpoe of bK_L.

A.3: Experimental

A bubble column 10.16 cm diameter and 250 cm height, was used for characterization of a set of plate spargers. Table A.1 shows the characteristics of each sparger. Air was selected as test fluid. The airflow was measured and controlled by mass flowmeter; experiments were performed with 5 mass air flowmeters (MKS instruments) covering ranges 0-5, 0-20, 0-30, 0-200 & 0-400 l/min. Temperature (Transduction Ltd. Model ICTD P/N1662) and pressure difference (Bailey model PTSDDD) were measured. All the above-mentioned instruments were connected to an interface and signal conditioner, Opto 22, with outputs monitored every second through a software package, Intellution IFix, installed on a PC. One side of the sparger was open to the atmosphere and once the pressure reached steady state, an average reading over 3 minutes was taken for each condition and set of variables.

Table A.1: Specifications of plate spargers

Sparger No.	Nominal Pore Diameter, μm	Sparger Diameter (D), cm	Sparger Thickness (t), cm
1	40	8.39	0.34
2	2	8.33	0.12
3	5	8.33	0.15
4	100	8.38	0.24
5	0.5	8.33	0.10
6	10	8.33	0.15

A.4: Sample Calculations

A sample calculation of permeability from the experimental data is presented in Table A.2. Air flowrate, referenced to 1 atm and 0°C, was adjusted to the temperature and pressure conditions inside the sparger using Equation A.5,

$$Q_m = \frac{T_m \times P_{St.} \times Q_{St.}}{T_{St.} \times P_m} \tag{A.5}$$

where,

Q_m : Flowrate adjusted to temperature and pressure, cm^3/s

$Q_{St.}$: Air flowrate at the mean pressure, cm^3/s

T_m : Air temperature, $^\circ K$

$T_{St.}$: Refrence temperature , 273.15 $^\circ K$

P_m : Algebric mean pressure , $(P_1+P_2)/2$, atm

$P_{St.}$: Refrence pressure, 1 atm

Table A.2: Typical calculation values

$Q_{St.}$ (l/min)	ΔP (cmH_2O)	$P_{st.}$ (atm)	P_m (atm)	$T_{St.}$ ($^\circ K$)	T_m $^\circ K$	Q_m (cm^3/s)	D (cm)	A (cm^2)	μ (Cp)	t (cm)	$K_{gcalculation}$ (Darcy)
3.99	0.96	1	1	273	293	71.3	8.33	54.5	0.018	0.15	3.8

Based on Darcy's law, plotting Q_m/A versus $\Delta P/t$ should give a line with a slope of K/μ and plotting of the inverse of the mean pressure ($1/P_m$) against the permeability calculated according to Equation A.2, should also result in a straight line with an intercept of K_L (permeability of liquid). Specimen plots for sparger No. 3 are presented in Figure A.2 (Q_m/A vs. $\Delta P/t$) and Figure A.3 (K_g vs. $1/P_m$). Since the best working range of mass flow meters is between 20%-80% of full scale, all calculations respected this range.

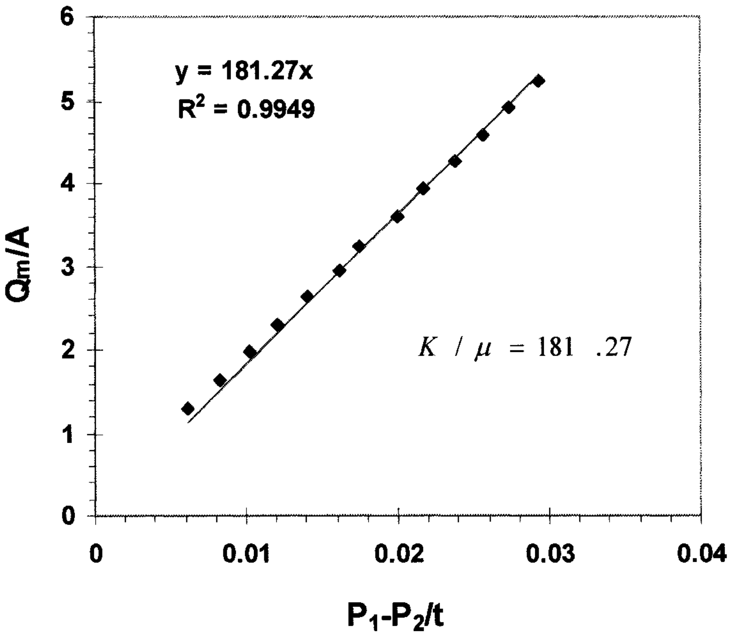


Figure A.2: Sparger # 3: Measurement of permeability to gas (K_g)

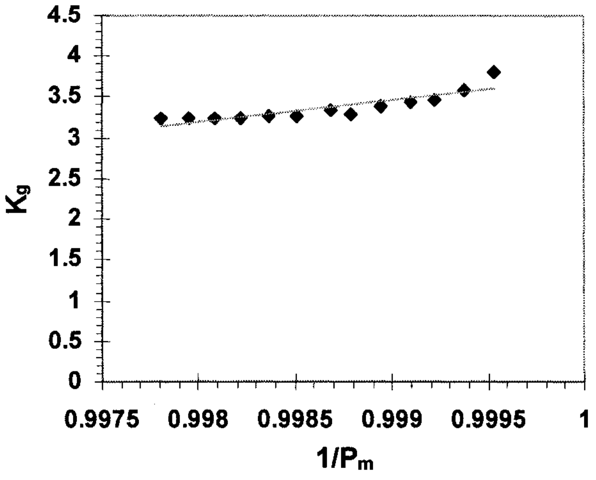


Figure A.3: Applications of Klinkenberg's model to estimate the permeability to liquid (K_L)

Figure A.4 presents a plot of flowrate versus pressure drop on log-log scales for all spargers. Table A.3 shows results of the permeability calculated for a set of plate spargers in the column using air as a test fluid.

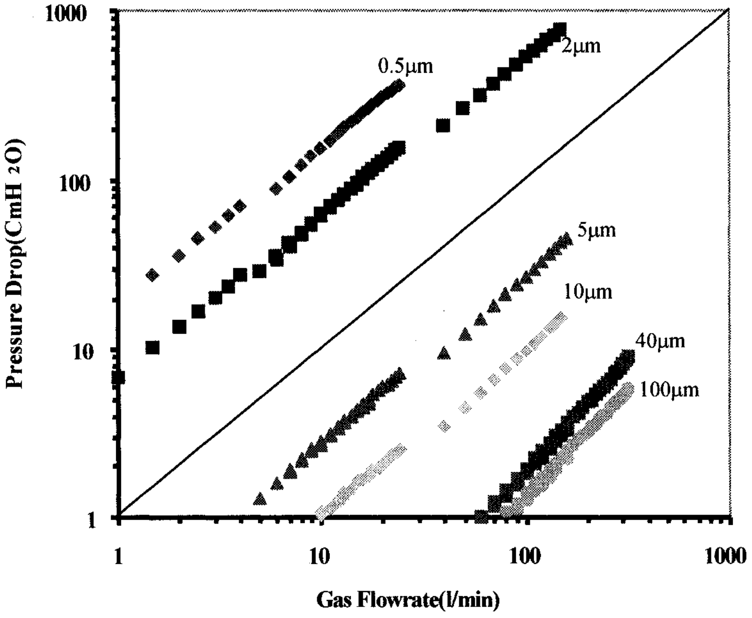


Figure A.4: Log-log representation of Q-ΔP data for a set of spargers

Table A.3: Results of Permeability calculation

Nominal Pore Diameter (μm)	Mass Flowrate (l/min)	$K_{gcalculation}$ (Darcy)	$K_{gmeasurement}$ (Darcy)	K_l (Darcy)
0.5	0-5	0.04	0.03	0.03
0.5	0-30	0.037	0.04	0.03
2	0-5	0.11	0.11	0.11
2	0-20	0.11	0.11	0.11
2	0-30	0.11	0.11	0.11
2	0-200	0.11	0.11	0.11
5	0-20	3.36	3.28	3.10
5	0-30	3.17	3.12	3.17
5	0-200	3.37	3.24	3.20
10	0-5	8.60	8.95	8.50
10	0-20	8.92	8.96	8.91
10	0-30	9.09	9.03	9.07
10	0-200	9.63	9.28	9.60
40	0-200	115.24	104.98	115
40	0-400	87.97	79.93	87
100	0-5	86.21	87.78	85
100	0-30	111.95	114.30	115
100	0-200	114.07	108.06	110
100	0-400	90.05	84.36	87

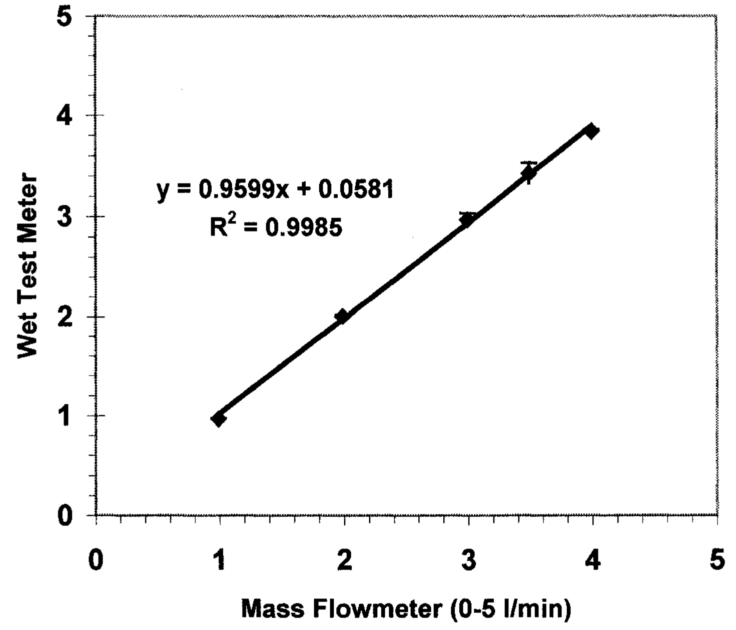
A.5: References

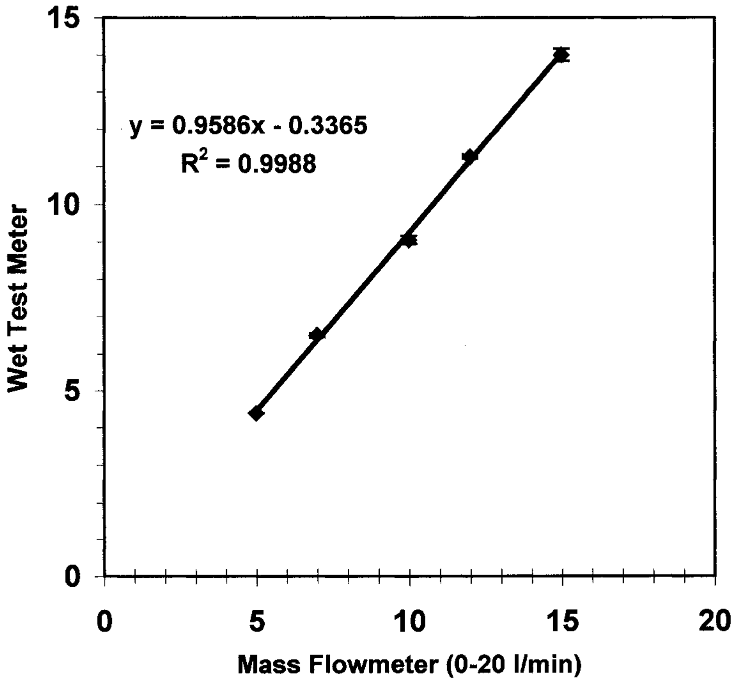
1 American Petroleum Institute, "Recommendation Practice for Determining Permeability of Porous Media", Third edition, 1956: 1-27.

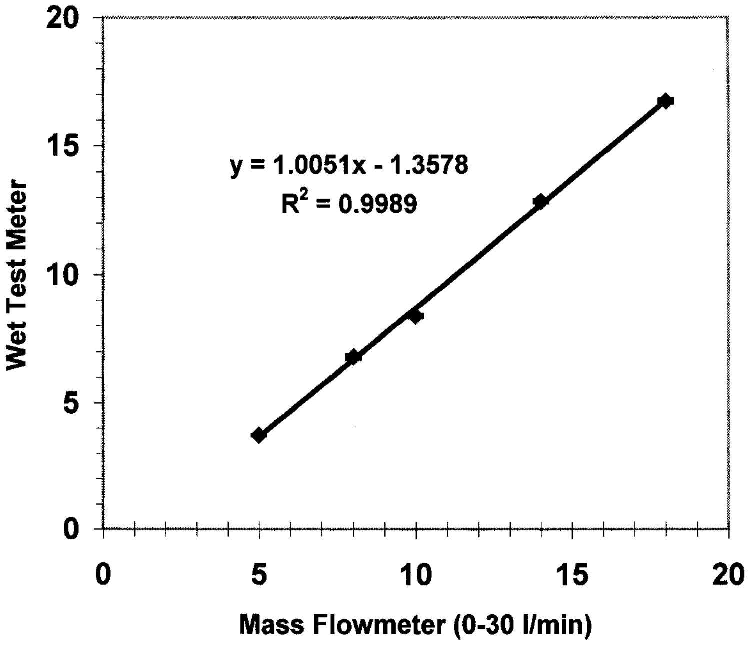
2 Escudero R.G. "Characterization of Rigid Spargers and Their Selection for Flotation Columns", Ph.D. Thesis, McGill University, 1998.

Appendix B: Calibration Curves

B.1: Mass Flowmeter







B.2: Pressure Transducer