Frothers and Frother Blends:
A Structure – Function Study

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Abstract

The presence of frother, either singly or as a blend, is common to most mineral flotation processes. Frothers have two main functions: provide target hydrodynamic conditions and promote froth stability. In the thesis hydrodynamics is measured by bubble size and gas holdup and froth stability by water overflow rate. These functions are related to frother chemistry, or more particularly, molecular structure. However, the structure – function link is not well understood and forms the theme of the thesis.

A methodology is developed to link one hydrodynamic function, bubble size reduction represented by CCC95 (critical coalescence concentration 95%), to frother structure represented by HLB (hydrophile-lypophile balance). The results indicate each frother family has a unique CCC95-HLB relationship. Empirical models are developed to predict CCC95 either from HLB or directly from frother structural parameters. Commercial frothers are shown to fit the relationships.

Use of dual-frother systems to achieve independent control over the two frother functions is tested. Blends of Alcohols with Polypropylene Glycols (PPG) and Polyethylene Glycols (PEG) are selected in pre-mixed and base/additive styles. The base/additive system 1-Butanol/PEG (EO > = 4) gives the independence sought but not 1-Butanol/PPG which causes an increase in bubble size. To explain the bubble size effect, frother partitioning is determined. This is achieved by development of two analytical techniques: high pressure liquid chromatography (HPLC) and nuclear magnetic resonance spectrometry (NMR) associated with total organic carbon analysis (TOC). The 1-Butanol/PPG blends show strong partitioning to the froth which corresponds to the increase in bubble size.

New frothers are synthesized to test the structure-function relationship by combining three groups: linear Alkyl-Ethoxy-Propoxylates ($C_nEO_lPO_m$) and

Alkyl-Propoxy-Ethoxylates ($C_nPO_mEO_l$). It is found that varying the number of PO groups, the length of Alkyl group chain, and the position of PO and EO could affect the two functions.

Résumé

Dans la plupart des processus de flottation, la mousse est communément présente soit seule, soit sous forme de mélange. Les mousses assument deux fonctions principales à savoir: créer les conditions hydrodynamiques et promouvoir la stabilité de la mousse. Dans cette thèse l'hydrodynamique est mesurée par la taille de la bulle et la rétention de gaz, tandis que la stabilité, par la vitesse de l'écoulement d'eau. Ces fonctions sont liées à la chimie des mousses et plus particulièrement à la structure moléculaire.

Une méthodologie qui permet de relier la fonction hydrodynamique à la taille de la bulle représentée par le CCC95 (concentration critique de coalescence 95%) et à la structure de la mousse représentée par le HLB (budget hydrophile-lyophile), a été développée. Les résultats montrent que chaque famille de mousse possède une relation CCC95-HLB unique. Des modèles empirique été développés afin de prédire le CCC95 soit à partir du HLB, soit directement à partir des paramètres structurels de la mousse. Les mousses commerciales s'accommodent de ces relations.

L'utilisation des systèmes à deux mousses visant un contrôle indépendant des deux mousses, a été testée. Les mélanges d'alcool avec les propylène-glycols (PPG) et les polyéthylène-glycols (PEG) ont été sélectionnés et préalablement mélanges et des additifs de base étaient utilisés. Le système Base/Additif 1-Butanol/PEG (EO>= 4) ont >prouvé l'indépendance recherchée à la différence de 1-Butanol/PPG qui a cause une augmentation de la taille de la bulle. Pour expliquer l'effet de la taille, la partition de la mousse a été déterminée. Cela a été réalisé grâce au développement de deux techniques: la chromatographie gazeuse de haute pression (HLPC) et la résonance magnétique (RMN) associée à l'analyse du carbone total (TOC). Les mélanges 1-Butanol/PPG ont révélé une forte partition avec la mousse qui correspond à l'augmentation de la taille de la bulle.

Des nouvelles mousses ont été synthétisées afin de tester la relation structure-fonction en combinant trios groupes: linéaire Alkyl-Ethoxy-propoxylates (C_nEOPO_m) et Alkyl-Propoxy-Ethoxylates ($C_n(PO_nEO$). Il a été observé qu'en faisant varier le nombre de PO groupes la longueur de la chaîne du groupe Alkyl et les positions PO et EO peuvent affecter les deux fonctions.

Contributions of Co-authors for Chapters 3, 4, 5 and 6

This thesis is manuscript-based and it includes the following four papers:

Chapter 3: Wei Zhang, Jan E. Nesset, Ramachandra S. Rao and James A. Finch, 2012. *"Characterizing Frother through CCC95-HLB Relationships"*. To be submitted.

Chapter 4: Wei Zhang, Xiang Zhou and James A. Finch, 2012. *"Dual Frother System: Gas Holdup, Bubble Size and Water Overflow Rate"*. To be submitted.

Chapter 5: Wei Zhang, Si-Ying Zhou and James A. Finch, 2012. *"Frother Partitioning in Dual-Frother Systems: Development of Analytical Techniques"*. To be submitted.

Chapter 6: Wei Zhang, Si-Ying Zhou, Xiang Zhou and James A. Finch, 2012. *"Synthesis and Characterization of New Polyglycol-Based Frothers: A Structure – Function Study"*. To be submitted.

All manuscripts are co-authored by Professor J. A. Finch in his capacity as research advisor. The first drafts were written by the author and edited by Prof. J. A. Finch. The initial proposal to use CCC95 – HLB to characterize structure – function relationship (Chapter 3) was made by Drs. Nesset and Rao. They also provided advice on the experimental design and contributed to the discussion of results. Mr. Xiang Zhou helped in gas holdup and water overflow rate in Chapters 4 and 6. Miss. Si-Ying Zhu contributed to Chapters 5 and 6 by demonstrating the nuclear magnetic resonance spectrometry technique.

Beyond the contribution of the co-authors, all the work presented in this dissertation was performed by the author.

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Nomenclature

Symbol	Units	Definition
J_g	cm/s	Superficial gas velocity, gas rate, air rate
E_g	%, fraction	Gas holdup or void fraction of gas in cell volume
J_{wO}	cm/s	The water overflow rate, was defined as the overflow mass rate (g/min) was converted to volume and divided by the column cross-sectional area, to give the water overflow rate (cm/s)
D_{32}	mm	Sauter mean diameter of the BSD, total volume of bubbles divided by total surface area of bubbles assuming spherical shape
D_L		Minimum bubble diameter, frother material constant
S_b	s^{-1}	Bubble surface area flux, total surface area of bubbles per unit area of cell per unit of time
CCC	ppm	Critical coalescence concentration
CCC95	ppm	Concentration for which 95% reduction in D32 has been reached
PPM, ppm	g/t	Concentration expressed as parts per million n
N		Number of measurements
RSD		Relative standard deviation
SSE		Sum of squared errors
RMSE		Root mean square error
R^2		Coefficient of determination
v/v		Volume ratio (volume/volume)
M.W.	g/mol	Molecular weight
HLB		Hydrophile-Lipophile Balance, empirical relationship measuring contribution of polar and non-polar groups for a frother in aqueous solution
PPG		Polypropylene Glycol
PEG		Polyethylene Glycol
DPG		Dipropylene Glycol
TPG		Tripropylene Glycol
MonoEG		Monoethylene Glycol
DEG		Diethylene Glycol
TEG		Triethylene Glycol
TetraEG		Tetraethylene Glycol
DPMEPro		Dipropoxy Monoethoxy Propanol
TPMEPro		Tripropoxy Monoethoxy Propanol
TPMEPen		Tripropoxy Monoethoxy Pentanol
TPDEPro		Tripropoxy Diethoxy Propanol

DETPPro		Diethoxy Tripropoxy Propanol
n		The number of alkyl group in the frother molecule
m		The number of PO group in the frother molecule
l		The number of EO group in the frother molecule
PO		Propylene Oxide
EO		Ethylene Oxide
RCS^{TM}		Reactor Cell System, Metso Minerals patented cell design
PIV		Particle imaging velocimetry
HPLC		High performance liquid chromatography
RI		Refractive Index
TOC		Total organic carbon analysis
NMR		Nuclear magnetic resonance spectrometry
δ	ppm	Chemical shift
MWCO		Molecular weight cut-off
THF		Tetrahydrofuran
D_2O		Deuterium oxide (solvent)
Rotovap		Rotary evaporator

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Chapter 1 – Introduction

1.1 Introduction

The technology of froth flotation, widely applied for processing mineral ores, is based on the capture of hydrophobic particles by air bubbles [Rao and Leja, 2004]. Surface-active agents called frothers are employed to produce fine and stable (i.e., non-coalescing) air bubbles to facilitate particle collection and transport to the froth (overflow) product [Crozier and Klimpel, 1989; Klimpel and Isherwood, 1991; Wheeler, 1994]. The other principal roles of frother is to promote froth formation while other roles may include reducing bubble rise velocity and increasing gas (air) holdup [Sam et al., 1996; Cho and Laskowski, 2002a,b; Laskowski, 2003; Laskowski et al., 2003; Grau et al., 2005; Pugh, 2007]. The use of frothers aids flotation performance by impacting both the quality (the *grade*) and quantity (the *recovery*) of the particles delivered to the froth product, which is usually the valuable mineral concentrate [Comley et al., 2007]. Given their importance in flotation, frothers are the subject of this thesis.

Frothers are usually non-ionic heteropolar surfactants, i.e., comprise hydrophilic (polar) groups, typically O and OH, and hydrophobic (non-polar) groups, typically hydrocarbon chains. Water dipoles readily interact (H-bond) with the polar groups of the frother, but not with the non-polar groups. As a result, the general understanding is that the heteropolar structure of the frother molecule leads to adsorption at the air-water interface (bubble surface) with the non-polar groups oriented towards the air side of the interface and the polar groups oriented towards the water side. Interface-related properties, e.g. surface tension, surface viscosity, and coalescence rate, are modified which lead to the two principal frother functions of importance in flotation: reduction in bubble size and increase in froth stability.

Laskowski [2003] was among the first to recognize the two functions and exploit in characterizing frothers to provide a basis for frother selection for a given duty. He also explored correlations between frother chemistry (structure) and function. However, the structure-function relationship remains poorly understood and choice of frother is usually empirical. The structure-function relationship is the theme of the thesis.

To develop the structure-function relationship we need suitable measurements. The prerequisite for the choice of ‘property’ is that it must be sensitive to the structure and be easy to measure. The properties selected in the thesis are: bubble size and gas holdup, which reflect the hydrodynamic conditions in the pulp phase; and water overflow rate, which represents froth stability. All three parameters are interrelated: generally, gas holdup is inversely related to bubble size [Azgomi et al., 2007]; and water overflow rate correlates positively with gas holdup [Moyo et al., 2007]. These correlations will be monitored throughout the thesis.

Among the properties, bubble size is perhaps the most important defining the surface area of air to collect and transport particles and water which in turn control froth stability. Rather than bubble size, however, we use the critical coalescence concentration (CCC). Introduced by Laskowski [2003] and coworkers [Cho and Laskowski, 2002a, b; Grau et al., 2005], CCC is the frother concentration giving the minimum Sauter mean bubble diameter and is useful in this thesis because itis characteristic of the frother type, i.e., chemistry or structure.

The measure of ‘structure’ ought to capture the heteropolar nature of frothers. The measure that has been proposed, and used here, is the hydrophile - lipophile balance (HLB) [Laskowski, 2003; Rao and Leja, 2004; Pugh, 2007]. The HLB number is a measure of the degree to which a surfactant is hydrophilic or hydrophobic. By varying the ratio of the hydrophobic groups to hydrophilic groups, the HLB number is changed.

In recent years, mixes of two frothers (dual frother systems or frother blends) have become popular in operations [Kumar et al, 1986; Tan et. al, 2005]. The reason given is improved control but exactly what is being achieved is not clear. Given that frother is added to serve two functions, reduce bubble size and stabilize froth, one possibility is that the dual frother system provides independent control over the two functions. Independence is difficult to achieve with a single frother since both functions are concentration-dependent.

In addition to designing frother blends, effort is being directed to development of new frother chemistries which may permit tailoring to the duty, for example improved coarse or fine particle recovery. The design must consider the frother structure [Klimpel and Isherwood, 1991; Harris and Jia, 2000; Cuppuccitti and Finch, 2007].

The purpose of this thesis is to examine the role of frother structure on frother functions. The thesis covers the aspects noted above: the CCC-HLB relationship (Chapter 3); dual frother systems (Chapters 4 and 5); and new chemistries (Chapter 6).

1.2 Thesis Objectives

The general objective is to determine the role of frother structure on frother functions using a laboratory bubble column and pilot mechanical flotation cell as the test vehicles. To accomplish, the following specific objectives are set:

1. To determine the dependence of CCC on HLB which requires:
    a) Determining Sauter mean bubble diameter versus concentration and fitting to a model to estimate CCC95;
    b) Quantifying structure by HLB using the Davies Equation;
    c) Modelling CCC95-HLB relationship.

2. To select dual frother blends based on component structure; determine the effect of dual frothers on the two functions; and investigate independent control over the two functions. This requires:
   a) Screening the candidate frothers according to their CCC95-HLB relationship;
   b) Examining two styles of blend: pre-mixed and base/additive;
   c) Developing analytical techniques (HPLC and NMR/TOC) to measure frother partitioning.

3. To synthesize new frothers with particular structures to provide target functions. This requires:
   a) Developing a methodology to design, synthesize and purify a class of new compounds based on sequencing hydrophilic and hydrophibic groups;
   b) Characterizing the compounds to indicate structure and purity;
   c) Correlating new frother structures to the two functions.

1.3 Thesis Structure

The thesis is ‘manuscript-based’. It comprises seven chapters, four of which (Chapters 3, 4, 5 and 6) stand by themselves and will be presented for publication. The chapters will have some repetition of the introductory material. As required, connecting texts to provide logical bridges between Chapters 3, 4, 5 and 6 are included separately in front of each chapter. The Chapters for the complete thesis are:

Chapter 1 (introduction): Flotation process and the role of frother are introduced. The thesis objectives and structure are presented.

Chapter 2 (literature review): Literature review on the effect of frothers on flotation emphasizing structure and functions, frother analysis and new classes of frothers.

Chapter 3 (characterizing frothers through CCC95-HLB relationships): This chapter describes a methodology to characterize frothers by relating impact on bubble size reduction represented by CCC95 (critical coalescence concentration) to frother structure represented by HLB (hydrophile-lypophile balance). Models are developed to predict CCC95 either from HLB or from frother structural parameters. Commercial frothers are shown to fit the relationships.

Chapter 4 (dual frother systems: gas holdup, bubble size and water overflow rate): In this chapter dual frother systems (blends) are investigated to determine combinations which provide independence over the two functions – pulp hydrodynamics and froth properties. Blends of Alcohols with Polypropylene Glycols and Polyethylene Glycols are the candidates, and pre-mixed and base/additive the blend styles.

Chapter 5 (frother partitioning in dual-frother systems: development of analytical techniques): Description, development and validation of two analytical methods to measure frother partitioning in dual frother system are presented. These techniques are: high pressure liquid chromatography (HPLC), and proton nuclear magnetic resonance spectroscopy (^{1}H NMR) associated with total organic carbon analysis (TOC).

Chapter 6 (synthesis and characterization of new polyglycol-based frothers: a structure‑function study): This chapter describes the synthesis of a new homologous series of linear Polyglycol-based frothers that consist of Ethylene Oxide (EO) and hydroxyl as hydrophilic groups and Propylene Oxide (PO) and alkyl as hydrophobic groups. The identities of the prepared frothers are confirmed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and total organic carbon (TOC) analysis. The effect of frother stucture and concentration on bubble size, gas holdup and water overflow rate are evaluated.

Chapter 7 (conclusions): the conclusions stemming from this thesis as well as contributions to original knowledge are given.

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Chapter 2 – Literature Review

2.1 Frother Chemistry and Flotation

Frothers have two prime functions in flotation: to reduce bubble size and increase froth stability. While many compounds can provide these functions, the most commonly used frothers in flotation are those containing non-polar water-repellent groups, as well as polar water avid groups [Harris and Jia, 2000; Cappuccitti and Finch, 2007]. The two major frother families of commercial importance today are Alcohols and Polyglycols [Klimpel and Isherwood, 1991; Laskowski, 1998]. Alcohol frothers ($C_nH_{2n+1}OH$) usually contain a single hydroxyl (OH) group and are restricted to 5 – 7 carbons either straight or branch chained. MIBC (methyl isobutyl carbinol) is the best-known frother in this group. Polyglycol frothers ($C_nH_{2n+1}(OC_3H_6)_mOH$ or $C_nH_{2n+1}(OC_2H_4)_lOH$) form a large class with varying molecular structure and molecular weight. Flottec 150 (F150) and Dowfroth 250 (DF250) are among the best-known examples in this group.

The frothing characteristics depend on the frother structure, e.g. the relative strength of the non-polar (hydrophobic) to polar (hydrophilic) groups. For each frother family, the length of hydrophobic to hydrophilic groups can be modified by changing the number of $-CH_2-$ groups in the alkyl chain in the case of Alcohols and Polyglycols, and/or number of Propylene Oxide (PO) or Ethylene Oxide (EO) groups in the case of Polyglycols. Varying the relative length of the hydrophobic to hydrophilic groups in the molecule changes its hydrophile-lipophile balance, or HLB [Laskowski, 2003].

The performance of frothers is dependent on their chemical structure [Pugh, 2007]. It has been reported that the maximum floatable particle size decreases by increasing branching, while selectivity increases [Klimpel and Hansen, 1988; Klimpel and Isherwood, 1991]. Schwarz [2004] claimed that increasing the molecular weight of

Polypropylene Glycol (PPG) frothers increases the volume of froth generated and she presumed there is an optimum molecular weight giving maximum froth stability, above which stability starts to decrease.

Summarizing, the structural properties of frothers such as the length of hydrocarbon (alkyl) chain and number of the PO groups may correlate with flotation performance. These structural properties are contained in the HLB concept and thus the HLB number may correlate with frother's functions in flotation. Measuring these functions is often referred to as frother 'characterization'.

2.2 Frother Characterization

2.2.1 Gas Dispersion

The so-called gas dispersion parameters have been studied intensively over the last 20 years [Gorain et al., 1997; Hernandez et al., 2003; Gomez and Finch, 2007]. These parameters comprise superficial gas velocity (J_g), gas holdup (E_g), bubble size (D_b) and bubble surface area flux (S_b). Several groups [Luttrell and Yoon, 1992; Gorain et al., 1997; Finch et al., 1999; Deglon et al., 2000; Hernandez et al., 2001; Comley et al., 2007] have shown that the overall flotation rate constant increases as bubble size is reduced. More commonly today this effect is incorporated in the bubble surface area flux, S_b, which combines the effect of superficial gas velocity (J_g) and Sauter mean bubble size (diameter, D_{32}) ($S_b = 6\ J_g\ /\ D_{32}$). Figure 2.1 shows rate constant vs. bubble surface area flux has a close to linear relationship. Since frother plays a key role in reducing bubble size, this figure also shows the important role of frother in flotation.

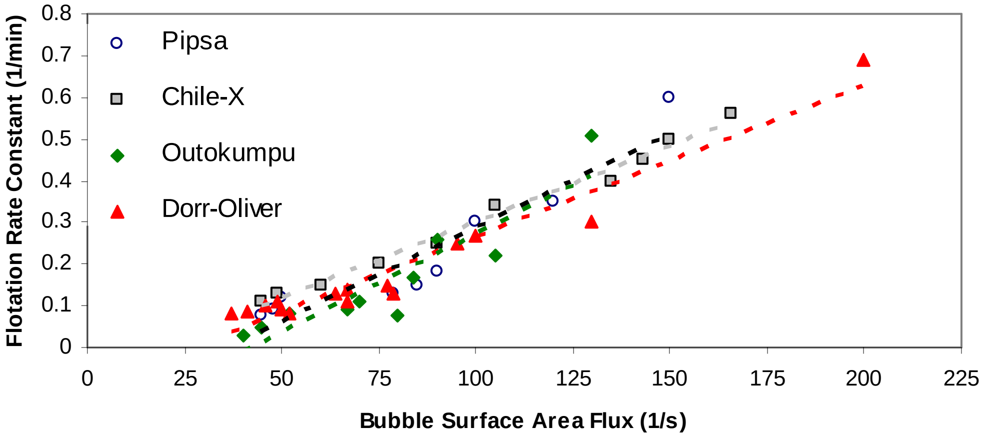

Figure 2.1: Flotation rate constant versus bubble surface area flux in four industrial flotation machines [Adapted from Nguyen and Schulze, 2004]

The action of frother in reducing bubble size is attributed to reduced rate of coalescence [Harris, 1976; Metso Minerals, 2002; Cho and Laskowski, 2002]. The concentration of frother in the pulp water determines the extent of bubble coalescence. The continued addition of frother has a diminishing effect resulting in bubble size reaching a limiting (minimum) value at a concentration now referred to as the critical coalescence concentration (CCC) [Cho and Laskowski, 2002]. Recognizing the difficulty in defining the end point of an exponential curve, Nesset et al. [2007] and Finch et al. [2008] used a model fit and estimated the CCC95, i.e. concentration achieving 95% of bubble size reduction compared to water alone. Laskowski [2003] proposed combining the CCC concept with a measure of foaming properties as a way to characterize frothers.

There is ample experimental evidence that frothers act to suppress coalescence. A recent study used the acoustic signal (sound) made when bubbles coalesce to follow the effect of frother [Kracht and Finch, 2009]. For common flotation frothers coalescence rate was found to decrease with increasing frother molecular weight. Although the mechanism by which frothers retard coalescence is still debated, evidence [Grau et al, 2005, Gélinas and Finch, 2005] suggests that they might bind water molecules to the bubble surface by hydrogen bonding, thus making it more difficult for the water to drain between approaching bubbles. This phenomenon can be considered the origin of a surface viscosity that is higher than the bulk [Ngyuen and Schulze, 2004]. Other researchers [Laskowski, 1998; Wang and Yoon, 2008] infer this mechanism also by reference to bubble hydration by frothers.

Gas holdup (E_g) in the 2-phase (air and water) system is readily determined from the hydrostatic pressure difference measured over a set distance [Gomez et al., 1995]. For three-phase pulps conductivity can be used in conjunction with Maxwell's model [Tavera et al., 2001]. Frother type and concentration influence E_g by controlling bubble size and bubble rise velocity [Azgomi et al., 2007; Rafiei et al., 2011].

The decrease in rise velocity of an air bubble due to frother is pronounced, as shown in Figure 2.2. The slowing down is attributed to the effect of a surface tension gradient force increasing drag [Duhkin et al., 1998]. This force also resists bubble deformation and recent work points to a relationship between shape and velocity [Wu and Gharib, 2002; Kracht and Finch, 2009; Gomez et al., 2010].

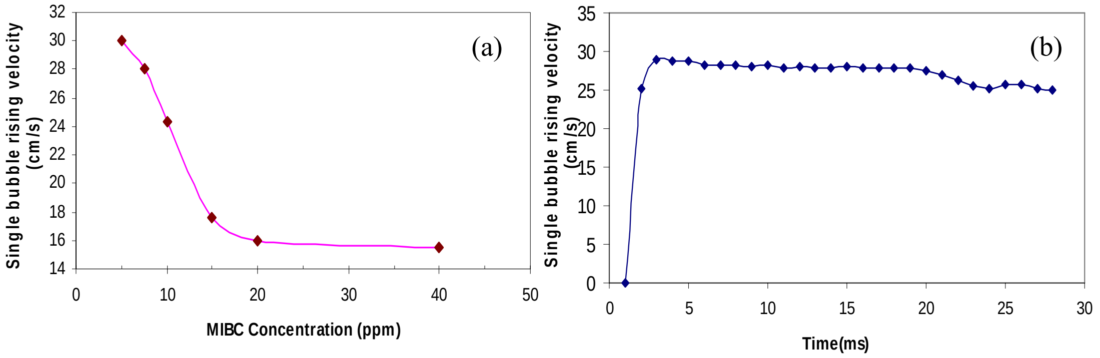

Figure 2.2: a) Single bubble (dia. 1.5 mm) velocity at 3 m from point of origin versus MIBC concentration; (b) Single bubble velocity versus time from point of origin in10 ppm MIBC [data provided by Tan, 2010]

Cappuccitti and Nesset [2009], based on the work of Azgomi et al. [2007] and Moyo et al. [2007], explored a method to classify frothers using gas holdup (E_g) vs. froth height to try to capture the two frother functions (control of bubble size and froth stability). The relationships readily identify frothers giving more control over froth stability, namely the Polyglycols, from those giving more control over gas holdup (i.e. bubble size), namely the Alcohols.

Finch et al. [1999] investigated the relationship between E_g and S_b using data from several sources, proposing that S_b can be determined from gas holdup. This implies a consistent relationship between gas holdup and bubble size. Azgomi et al. [2007] examined the correspondence of gas holdup with bubble size, an example being Figure 2.3 (a). This shows the relationship is not straightforward: at low concentration while bubble size is decreasing gas holdup remains almost constant while at high concentration bubble size (at least the D_{32}) becomes constant and gas holdup continues to increase. Figure 2.3 (b) offers a possible explanation: at low concentration (e.g. <5 ppm) bubble rise velocity has not started to decrease while at high concentration it continues to decrease.

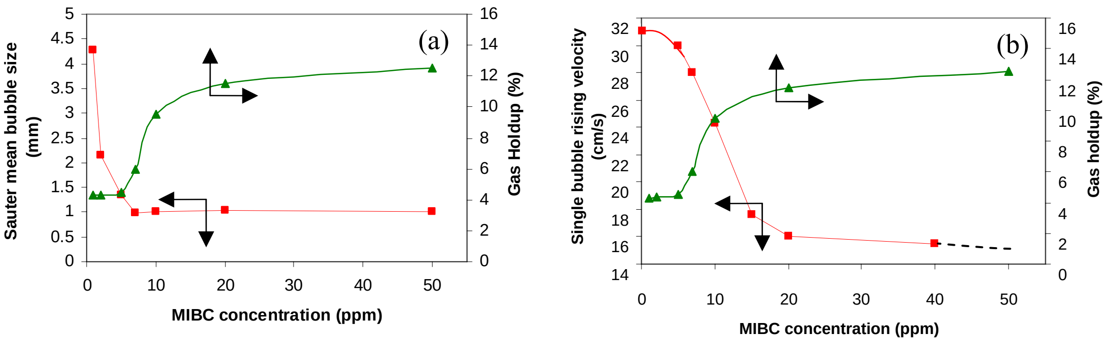

Figure 2.3: a) Gas holdup and bubble size vs. frother concentration [Azgomi et al., 2007]; b) Gas holdup and single bubble rising velocity vs. frother concentration [Azgomi et al. 2007 and Tan, 2010]

Azgomi et al. [2007] found a frother chemistry effect on gas holdup: for instance, 1-Pentanol and F150 could give the same gas holdup but with bubbles in 1-Pentanol being significantly smaller than in F150. This implies bubbles in 1-Pentanol rise faster than equal-sized bubbles in F150 and this proved to be the case, for bubbles in swarms [Acuna and Finch, 2010] and as single bubbles [Rafiei et al., 2011]. To interpret the effect of frother chemistry on gas holdup, the combined influences on bubble size and velocity must be considered.

2.2.2 Stabilizing Froth

Froth is a dynamic system in which solid and water movement is governed by the flow of air bubbles into the froth from the pulp, from froth interface to the top of the froth, and by bubble coalescence. The term “froth stability” is understood herein as the ability of bubbles in froth to resist coalescence and bursting [Triffett and Cilliers, 2004]. In other words, more stable froth has fewer coalescence and bursting events. According to Shkodin and Tikhomivova [1951] at the first stage of froth formation (i.e., at the base of the froth), bubbles are separated by a liquid film in the order of ca. 1 μm. The film comprises solvated envelopes (hydrated layers) with properties different from those of the ‘free’ water, as illustrated in Figure 2.4. On drainage the film thins and the hydrated layers come into contact between neighbouring bubbles.

The next stage in coalescence involves removal of the liquid from the contacting hydration layers. Depending on the nature of the layer, which reflects frother chemistry, drainage and coalescence can be rapid (e.g. with Alcohol frothers) or the film be more persistent (e.g. with some Polyglycols). Gravity and capillary effects in addition to the properties of the hydration layer govern the water drainage. There is a resultant transition in bubble size as froth ‘ages’, i.e., as you go from the base upwards.

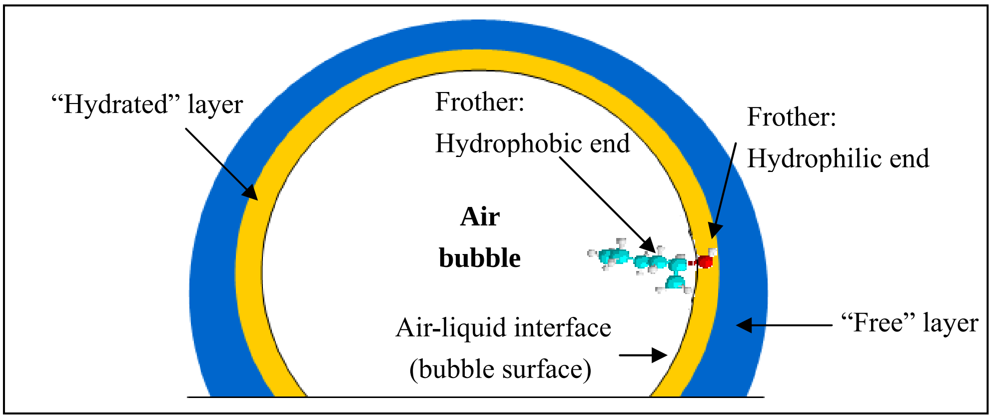

Figure 2.4: Frother alignment at the bubble surface and the formation of the 'bound hydrated' and 'free' layers [After Gélinas and Finch, 2005]

Mechanistic modeling of froths in flotation systems has accelerated over the last decade. The starting description [e.g. Neethling et al., 2003] sees bubbles in the froth as surrounded by thin lamellae (the hydrated layer) and when three (or more) bubbles meet, a "reservoir" (Plateau border region) is formed at the intersection (Figure 2.5). Most of the water in froth is contained in the Plateau border region with only a small fraction residing in the lamellae. A method was proposed by Zhang et al. [2010] to determine an equivalent water thickness (effectively the water content in Plateau border) associated with the bubble surface area exiting via the froth overflow. Testing a range of frothers they found that a frother with higher HLB number (e.g. F150, HLB = 8.625) creates a thicker film (17.6 μm) while lower HLB number frothers (e.g. FX160-05, HLB = 7.11) create a thinner (8.8 μm) film. As the film thickness changes, so does the water overflow rate to the froth.

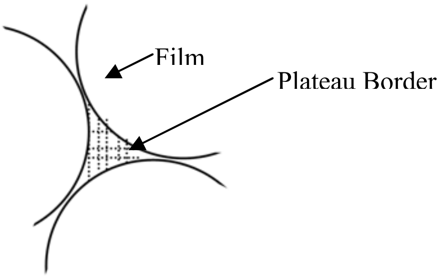

Figure 2.5: Schematic of the Plateau border at the junction of three bubbles in the froth

Froth stabilization can be quantified by measurements such as equilibrium froth height and water overflow rate. Water overflow rate is more reliable than froth height [Elmahdy and Finch, 2009], and is also important in flotation as it controls particle recovery by entrainment [Lynch et al., 1981]. Water overflow rate has been the subject of modeling efforts, both empirical (Zheng et al., 2006) and fundamental (Neethling et al., 2003; Stevenson et al., 2003). Moyo et al. [2007] found that water overflow rate correlated against gas holdup in the bubbly zone (the aerated solution below the froth) and the trends were characteristic of frother type. Both of Moyo et al. [2007] and Zhang et al. [2010] showed that water overflow rate was closely linked to frother chemistry. Measurement of water overflow rate can be readily extended to three-phase systems to reveal the added effect of solids [Melo and Laskowski, 2007; Kuan and Finch, 2010]. The use of water overflow rate to characterize frothers will be used in this thesis.

2.3 Frother Partitioning and Measurement of Frother Concentration

In the pulp (or bubbly zone in two-phase tests) frother is adsorbed on the surface of the rising bubbles and is deposited in the overflow water as the bubbles burst. The released frother increases the concentration in the overflow water compared to the frother added (i.e., the feed) or in the underflow. This re-distribution between pulp and froth is referred to as 'partitioning'. Frother partitioning is a consequence of adsorption and bubble movement through the pulp and froth zones, thus its measurement may provide information to interpret observations in the zones (e.g. bubble size, gas holdup and water overflow rate), and interactions between the zones [Gomez and Finch, 2011].

Determining partitioning requires measurement of frother concentration. Several analytical techniques have been developed, including: gas chromatography [Tsatouhas et al., 2005]; total organic carbon [Hadler et al., 2005; Zhang et al, 2010]; calibrations of bubble size and gas gold-up vs. frother concentration [Weber et al., 2003]; and colorimetry [Gélinas and Finch, 2005; 2007; Zangooi et al., 2010]. Among these, the colorimetric technique was designed for use in-plant. The colorimetric technique was first applied to MIBC by Parkhomovski et al. [1976]. The technique was successfully extended to a wide range of commercial frothers [Gélinas and Finch, 2005]. This technique is based on the Komarowsky reaction and color formation is due to the hydration of the frother by sulphuric acid, and subsequent reaction with an aldehyde. The color intensity is proportional to concentration over a certain ppm range, which is used for constructing a calibration curve of absorbance versus concentration [Gomez and Finch, 2011].

Gélinas and Finch [2005; 2007] using colorimetry were among the first to measure partitioning. They found relatively little partitioning of MIBC at one plant but significant partitioning of F150 at a second, detecting up to 100 ppm in the overflow (i.e. froth) compared to ca. 1 ppm in the pulp. The observation explained the F150 enrichment in downstream banks which made operation difficult. Zhang et al. [2010] analyzing by total organic carbon (TOC) confirmed this stronger partitioning of F150 compared to MIBC through lab-scale two-phase (air-water) tests.

None of the techniques have been applied to frother blends. An objective of this thesis is to develop analytical techniques suited to dual frother systems.

2.4 New Frother Chemistries

Recent trends in developing new frothers have been taken two directions, one focusing on modifying known frothers [SME Research Forum, 2000], and the other emphasizing synthesis of new frothers (including frother blends) [Klimpel and Isherwood, 1991; Harris and Jia, 2000; Cappuccitti and Finch, 2007; Elmahdy and Finch, 2009].

An increasing trend in practice is to use blends of frothers with the aim of exploiting any synergistic effects. The recognition that frothers have rather defined optimal particle sizes ranges for flotation led to frother blending or "balancing" by Klimpel[1995]. Most work has considered blends of Alcohols with Polyglycols. One study mixed frothers on the basis of their relative CCC and concluded that the Polyglycol dominated [Laskowski et al., 2003]. A second study considered only froth properties and reported a synergistic effect: froth height with the blend was larger than the sum of froth height formed by each frother alone [Tan et al., 2005]. Elmahdy and Finch [2009], pursuing the notion of independent control of the two functions using Alcohol/Polyglycol blends, found the same synergistic effect on froth properties reported by Tan et al. [2005] but also found a negative effect on bubble size which increased in the blend compared to the frothers alone.

A new group of synthetic frothers consisting of Propylene Oxide (PO) and Aliphatic Alcohols, such as Hexanol$(PO)_2$, Pentanol$(PO)_2$ and MIBC$(PO)_2$ were introduced by Klimpel and Isherwood [1991]. They were developed to try to broaden the recoverable particle size range compared to the parent alcohol alone. Harris and Jia [2000] claimed that a new class of frothers created by adding a sulphur atom to Polyalkoxylate increased copper and moly recovery from a porphyry ore. In the most recent effort, Cappuccitti and Finch [2007] developed a new class of frothers from the reaction of C-1 to C-4 Aliphatic Alcohols with 0.2-5 moles of Ethylene Oxide (EO). A new frother (Butanol with 1.5 EO) was found suitable to replace MIBC, one of the objectives of the exercise. This thesis will explore the relationship between frother chemistry and properties by designing and characterizing a series of frother blends (Chapter 4), and new synthetic frothers (Chapter 6).

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Chapter 3 – Characterizing Frothers through CCC95-HLB Relationships

Abstract

Frothers are surfactants commonly used to reduce bubble size in mineral flotation. This chapter describes a methodology to characterize frothers by relating impact on bubble size reduction represented by CCC (Critical Coalescence Concentration) to frother structure represented by HLB (Hydrophile-Lypophile Balance). Thirty-six surfactants were tested from three frother families: Aliphatic Alcohols, Polypropylene Glycol Alkyl Ethers and Polypropylene Glycols, covering a range in alkyl groups (represented by n, the number of carbon atoms) and number of Propylene Oxide groups (represented by m). The Sauter mean size (D_{32}) was derived from bubble size distribution measured in a 0.8 m^3 mechanical flotation cell. The D_{32} vs. concentration data were fitted to a 3-parameter model to determine CCC95, the concentration giving 95% reduction in bubble size compared to water only. It is shown that each family exhibits a unique CCC95-HLB relationship dependent on n and m. Empirical models were developed to predict CCC95 either from HLB or directly from n and m. Commercial frothers of known family are shown to fit the relationships. This ability to estimate CCC95 from family/HLB information is a step in modeling the role of frother in controlling bubble size in flotation machines.

3.1 Introduction

Flotation, widely used for processing mineral ores, is based on the capture of hydrophobic particles by air bubbles [Rao and Leja, 2004]. In the process surface-active agents known as frothers are commonly employed to aid production of fine air bubbles which facilitates particle capture and transport.

Bubbles in flotation machines in the absence of frother exhibit a wide, often bi-modal size range with a Sauter mean size (diameter, D_{32}) ca. 4 mm where the addition of sufficient frother narrows to uni-modal distribution of Sauter mean size typically ca. 1 mm [Nesset et al., 2007]. This reduced bubble size enhances flotation kinetics. Treating flotation as a first order kinetic process, Gorain et al. [1997; 1998] showed that the flotation rate constant increased inversely with bubble size ($1/D_b$) a dependence used in the JKSimFloat simulator [Harris et al., 2002]. Others have suggested an even stronger dependence, as high as $1/D_b^3$ [Yoon, 1993]. Recent plant-based work showed dependence on $1/D_b^2$ [Hernandez-Aguilar, 2011]. Regardless, it is evident that flotation rate is related to bubble size and thus to the effect of frother on bubble size.

Three frother families are the subject of the present work: Aliphatic Alcohols ($C_nH_{2n+1}OH$), PPGAE (Polypropylene Glycol Alkyl Ethers, $C_nH_{2n+1}(OC_3H_6)_mOH$) and PPG (Polypropylene Glycols, $H(OC_3H_6)_mOH$), the latter two sometimes lumped as 'Polyglycols'. The ambition is studying surfactants from these three families to determine the link between frother's role in reducing bubble size measured by CCC (critical coalescence concentration) and frother structure measured by HLB (hydrophile-lipophile balance); i.e., to forge a structure-function relationship. Some background will justify the choice of CCC and HLB.

3.2 Critical Coalescence Concentration and Hydrophile-Lipophile Balance

The general dependence on frother concentration (C) is that D_{32} decreases exponentially to reach a minimum size at some concentration [Finch and Dobby, 1991]. This action is usually ascribed to frothers reducing coalescence [Harris, 1976]. Combining these points Cho and Laskowski [2002] introduced the term critical coalescence concentration (CCC) to describe the concentration giving the minimum bubble size. Laskowski [2003] showed that all frothers produced a similar D_{32}-C trend, differing only in their CCC, for example DowFroth 250 with CCC 9.1 ppm and MIBC 11.2 ppm. This self-similarity enabled a unique trend line for all frothers by plotting D_{32} against the normalized concentration

C/CCC.

Laskowski [2003] described a graphical method to estimate CCC. Recognizing the difficulty in identifying the end point of an exponential function Nesset et al. [2007] substituted a 3-parameter model to fit the D_{32}-C data and estimate CCC as the concentration giving 95% reduction in bubble size compared to that in water alone, termed the CCC95. The 3-parameter model was presented as:

$$D_{32} = D_L + A \cdot Exp(-B \cdot C) \tag{3.1}$$

where D_L is the minimum (limiting) bubble size, A the bubble size reduction (initial, zero-frother, D_{32} minus D_L), and B the decay constant, which depends on the frother in question.

The normalized trend then becomes:

$$D_{32} = D_L + a \cdot Exp(-b \cdot \frac{C}{CCC95}) \tag{3.2}$$

where D_L, *a* and *b* have the same meaning but unique values.

It is evident in the model (Eqn. 3.2) that other CCCx values could be quoted; for example CCC75 would mean the concentration giving 75% reduction in bubble size from water alone.

Grau et al. [2005] suggested CCC is a material constant. Nesset et al. [2007; 2012] explored the dependence of CCC95 on operating variables, for example showing it was independent of impeller speed over a wide range in forced air mechanical flotation machines but increased with air rate. Both research groups employed mechanical machines and although data on other flotation devices are limited the CCC appears to depend on machine type but the the D_{32}-C trends are consistent. While the CCC95 is, therefore, not entirely a material constant it does meet the criterion here of quantifying the role of frother type in effecting bubble size reduction. Consequently CCC95 is our measure of frother function.

The hydrophile-lipophile balance (HLB) is one of the most widely used indicators of a surfactant's suitability for a given application. It offers a measure of the tendency of surfactant to partition between oil and water. Since its introduction by Griffin [1949] there have been several attempts to develop a rapid and reproducible technique to determine HLB both experimentally and computationally [Davies, 1957; Mittal and Lindman, 1984; Proverbio et al., 2003; Wu et al., 2004]. Among all, the Davies method has been most widely used [Davies, 1957; Davies and Rideal, 1961]. Davies assumed that HLB was an additive and constitutive indicator with hydrophilic and lipophilic (hydrophobic) group numbers assigned to various structural components. In the Davies' approach the HLB is given by:

$$\text{HLB}=7+\sum(\text{hydrophilic group numbers})+\sum(\text{lipophilic group numbers}) \qquad (3.3)$$

Typically HLB values range between 1 and 20 [Tanaka and Igarashi, 2005], with high numbers indicating high water solubility and a low numbers meaning poor water solubility. According to Tanaka and Igarashi [2005], applications for different ranges of HLB values are shown in Table 3.1:

Table 3.1 − Correlation of HLB and application

HLB value	***Application***
1.5-3	Antifoaming agents
3.5-6	Water-in-oil emulsifiers
4-10	Frothers
7-9	Wetting agents
8-18	Oil-in-water emulsifiers
10-20	Collectors
13-15	Detergents
15-18	Solubilizers

The group numbers related to the present investigation are listed in Table 3.2.

Table 3.2 − The selected group number used in the Davies method of estimating HLB

Functional group	***Group contribution number***
Hydrophilic	
-OH	1.9
-O-	1.3
Lipophilic (or hydrophobic)	
-CH-; CH_2-; -CH_3-; =CH	-0.475

Example calculations are given for 1-Pentanol (Eqn. 3.4a) where we have 1 OH group and 5 C atoms in alkyl chain (i.e. C_5H_{11}), and Dipropylene Glycol ($H(OC_3H_6)_2OH$) (Eqn. 3.4b) where we have 2 OH groups and 6 C atoms in alkyl chain as well as 1 O atom:

$$HLB_{\text{1-Pentanol}} = 7+1.9-(5*0.475) = 6.625 \qquad (3.4a)$$

$$HLB_{\text{Dipropylene Glycol}} =7+ (2*1.9)+1.3-(6*0.475) = 9.25 \qquad (3.4b)$$

Laskowski [2003] and Pugh [2007] have discussed a link between frother functions and HLB. Laskowski noted that frothers with low CCC values had low HLB numbers, i.e., were more hydrophobic than frothers with higher CCC values, but no general correlation emerged. His data base was dominated by commercial frothers and did not include Polypropylene Glycols. In this study a range of pure surfactants from the three families is studied, varying both n in the alkyl group and m the number of Propylene Oxide groups. Establishing a correlation between CCC and HLB would be a step towards predicting bubble size in flotation systems from frother structure and might lead to new frother formulations with tailored properties.

3.3 Experimental

3.3.1 Apparatus

An AutoCAD sketch of the set-up to measure bubble size is shown in Figures 3.1 and 3.2. The nominal volume of the cell is 800 L, with a standard test volume of 700 L being employed. The impeller diameter was 21 cm and that of the outside diffuser 33 cm. A feature of the design is the baffle ring at 40 cm from the bottom of the tank (32 cm below water surface) which divides the turbulent zone around the impeller from the quiescent zone above where bubble size is determined. Air supply was from a compressed air system and manipulated via a 400 LPM KMS^{TM} mass flow meter.

Bubble sizing was the sampling-for-imaging (SFI) technique using the McGill Bubble Size Analyzer (MBSA) [Hernandez-Aguilar et al., 2002; Gomez and Finch, 2007]. The sampling tube of the MBSA was positioned 33 cm from the central shaft (19 cm from the wall) and 52 cm from the bottom of the tank (20 cm below the water surface). This location inside the quiescent zone had been established previously as being both representative of the average air rate in the cell and giving reproducible data [Nesset et al., 2007]. All experiments were run under the following conditions: air superficial velocity (J_g, i.e., volumetric air rate divided by cell cross-sectional area) 0.5 cm/s; room temperature 20-22°C; and impeller speed 1500 rpm (equivalent to 5.73 m/s tip speed). The air velocity was selected to correspond to the 'base' air rate in the bubble size modeling work of Nesset et al. [2007; 2012]; and the impeller speed was selected as being well within the range determined to have no impact on bubble size [Nesset et al., 2007; 2012].

Experiments were conducted in a water-air system. The cell was filled with Montréal tap water one day before a test to equilibrate the water to room temperature. Frother solutions were prepared for the cell (cell concentration) and for the MBSA assembly (chamber concentration) independently. The chamber concentration was kept at least above CCC75 of the frother to prevent coalescence in the sampling tube [Zhang et al., 2009]. Fifteen minutes of agitation at 4200 rpm without air prior to testing ensured the frother was fully mixed.

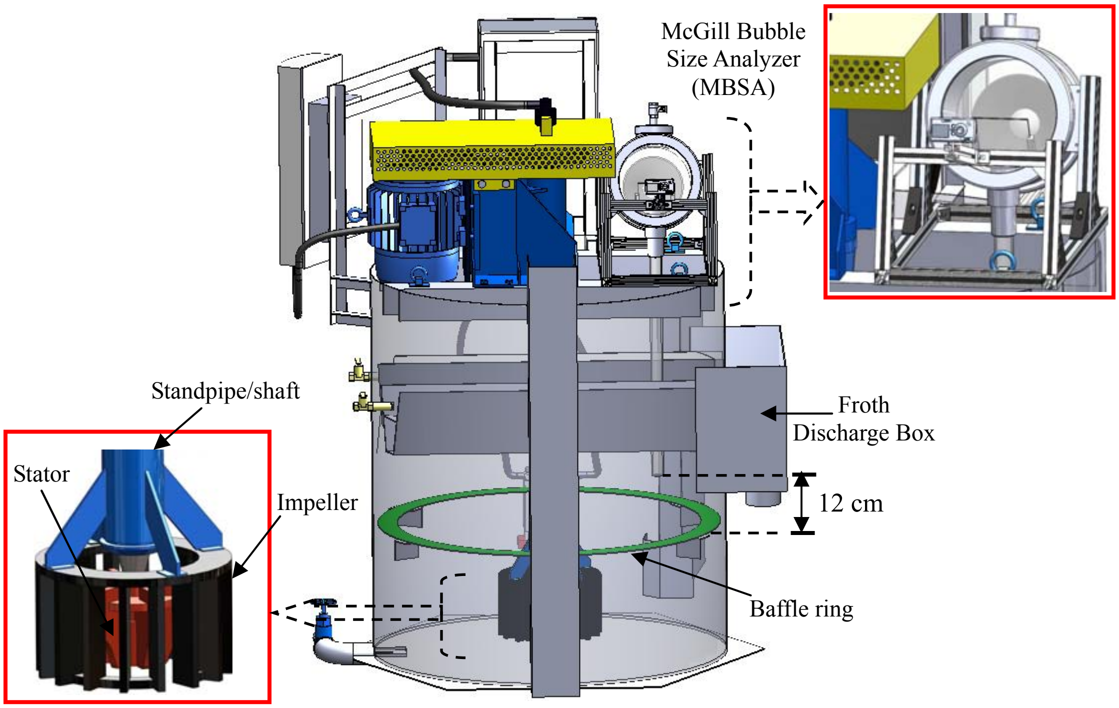


Figure 3.1: Schematic CAD drawing of Metso RCS^{TM} 0.8 m^3 mechanical cell and accessories

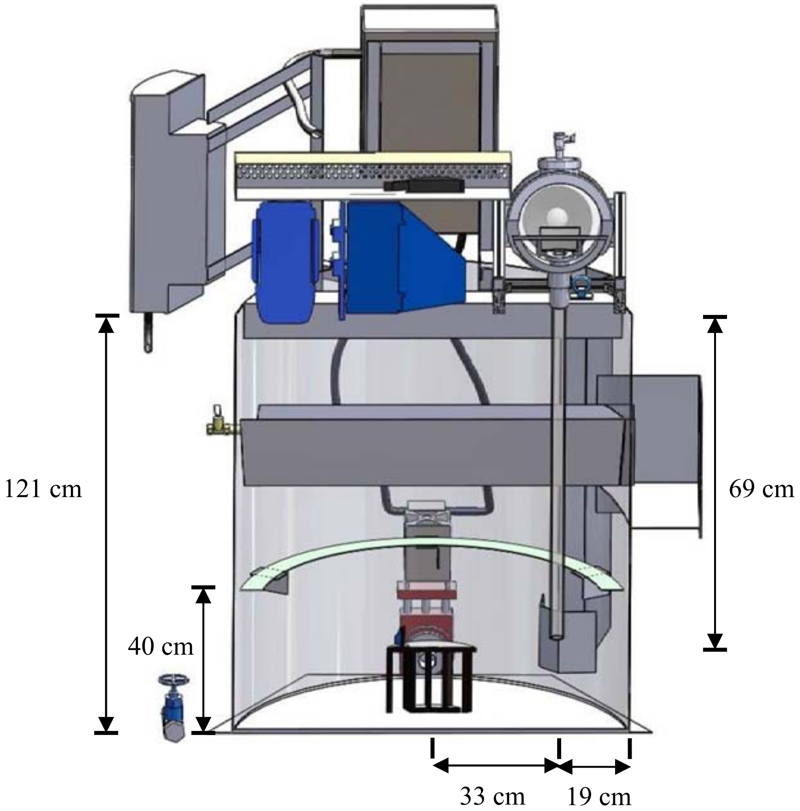


Figure 3.2: A cut-away view of Metso RCS^{TM} 0.8 m^3 mechanical cell showing dimensions and location of MBSA sampling tube

Frother was added incrementally to give up to twenty concentration points ranging up to 200 ppm. This number of points ensures reliable estimation of the three fitted parameters. The bubble size data were corrected and reported at standard temperature and pressure. Up to 100 000 bubbles were counted.

The SFI technique was validated using particle image velocimetry (PIV). For this a bubble column (110 cm x 10 cm) was used to provide the necessary transparent wall for the PIV laser light. Bubbles were generated at a stainless steel sparger (5 μm nominal pore size). The bubble size was measured by PIV at the same location as the MBSA sampling point. The PIV apparatus (model: Gemini 200 - 15 Hz) consisted of two CCD cameras (lens model: Nikon AF 50 mm) and laser synchronizer (model: 630149-G). The bubbles which passed the laser plane were observed in the PIV images. The imaged area was 74 x 92.5 mm giving a smallest detectable bubble size of about 0.3 mm (0.1 mm for SFI technique). A threshold method was used to identify bubbles from the PIV images. Some 100 images comprising 1000 -15 000 bubbles were recorded in each experiment.

3.3.2 Reagents

The surfactants from the three frother families are identified in Table 3.3a which shows the range in n and m and corresponding range in HLB (note, Polyglycol Monoethyl Ethers (i.e. n = 2) are not available). All were reagent grade from Aldrich-Sigma (98%~99.9% purity). Several commercial frothers were included and are listed in Table 3.3b.

Table 3.3a − Frother families and range of surfactants (n, m HLB) used in the study

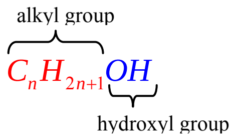
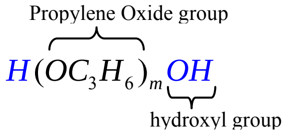
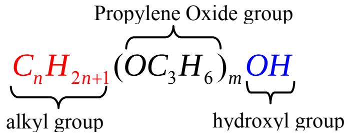
Frother family	***Chemical structure***	***n***	***m***	***HLB***
Aliphatic Alcohols	 $\overbrace{C_nH_{2n+1}}^{\text{alkyl group}}\underbrace{OH}_{\text{hydroxyl group}}$	3-8	-	5-7.5
Polypropylene Glycols (PPG)	 $H\overbrace{(OC_3H_6)_m}^{\text{Propylene Oxide group}}\underbrace{OH}_{\text{hydroxyl group}}$	0	3-17	7.4-9.3
Polypropylene Glycol Alkyl Ethers (PPGAE)	 $\underbrace{C_nH_{2n+1}}_{\text{alkyl group}}\overbrace{(OC_3H_6)_m}^{\text{Propylene Oxide group}}\underbrace{OH}_{\text{hydroxyl group}}$	1,3,4	1-7	6.5-8.3

Table 3.3b − Commercial frothers used in the study

Frother Family	***Commercial Frother Type***	***Supplier***	***n***	***M***	***Molecular Weight***	***HLB***
Aliphatic Alcohols	FX120-01	Flottec	6	-	102	6.05
Polypropylene Glycol (PPG)	F150	Flottec	0	7	425	8.625
Polypropylene Glycol Alkyl ether (PPGAE)	DowFroth 250	Dow Chemical	1	4	264	7.83
	DowFroth 1012	Dow Chemical	1	6.7	398	7.48
	FX160-01	Flottec	1	3.8	251	7.86
	FX160-05	Flottec	3	2.5	207	7.11
	F160	Flottec	4	2.5	217	6.63

3.4 Results

3.4.1 Reliability and Validation

Figure 3.3 shows Sauter mean bubble size (D_{32}) as a function of concentration for three repeats for the commercial frother DowFroth 250 (DF 250). Full repeat tests (i.e. including solution preparation) were conducted by two different operators at three different times. The D_{32}-C curves were consistent and the 95% confidence interval on the calculated CCC95 was 0.6%, which is too small to indicate on the plot.

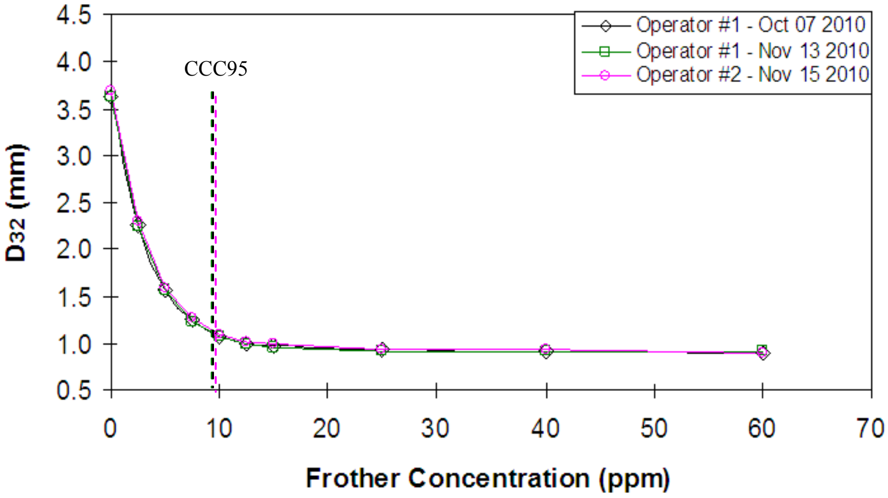


Figure 3.3: Reliability: inter-operator and intra-operator duplicated experiments at same conditions for DF 250

In validating the SFI technique, PIV was used simultaneously to determine bubble size at selected concentrations with DF 250. The results (Figure 3.4) show that the D_{32} from SFI is in good agreement with the D_{32} from PIV. The results confirm the reliability (Figure 3.3) and validity (Figure 3.4) of the SFI technique.

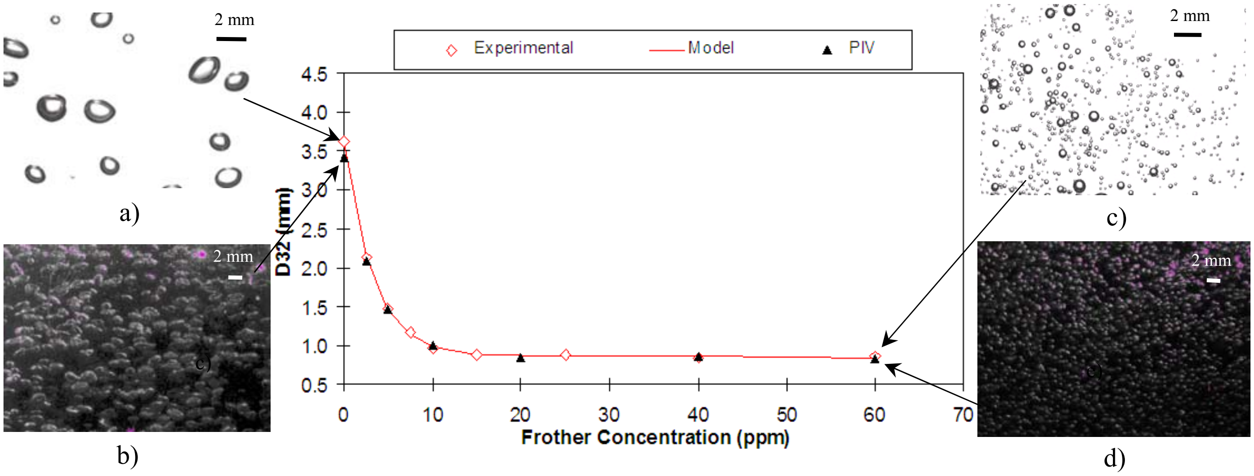


Figure 3.4: Validation: Sauter mean bubble size as a function of frother DF 250 concentration measured by the SFI technique (diamonds) and the PIV technique (triangles); a) Example image at 0 ppm concentration by SFI technique; b) Example image at 0 ppm concentration by PVI technique; c) Example image at 60 ppm concentration by SFI technique; d) Example image at 60 ppm concentration by PIV technique (Note, line is the 3-parameter model fit to the SFI D_{32}-C data.)

3.4.2 CCC95 vs. HLB

The trend in Figure 3.3 was repeated for all frothers, as illustrated in Figure 3.5 for selected surfactants with the CCC95 indicated. Table 4 gives the CCC95 and D_L results (from fitting to the 3-parameter model, Eqn. 3.1) for all reagents tested with their corresponding molecular weight (MW) and HLB. The literature CCC values included for reference are in agreement with the current values.

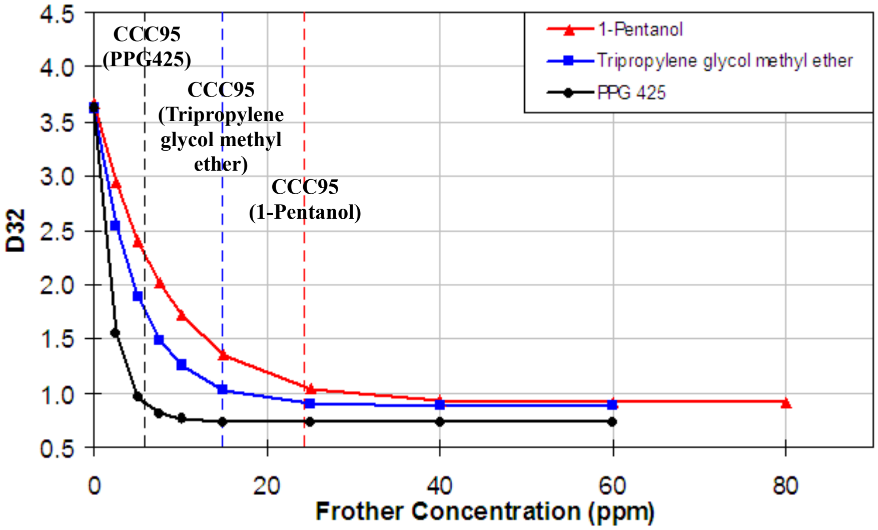


Figure 3.5: The effect of frother addition on D_{32} for 3 frother types; the location of CCC95 and that D_L depends on frother type is noted

Table 3.4 − Summary of properties and CCC95 and D_L determined for the tested surfactants

Frother Family	*Frother Type*	*n*	*m*	*Calculated HLB*	*Molecular Weight (g/mol)*	*Grau and Laskowski, 2006*	*Current Work*		
						CCC (ppm)	**CCC95 (ppm)**	**CCC95 (mmol/L)**	**D_L (mm)**
Aliphatic Alcohols	**1-Propanol**	3	-	7.48	60	-	236	3.92	0.87
	1-Butanol	4	-	7	74	-	63.	0.85	0.88
	1-Pentanol	5	-	6.53	88	-	25	0.29	0.92
	1-Hexanol	6	-	6.05	102	11	11	0.11	1.00
	1-Heptanol	7	-	5.58	116	-	8	0.072	1.08
	1-Octanol	8	-	5.1	130	-	8	0.060	1.15
	2-Propanol	3	-	7.48	60	-	307	5.10	0.86
	2-Butanol	4	-	7	74	-	77	1.04	0.88
	2-Pentanol	5	-	6.53	88	-	30	0.34	0.91
	2-Hexanol	6	-	6.05	102	-	11	0.11	1.01
	2-Heptanol	7	-	5.58	116	-	9	0.080	1.08
	2-Octanol	8	-	5.1	130	-	8	0.062	1.12
	3-Pentanol	5	-	6.53	88	-	41	0.47	0.93
	3-Hexanol	6	-	6.05	102	-	13	0.12	1.00
Polypropylene Glycol Ethers	**Propylene Glycol Methyl Ether**	1	1	8.28	90	47	44	0.48	0.84
	Propylene Glycol Propyl Ether	3	1	7.33	118	-	29	0.25	0.88
	Propylene Glycol Butyl Ether	4	1	6.85	132	-	21	0.16	0.92
	Di(Propylene Glycol) Methyl Ether	1	2	8.13	148	25	26	0.18	0.83
	Di(Propylene Glycol) Propyl Ether	3	2	7.18	176	-	16	0.094	0.89
	Di(Propylene Glycol) Butyl Ether	4	2	6.7	190	-	12	0.066	0.91
	Tri(Propylene Glycol) Methyl Ether	1	3	7.98	206	17	15	0.073	0.89
	Tri(Propylene Glycol) Propyl Ether	3	3	7.03	234	-	11	0.045	0.92
	Tri(Propylene Glycol) Butyl Ether	4	3	6.55	248	-	7	0.029	0.96

Polypropylene Glycols	**Di Propylene Glycol**	-	2	9.25	134	-	53	0.40	0.71
	Tri Propylene Glycol	-	3	9.125	192	-	33	0.17	0.69
	Tetra Propylene Glycol	-	4	9	250	-	22	0.088	0.71
	Polypropylene Glycol 425	-	7	8.625	425	-	6	0.014	0.74
	Polypropylene Glycol 725	-	12	8	725	-	7	0.0091	0.79
	Polypropylene Glycol 1000	-	17	7.375	1000	-	8	0.0084	0.88
Commercial frothers	**FX120-01**	6	-	6.05	102	-	11	0.10	0.98
	DowFroth250	1	4	7.83	264	9	10	0.038	0.85
	DowFroth1012	1	6.7	7.48	420	6	6	0.014	0.86
	FX160-05	3	2.5	7.11	207	-	15	0.074	0.90
	FX160-01	1	3.8	7.86	251	-	12	0.048	0.88
	F150	-	7	8.625	425	-	6	0.014	0.76
	F160	4	2.5	6.63	217	-	8	0.037	0.95

Laskowski [2003] considered a dependency between the CCC and molecular weight. This is tested in Figure 3.6 which shows trends dependent on family. Nesset et al. [2012] correlated CCC95 in ppm against HLB/MW for a selection of commercial frothers; this is tested in Figure 3.7 for all 36 frothers. The trend for the Alcohols is consistent but for the Polyglycols it becomes progressively scattered. In addition, the correlation is a rather mixed association, the use of ppm distancing it from a fundamental in favour of a practical basis.

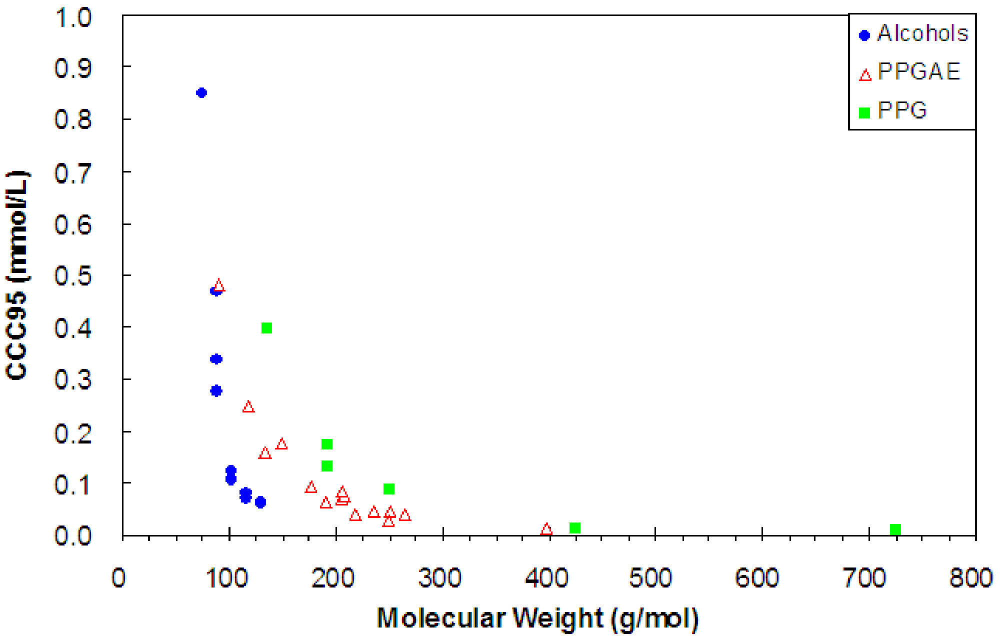


Figure 3.6: CCC95 (mmol/L) versus molecular weight for the 36 frothers

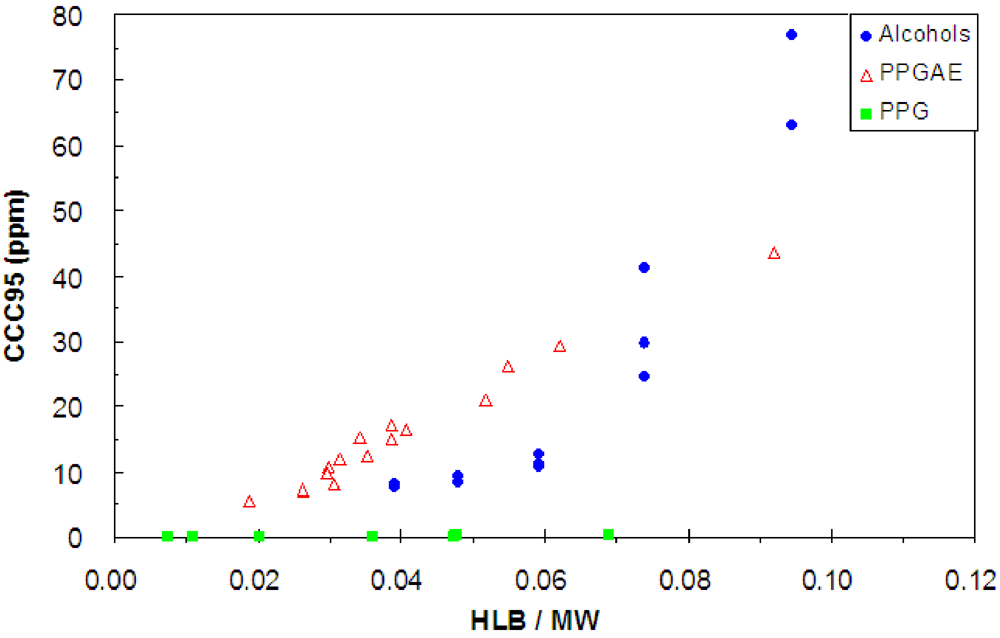


Figure 3.7: CCC95 (ppm) versus HLB / molecular weight for the 36 frothers

Figure 3.8a shows the CCC95-HLB relationship for the Aliphatic Alcohols. Starting with Propanol there is a sharp decrease in CCC95 as HLB decreases which levels off above 6 carbons (n = 6 or C-6). For C < 6 there is an increasing isomer effect, i.e., effect of position of the OH group, which is illustrated by comparing Hexanol and Pentanol in Figure 3.8b. For practical purposes, however, since such short chain Alcohols are not employed as frothers, the isomer effect can be ignored. The commercial frother FX120-01 is seen to fit the trend.

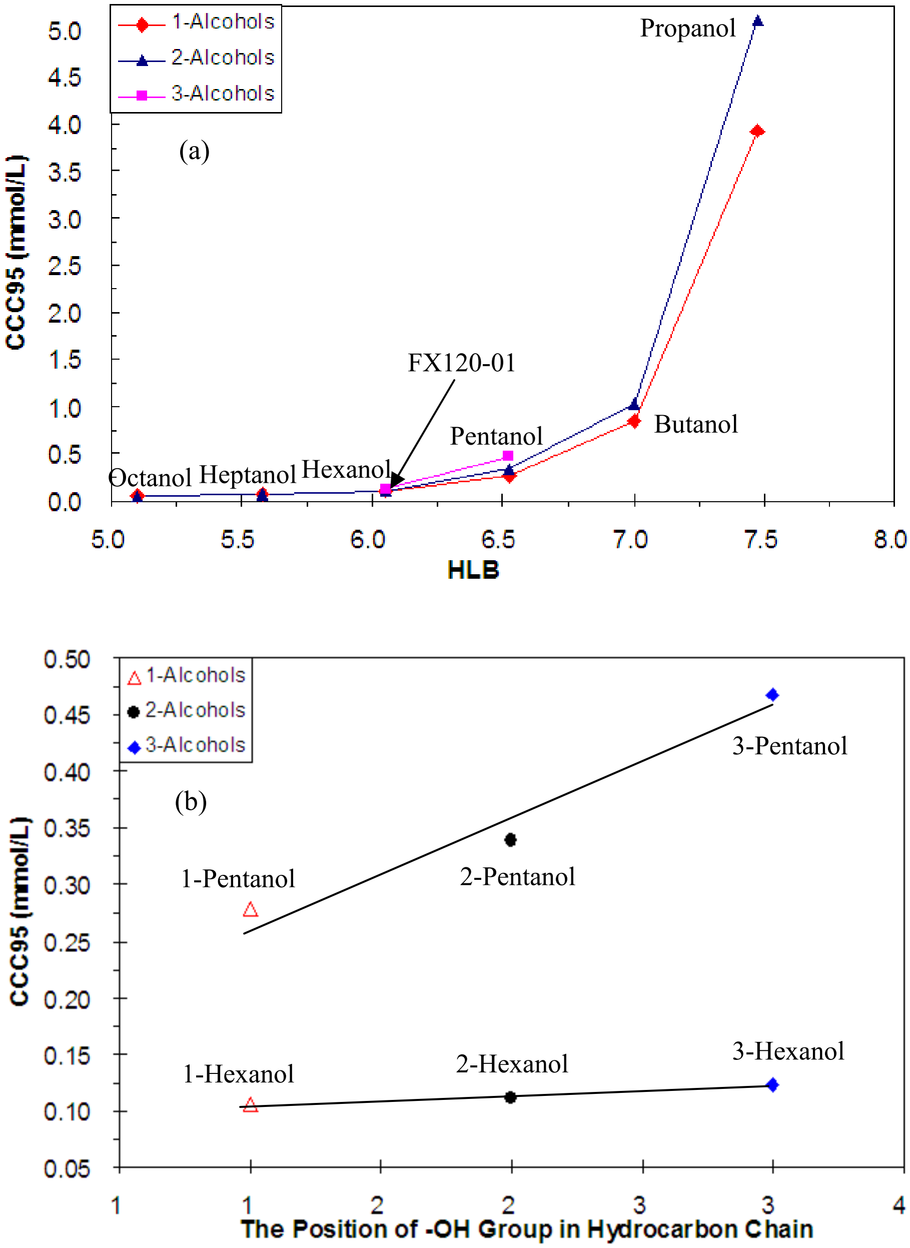


Figure 3.8: a) CCC95 versus HLB for the isomers of Pentanol and Hexanol (i.e., 1-Alcohol, 2-Alcohol and 3-Alcohol); b) the effect of –OH group position on CCC95 for Pentanol and Hexanol isomers

Figure 3.9 shows CCC95 vs. HLB for the two Polyglycol families, in this case as a function of m for a given n. There is a pattern: CCC95 decreases with increasing m in a series of parallel or self-similar plots which trend to lower HLB with increasing n. For n = 0 (i.e., Polypropylene Glycols) m = 1 was tested but showed no bubble size reduction up to 13 mmol/L (1000 ppm). The commercial frothers are shown to fit the pattern.

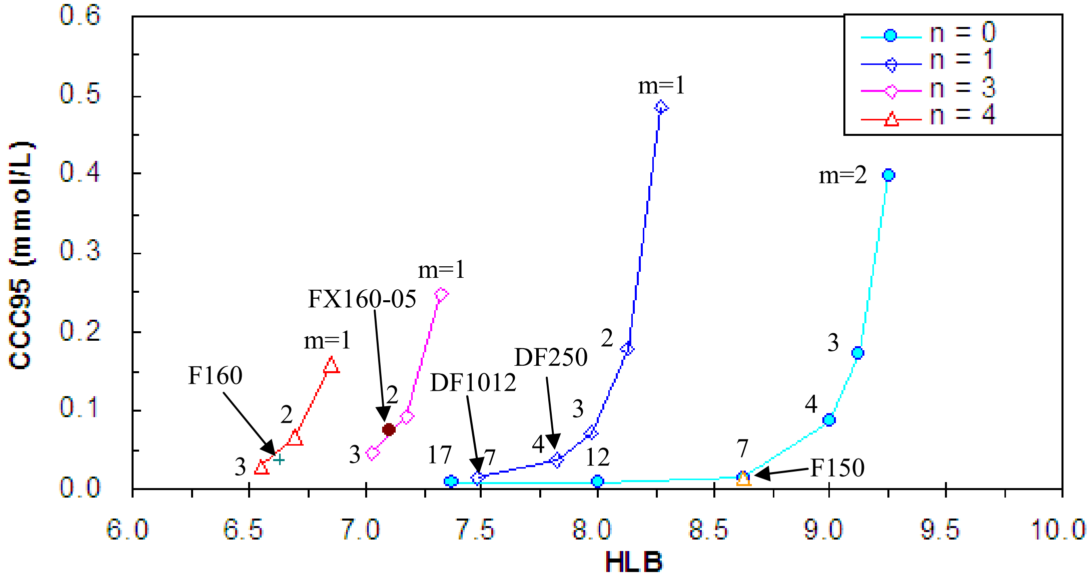


Figure 3.9: CCC95 versus HLB for the Polyglycols as function of m for a given n

3.4.3 Developing a CCC-HLB Model

The trends in Figures 3.8a and 3.9 show consistent patterns that can be fitted to the following exponential equation:

$$CCC95 = \alpha \cdot Exp(\beta \cdot HLB) \tag{3.5}$$

where α and β are constants that depend on the family (i.e., n). Table 3.5 gives the values for the Polyglycols and 1-Alcohols.

Table 3.5 − The tested range of n and m and corresponding constants in Eqn. 3.5 and goodness-of-fit relationships for the data shown in Table 3.4

Family	***n***	***m***	***α***	***β***	***Precision***				
					Data Points, N	**R^2**	**$R^2_{Adjusted}$**	**SSE**	**RMSE**
1-Alcohol	3-8	0	**1.52E-10**	**3.207**	6	0.9815	0.9769	0.002136	0.02311
Polypropylene Glycol	0	2-17	**4.76E-17**	**3.951**	6	0.9615	0.942	0.006069	0.04498
Polypropylene Glycol Methyl Ether	1	1-7	**1.61E-18**	**4.855**	6	0.9745	0.9682	0.004049	0.03181
Polypropylene Glycol Propyl Ether	3	1-3	**3.15E-19**	**5.624**	4	0.9937	0.9905	0.0001581	0.008891
Polypropylene Glycol Butyl Ether	4	1-3	**9.58E-20**	**6.125**	4	0.9972	0.003891	3.027E-5	0.003891

The α and β can be linked to n as follows:

$$\alpha = 4.74 \cdot 10^{-17} \cdot \exp(-3.497 \cdot n) + 1.956 \cdot 10^{-19} \cdot \exp(-0.001452 \cdot n) \qquad (3.6)$$

$$\beta = \frac{6.985 \cdot n + 4.814}{1.455 + n} \qquad (3.7)$$

3.4.4 Developing CCC95 Model as a Function of n and m

3.4.4.1 Polyglycols

Figure 3.10 presents HLB values versus m, which shows simple linear relationships. Taking 0.15 as the average slope this yields:

$$HLB = -0.149 \cdot m + \gamma \qquad (3.8)$$

where γ depends on n (see inset).

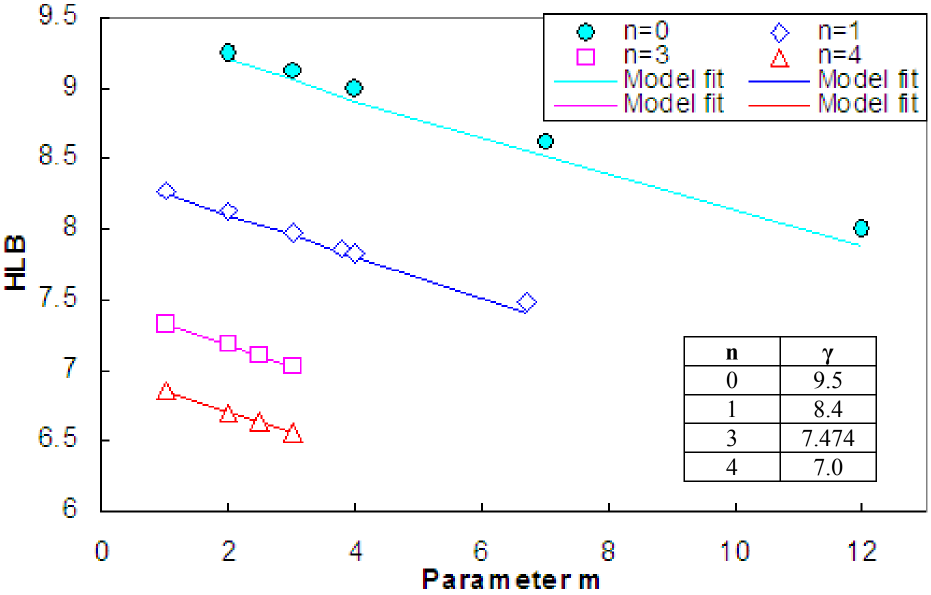


Figure 3.10: HLB for the Polyglycols as function of m for a given n

The γ is then correlated to n, yielding:

$$\gamma = \frac{5.158 \cdot n + 29.9}{3.152 + n} \tag{3.9}$$

To define the relationship between HLB and parameters m and n, Eqns. 8 and 9 are combined:

$$HLB = -0.149 \cdot m + \frac{5.158 \cdot n + 29.9}{3.152 + n} \tag{3.10}$$

The expressions for α (Eqn. 3.6), β (Eqn. 3.7) and HLB (Eqn. 3.10) are inserted into Eqn. 3.5 to obtain an overall expression for CCC95 as a function of m and n. After re-arranging and gathering terms one obtains:

$$CCC95(mmol/L) = [4.74 \cdot 10^{-17} \cdot \exp(-3.497 \cdot n) + 1.956 \cdot 10^{-19} \exp(-0.001452 \cdot n)] \cdot \exp[(\frac{6.985 \cdot n + 4.814}{1.455 + n}) \cdot (-0.149 \cdot m + \frac{5.158 \cdot n + 29.9}{3.152 + n})] \tag{3.11}$$

The Equation, while cumbersome, gives an excellent fit (Figure 3.11) for n = 1, 3 and 4 and acceptable one for n = 0. It is evident, therefore, that knowing m and n for Polyglycols, in essence the structure, CCC95 can be predicted.

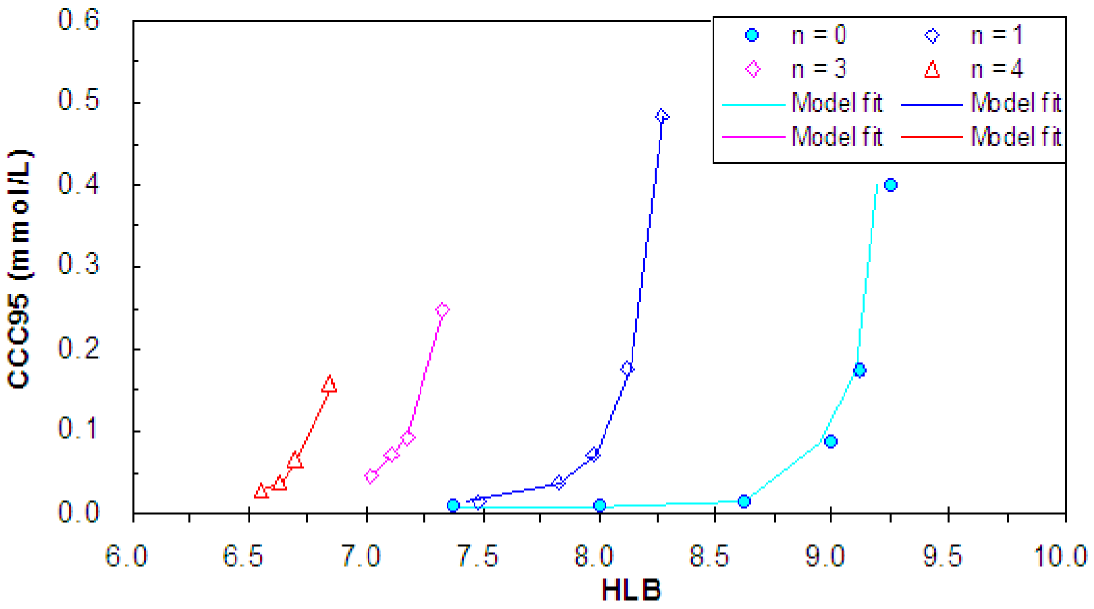


Figure 3.11: Model (Eqn. 3.11) fit CCC95 versus HLB data for the Polyglycols plotted as function of m for a given n

3.4.4.2 1-Alcohols

Applying the same approach as described for Polyglycols, the CCC95 for 1-Alcohols can be expressed by the general relationship:

$$CCC95(mmol/L) = 1.5249 \cdot 10^{-10} \cdot \exp[3.207 \cdot (\frac{-75.17 \cdot n + 1490.44}{166 + n})] \qquad (3.12)$$

The experimental data and model fit (line) are shown in Figure 3.12; it is evident that the CCC95 of 1-Alcohols can be predicted if n is known.

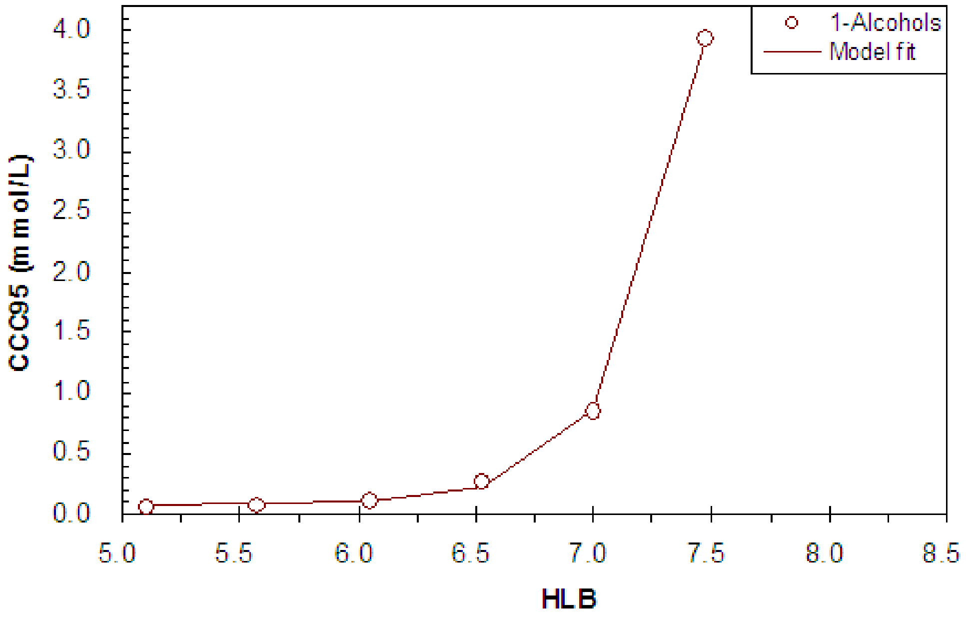


Figure 3.12: Model (Eqn. 3.12) fit to CCC95 versus HLB data for the 1-Alcohols

3.4.5 D_L and HLB

Nesset et al. [2007] suggested that the minimum bubble diameter (determined from the model fit, Eqn. 3.1, D_L) tended to decrease as CCC95 increased, i.e., as HLB increased. Figure 3.13 expands the database and confirms this trend, showing a linear decrease in D_L as HLB increases fitted by:

$$D_L = -0.072 \cdot HLB + 1.43 \tag{3.13}$$

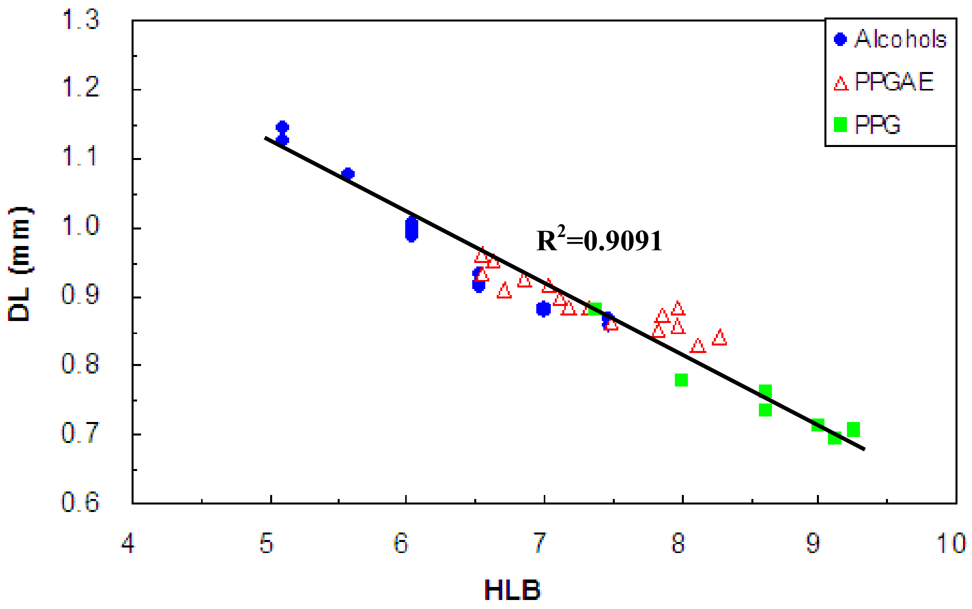


Figure 3.13: Minimum bubble size D_L versus HLB for all surfactants tested: the line is the regression model, Eqn. 3.13

3.5 Discussion

In most flotation systems frothers have the key function of controlling bubble size. Consequently understanding and predicting their action is of interest to modellers and plant operators. The approach here was to explore a structure-function relationship. To quantify structure HLB was used as it encompasses the hydrophilic-hydrophobic (amphipathic) character that controls adsorption at the air-water interface, which arguably is the basis for frother action. The function, bubble size reduction, was quantified through the CCC concept derived from the plot of Sauter mean diameter (D_{32}) versus concentration (C). The D_{32} was calculated from bubble size distribution obtained using the sampling-for-imaging technique (SFI) and validated against a second, PIV-based method. The subsequent estimation of CCC95 from a model fit to the D_{32} vs C data proved reliable, confirmed with a second operator and by showing CCC95 values were similar to published data. The large cell volume (700 L water) aided reliability by permitting sufficient chamber surfactant concentration to avoid coalescence, which improves data reliability at cell concentrations well below CCC95 and thus improves the fit to Eqn 3.1.

Efforts along this structure-function approach by Laskowski [2003] and Nesset et al. [2007; 2012] laid a foundation. Suggested correlations involving molecular weight were explored in Figures 3.6 and 3.7 but were not pursued in favour of using HLB alone. What is revealed is a family-based CCC-HLB pattern, confirming a possibility considered by Pugh [2007]. For the Alcohols the trend was a rapid decrease in CCC95 as HLB was reduced as number of carbons (n) was increased (Figure 3.8a). The same observation was made by Keitel and Onken [1982] studying the inhibition of bubble coalescence by various solutes in a bubble column. They found for Aliphatic Alcohols that the limiting concentration decreased with increasing n to approach a limiting value for $n > 6$. Drogaris and Weiland [1983] studied coalescence between bubble pairs generated at two adjacent capillary orifices in stagnant liquid and also found that coalescence inhibition improves with increasing chain length for Alcohols. The work here also identifies an effect of the position of the OH (i.e., an isomer effect) (Figure 3.8b). Given this only becomes significant for $C < 5$ and these currently are not employed commercially we chose to ignore the isomer effect in subsequent analysis.

The pattern for Polyglycols was CCC95 decreased as m increased in a series of self-similar plots shifting to lower HLB as n was increased (Figure 3.9). Although the PPGAEs and PPGs are usually considered as separate families, the pattern suggests they can be treated as one. Moreover, the Alcohols show a similar trend when plotted for a given m (Figure 3.8a), suggesting all the tested surfactants share some family traits. These patterns are new findings.

While a universal CCC95-HLB relationship (i.e., one independent of n and m) remains elusive, the large database permitted development of empirical models, which fit the results for Polyglycol (Figure 3.11) and 1-Alcohols (Figure 3.12). Thus it is possible to deduce CCC95 knowing n and m, either directly via Eqns. 3.11 (Polyglycols) or 3.12 (1-Alcohols), or from HLB via Eqn. 3.5 and Table 3.5. Either approach represents a significant step towards a first structure-based prediction of the impact of frother on bubble size in flotation machines. From the present work the prediction relates directly to mechanical flotation machines but the trends are considered applicable to all machines. Future work may see a relationship between CCC and machine type enabling the present results to be generalized.

One reason for the failure to find a universal relationship may be the Davies definition of HLB and the group numbers assigned. The results for Alcohols show that position of the OH group influences CCC95: as OH moves away from the end position CCC95 increases and this becomes more pronounced as chain length (n) decreases. This might result from an effect on orientation of the surfactant molecule at the air-water interface which becomes more significant as the molecule becomes smaller and thus the impact on CCC95 increases. The OH group number should reflect its position in the molecule. Likewise, the unique number for all CH groups can be questioned. With a sufficient database perhaps new empirical group numbers could be deduced that apply to prediction of CCC95. There are precedents for such modifications [Lin et al., 1971; 1973; 1976; Lin, 1976; McGowan, 1990; Sowada and McGowan, 1992].

There are alternatives to HLB. We are exploring the use of nuclear magnetic resonance (NMR) spectroscopy to determine the H-ratio to quantify the hydrophilic-hydrophobic balance [Zhang, et al, 2012]. NMR also gives structure which for commercial frothers may prove a necessary first step. This work will form part of a future report.

While the emphasis was CCC95 it is evident that the minimum Sauter mean bubble size (D_L) is not constant but decreases as HLB increases. The observation has a practical impact: if a process requires finer bubbles then a surfactant of higher HLB is suggested, the cost being the high associated concentration to reach CCC95. The observation also raises a fundamental question. The CCC concept implies frother is involved only in preserving the bubble size produced by the machine; i.e., the machine produces, frother preserves hypothesis. This means that D_L is the machine-produced size and should be invariant for given machine operating conditions. Figure 3.13 shows this is not the case and argues that frothers play some role in breakup of the air mass in creating the initial size, which subsequently the frother preserves. From Figure 3.13 this would mean that surfactants with higher HLB, i.e., lower hydrophobicity, such as Pentanol over Hexanol, are more effective in promoting breakup for which no mechanism is immediately forthcoming.

3.6 Conclusions

A structure-function approach to characterizing frothers was explored using Hydrophile-Lypophile Balance (HLB) to represent chemical structure and Critical Coalescence Concentration (CCC) to represent the bubble size reduction function. The tests were conducted in a 0.8 m^3 mechanical cell on 36 pure surfactants and commercial frothers of Aliphatic Alcohol, Polypropylene Glycol Alkyl Ether and Polypropylene Glycol (Polyglycol) families. The result was a series of self-similar CCC-HLB trends dependent on n (number of C-atoms in alkyl group) and m (number of Propylene Oxide groups). The Alcohol data also showed an isomer effect at $n < 5$. Empirical models were developed for the Polyglycols and 1-Alcohols showing that CCC could be predicted knowing n and m, i.e., knowing the structure. This finding is a significant step towards modeling the effect of frother on bubble size in flotation systems.

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Connecting Texts between Chapters 3 and 4

In order to characterize single frother's structure – function relationship, Chapter 3 developed a methodology to link one hydrodynamic function, bubble size reduction represented by CCC (critical coalescence concentration), to frother structure represented by HLB (hydrophile-lypophile balance). Chapter 4 will investigate if knowing the CCC-HLB relationships found in Chapter 3 that the independence over the two functions (hydrodynamic and froth properties) could be achieved by using dual-frother systems (or blends).

Chapter 4 – Dual Frother Systems: Gas Holdup, Bubble Size and Water Overflow Rate

Abstract

In flotation, frothers commonly provide two functions: control of pulp hydrodynamic properties and control of froth properties. In this chapter dual frother systems (blends) are investigated to determine combinations which provide independence over these two functions. A bubble column was used on a two-phase air-water system. Sauter mean bubble diameter (D_{32}) and gas holdup (E_g) were the hydrodynamic properties and water superficial overflow rate (J_{wO}) was the froth property. Blends of Alcohols with Polypropylene Glycols (PPG) and Polyethylene Glycols (PEG) were the candidates. Pre-mixed frother blends did not provide independence. The second approach was to use Alcohols as base and PPGs and PEGs as additives. Candidate blends were eliminated for a variety of reasons: with 1-Hexanol/TetraEG, J_{wO} converged to roughly the same level as TetraEG concentration was increased; with 1-Butanol/PPG,, D_{32} increased upon addition of PPG. The search was eventually successful: 1-Butanol/PEG blends gave independent control provided PEG had four or more EO groups. The increase in D_{32} noted with 1-Butanol/PPG blends was traced to partitioning of 1-Butanol to the froth which reduced 1-Butanol concentration below its critical coalescence concentration.

4.1 Introduction

In flotation, a frother has two main functions: to help provide the desired hydrodynamic properties in the pulp and the desired properties of the froth [Zieminski et al., 1967; Klimpel and Isherwood, 1991; Laskowski, 1998, Finch et al., 2006]. Their ability to do this is generally ascribed to reduced coalescence [Harris, 1976; Harris, 1982]. Other roles might be promoting bubble break-up [Grau and Laskowski, 2006; Finch et al., 2008; Kracht and Finch, 2009] and reducing bubble rise velocity [Azgomi et al., 2007;

Bulatovic, 2007].

The frothers most commonly used in flotation are compounds containing nonpolar, hydrophobic groups (e.g. alkyl groups) and polar, hydrophilic groups (e.g. oxygen and hydroxyl groups). The most widely used commercial frothers are Aliphatic Alcohols (general formula: $C_nH_{2n+1}OH$) and Polyglycols [Booth and Freyberger, 1962; Klimpel and Hansen, 1988]. For Polyglycols there are four sub-families: Polypropylene Glycols ($H(OC_3H_6)_mOH$), Polypropylene Glycol Alkyl Ethers ($C_nH_{2n+1}(OC_3H_6)_mOH$), Polyethylene Glycols ($H(OC_2H_4)_lOH$) and Polyethylene Glycol Alkyl Ethers ($C_nH_{2n+1}(OC_2H_4)_lOH$). Strictly, Polyethylene Glycols are not “conventional” frothers since they do not provide adequate bubble size reduction and frothing; however, Cappuccitti and Finch [2007] indicate that they might function in concert with Alcohols. A number of synthesized frothers consisting of various numbers of Ethylene Oxide (Ethoxy, EO) or Propylene Oxide (Propoxy, PO) have been commercialized in recent years [Cappuccitti and Finch, 2007]. These frothers are represented by the general formula $R(X)_nOH$ where R = H or straight or branched chain C_1 to C_4 alkyl radials, and X = EO or PO.

Based on the progress correlating frother chemical structure and effective size of particle floated, it has been recognized that a single frother generally cannot float the broad particle size distribution typical of a flotation feed [Klimpel, 1995]. Alcohol frothers tend to be more effective for fine-particle recovery than for coarse particle recovery while Polyglycol frothers are more effective for coarse particle flotation. It seems that for high recovery a mix of Alcohol and Polyglycol frothers may offer an advantage. Another argument for mixed frothers is that there are two functions: a single frother probably means a compromise on hydrodynamic or froth properties while a dual frother system offers a possibility to independently control both [Elmahdy and Finch, 2009].

Little attention has been directed to characterizing mixed frothers. There is no accepted technique for their evaluation and selection relies on empirical testing. Attempts to provide guidelines are mostly based on interpretation of flotation plant surveys [Klimpel and Hansen, 1988]. More recently, Laskowski and co-workers [Laskowski, 2003; Laskowski et al., 2003 and Laskowski, 2004] and others [Pugh, 2007; Zhang et al., 2012] have introduced the possibility of selecting blends based on parameters such as CCC (critical coalescence concentration) and HLB (hydrophile-lipophile balance).

Characterization should capture both hydrodynamic and froth properties [Laskowski, 2003; Cappuccitti and Nesset, 2009]. Hydrodynamic parameters include bubble size and gas holdup as a function of gas rate and the derived parameter, bubble surface area flux. These parameters correlate with the effect of frother on flotation kinetics [Luttrell and Yoon, 1992; Gorain et al., 1997; Finch et al., 1999; Deglon et al., 2000; Hernandez et al., 2001; Comley et al., 2007]. Plant evaluation using hydrodynamic measurements have had a significant impact on flotation practice over the past decade [Cooper et al., 2004; Hernandez-Aguilar et al., 2006; Hernandez-Aguilar and Reddick, 2007; Pyecha et al., 2006; Nesset et al., 2005, Nesset et al., 2006].

Froth properties can be measured in various ways, for example by equilibrium froth height and water overflow rate. In our experience froth volume is not always stable making determination of froth height unreliable [Elmahdy and Finch, 2009]. We favour water overflow rate to characterize froth stability [Araya et al., 2011]. Moyo et al. [2007] and Zhang et al. [2010] showed that water overflow rate was linked to frother type (i.e., "structure" or "chemistry"); and the measurement can be extended to three-phase systems [Melo and Laskowski, 2007; Kuan and Finch, 2010].

The prior works on dual frothers focussed on blends of Alcohol and Polyglycols. One study mixed frothers on the basis of their relative CCC and concluded that the Polyglycol dominated [Laskowski et al., 2003]. A second study considered only froth properties and reported a synergistic effect: froth height with the blend was larger than the summation of froth height formed by the frothers alone [Tan et al., 2005]. Elmahdy and Finch [2009] pursued the notion of independent control of the two functions using Alcohol/Polyglycol blends. They suggested a small addition of Polyglycol (1 to 2 ppm) to Alcohol as base did offer some independence observing that overflow rate could be varied while bubble size remained constant. They found the same synergistic effect on froth properties reported by Tan et al. [2005] but also found a negative effect on bubble size which increased in the blend compared to the frothers alone.

The purpose of this chapter is to characterize dual Alcohol/Polyglycol frother systems by measuring bubble size, gas holdup and water overflow rate with the objective of determining blends that achieve independent control over hydrodynamic and froth properties.

4.2 Experimental

4.2.1 Apparatus

A bubble column, 350 cm x 10 cm diameter (28 L), was the test rig (Figure 4.1). A stainless cylindrical porous sparger (6 cm high x 2.5 cm diameter) of 5 μm nominal pore size (diameter) was positioned vertically at the base of the column to disperse the air. This sparger was selected as it gave significant bubble size and gas holdup changes for all the frothers tested. Operation was continuous with the feed (frother solution) controlled by a peristaltic pump (Cole Palmer model 7520-25) and overflow and underflow recycled to the feed tank to close the loop. The underflow rate was fixed at 1600 g/min. A calibrated mass flow meter (MKS instruments model M100B53CS18V) was used to maintain superficial air flow velocity (J_g) at 0.5 cm/s. A differential pressure transmitter (Bailey model PTSDDD) was tapped between 260 cm and 329.5 cm above the sparger to determine gas holdup (E_g). As a backup, three 2.5 cm wide stainless ring electrodes separated by acrylic sections 7.5 cm wide were mounted around the mid-section to estimate gas holdup from conductivity [Tavera et al., 2001]. Bubble size measurements were made using the McGill Bubble Size Analyzer (MBSA) [Gomez and Finch, 2007] and are reported as the Sauter mean diameter (D_{32}). Froth height was maintained at 0.5 cm (5 mm) by manipulating the feed pump speed. Timed samples of underflow and overflow were taken to measure flow rate and frother concentration when the system was in steady state, as determined by stable gas holdup readings. All unused samples were returned to the feed tank. The water overflow rate was measured as mass/unit time, converted to volume and divided by the column cross-sectional area to give superficial velocity (J_{wO}). Water was Montréal tap allowed to reach room temperature (20~22°C) prior to a test. Temperature was recorded (Thermopar type K) to correct the superficial air velocity and conductivity values to standard temperature of 25°C.

4.2.2 Methodology

All testing was performed in the two-phase, air-water system. Frother was weighed and mixed (stirred at least 15 minutes without air) with 50 L water in the feed tank before being transferred to the column. Mixing was important for the longer chain alcohol frothers (i.e., lower HLB, lower solubility reagents). The frother concentration prepared for the MBSA assembly (chamber concentration) was high enough to prevent bubble coalescence [Zhang et al, 2009]. Prior to each experiment, the column was rinsed in hot water and the sparger sonicated for at least half an hour. The feed tank, sampling buckets, froth discharge launder and other accessories were cleaned carefully first by acetone and then distilled water to eliminate contaminants.

The start-up procedure was to set the air rate, allow froth to form then alter pump speed to bring the level to the 5 mm froth depth. Steady state (stable gas holdup) was reached in about 10-25 minutes depending on the frother type. Some conditions were replicated to establish reliability.

In some cases to help interpret the results, frother concentration was determined by reversed-phase high performance liquid chromatography (HPLC). The HPLC analysis was carried out using a Hypersil ODS column (series number: 93108-8, particle size 5 microns, 150 x 4.60 mm) with a refractive index detector (HP model series 1047A). Data acquisition and peak area integration were performed using HP data system (model series 1050). Full details of the chromatographic conditions, resolution of each frother in the blend, and calibration of each frother are reported in Chapter 5.

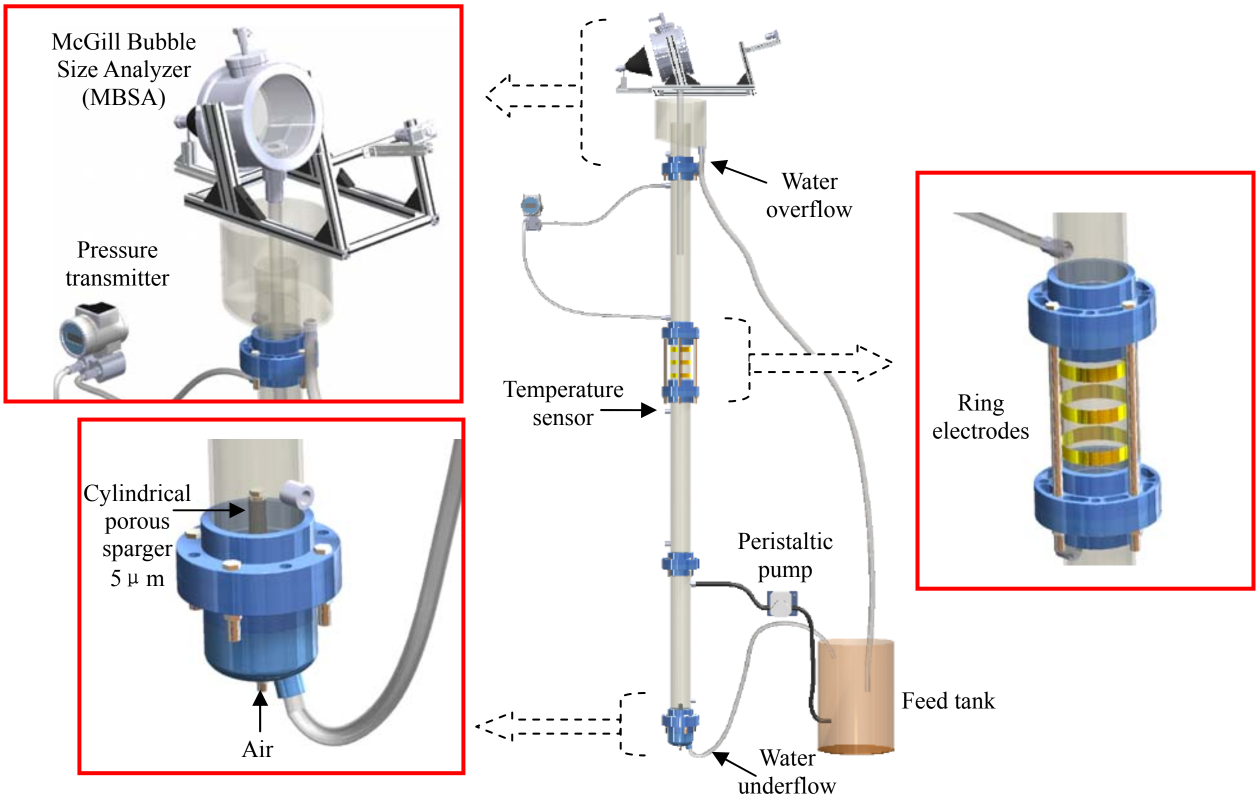


Figure 4.1: The set-up of continuous bubble column and accessories

4.2.3 Frothers

The frothers tested are listed in Table 4.1, selected to cover a range of HLB, CCC and molecular weight. All were reagent grade from Sigma-Aldrich (identified as 99% purity or higher), as verified by proton nuclear magnetic resonance (^{1}H-NMR) spectrometry. (Details on NMR analysis are given in Chapter 5.)

Table 4.1 – Frothers tested

Frother Family	***Frother Type***	***Calculated HLB (Davies methodl)***	***CCC95* (ppm)***	***Molecular Weight (g/mol)***	***Chemical Formula***
Alcohols	1-Butanol	7	63.2	74	$CH_3CH_2CH_2CH_2OH$
	1-Hexanol	6.05	10.8	102	$CH_3CH_2CH_2CH_2CH_2CH_2OH$
Polypropylene Glycols	Dipropylene Glycol	9.25	53.5	134	$H(C_3H_6O)_2OH$
	Tripropylene Glycol	9.125	33.3	192	$H(C_3H_6O)_3OH$
Polyethylene Glycols	Monoethylene Glycol	11.1	-	62	$H(C_2H_4O)OH$
	Diethylene Glycol	11.5	-	106	$H(C_2H_4O)_2OH$
	Triethylene Glycol	11.8	-	150	$H(C_2H_4O)_3OH$
	Tetraethylene Glycol	12.1	-	194	$H(C_2H_4O)_4OH$
	PEG 300**	12.9	-	300	$H(C_2H_4O)_{6.4}OH$
	PEG 400	13.7	-	400	$H(C_2H_4O)_{8.7}OH$

* Data from Zhang et al., [2012]

** 300 is molecular weight (300 g/mol)

Two styles of dual frothers were employed: pre-mixed and base/additive.

4.2.3.1 Pre-Mixed Frothers

The pre-mixed frothers were 1-Hexanol or 1-Butanol with Polyethylene Glycol (PEG) or Polypropylene Glycol (PPG). The mixtures were made up to a certain mole ratio of Alcohol to EO or PO by adding the required amount of PEG or PPG (Table 4.2). The blend concentration is reported as ppm. The selected frothers were mixed vigorously for ca. 15 minutes and left for at least 12 hours prior to testing in order to achieve solution homogeneity. Samples were taken from the top and bottom of the solution to verify homogeneity and the mole ratio using ^{1}H-NMR.

Table 4.2 – Pre-mixed frothers tested and molar ratios

Pre-Mixed Frother Components				***Molar Ratio***
1-Hexanol	-	Polypropylene Glycol	-	Hexanol/PO $\frac{1}{0.05}$ $\frac{1}{0.1}$ $\frac{1}{1}$ $\frac{1}{2}$ $\frac{1}{4}$
1-Hexanol	-	-	Polyethylene Glycol	Hexanol/EO $\frac{1}{1}$ $\frac{1}{2}$ $\frac{1}{3}$ $\frac{1}{4}$
-	1-Butanol	Polypropylene Glycol	-	Butanol/PO $\frac{1}{0.1}$ $\frac{1}{1}$ $\frac{1}{4}$
-	1-Butanol	-	Polyethylene Glycol	Butanol/EO $\frac{1}{1}$ $\frac{1}{2}$ $\frac{1}{4}$

4.2.3.2 Base/Additive Frothers

In this style one frother is kept at constant concentration (the base) while changing the concentration of the other (the additive). Table 4.3 summarizes the base/additive frothers tested.

Table 4.3 – Base/additive frothers and concentration range

Base/Additive Frother Type	***Base Frother***	***Additive Frother***
	Concentration range (ppm)	Concentration range (ppm)
1-Hexanol/TetraEG	10-100	5-150
1-Butanol/DPG	30-80	5-200
1-Butanol/TPG	10-100	5-150
1-Butanol/MonoEG	30-100	5-200
1-Butanol/DEG	30-100	5-200
1-Butanol/TEG	30-100	5-200
1-Butanol/TetraEG	10-200	5-200
1-Butanol/PEG 300	30	5-200
1-Butanol/PEG 400	30	5-200

4.3 Results

4.3.1 Reliability

Replicate tests were conducted for the base/addtive frother system 80 ppm 1-Butanol/ Dipropylene Glycol (DPG) to establish precision for gas holdup (E_g) and water overflow rate (J_{wO}) (Figure 4.2). The trial was divided in two: inter-operator (i.e., different operators ran experiments on the same day) and intra-operator (i.e., same operator ran experiments on different days). The results (Figure 4.2) show high precision (repeatability). It is noted that the first two gas holdup points (i.e., up to a few ppm frother) showed more variability compared to gas holdup at higher concentrations. This could be attributed to coalescence (a random event); or as Tang and Heindel [2005] proposed, to the use of tap water for which they observed time-dependent gas holdup attributed to changes in concentration of volatile coalescence-inhibiting contaminants in the water.

The reliability and validity of the bubble size measurement and frother concentration analysis are reported in Chapters 3 and 5, respectively.

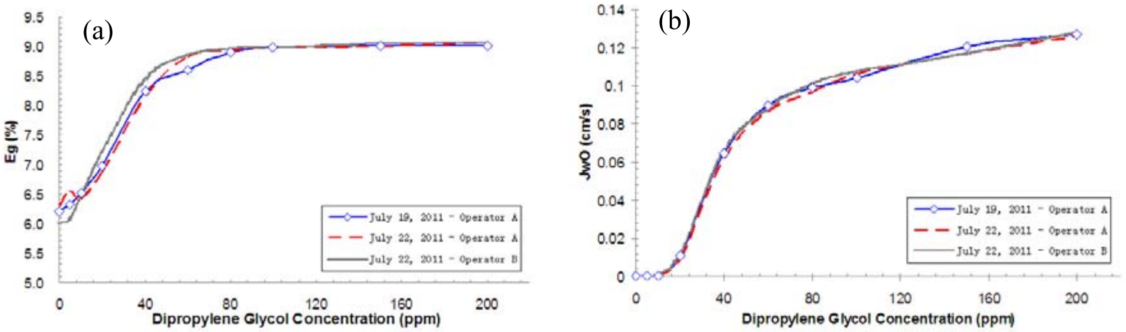


Figure 4.2: Validation test: (a) gas holdup, E_g; and (b) water overflow rate, J_{wO}, as a function of Dipropylene Glycol concentration (additive) to of 80 ppm 1-Butanol (base)

4.3.2 Pre-Mixed Style

Figure 4.3 shows gas holdup (E_g), water overflow rate (J_{wO}) and bubble size (D_{32}) as a function of concentration of the pre-mixed frother 1-Hexanol and Polypropylene Glycol (PPG) for a series of Hexanol/PO mole ratios. Both E_g and J_{wO} increase significantly with concentration up to ca. 20-30 ppm and with mole ratio up to 1/1; decreasing mole ratio from 1/0.05 to 1/1 increased gas holdup by ca. 40% and virtually doubled water overflow rate.

The trend in bubble size shows the expected decrease with increasing concentration corresponding to the increase in gas holdup. But the effect of mole ratio is not as expected: decreasing the ratio increased bubble size which does not correlate with its effect on increasing gas holdup. A similar observation was made with pre-mixed 1-Butanol/Polypropylene Glycol (see Appendix). Polyglycols can have a greater impact on slowing bubble rise than Alcohols [Rafiei et al., 2011] and this may offset the effect of the increase in bubble size on reducing gas holdup.

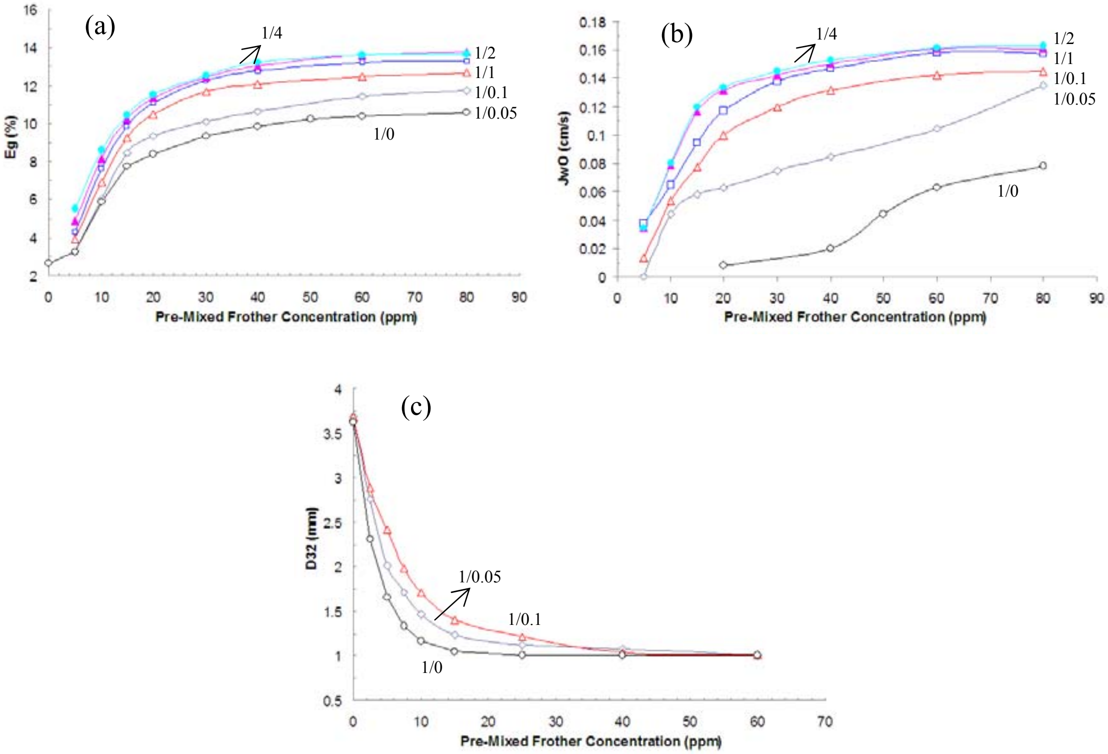


Figure 4.3: Effect of pre-mixed Hexanol/Propylene Oxide frothers on (a) gas holdup – E_g; (b) water overflow rate – J_{wO}; and (c) bubble size – D_{32}

Figure 4.4 shows the results for pre-mixed 1-Hexanol/Polyethylene Glycol. In this system the addition of EO generally decreases both E_g and J_{wO}, albeit marginally, and retains the expected correlation between E_g and D_{32}. Pre-mixed 1-Butanol/Poylethylene Glycol shows similar trends (see Appendix).

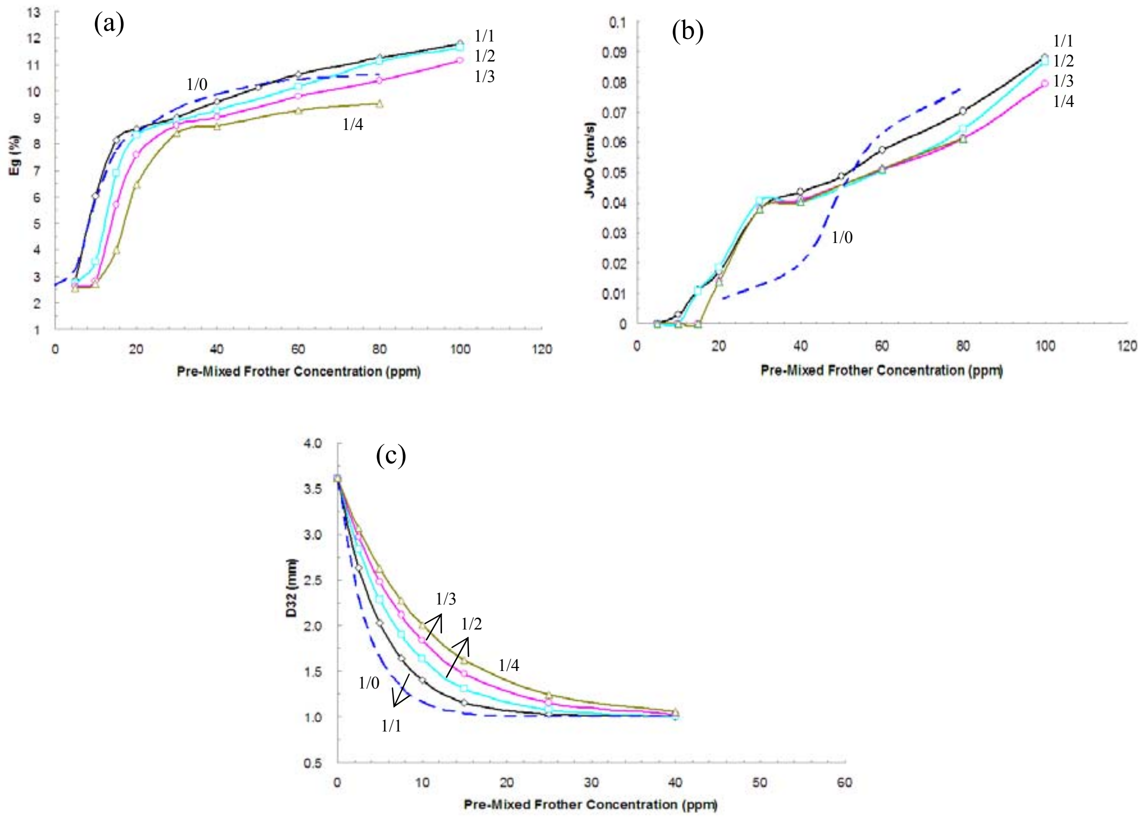


Figure 4.4: Effect of pre-mixed 1-Hexanol/Ethylene Oxide frothers on (a) gas holdup – E_g; (b) water overflow rate – J_{wO}; and (c) bubble size – D_{32}

As summarized in Table 4.4, no candidate pre-mixed style blend provided independent control over the two frother functions. Attention thus focussed on the base/additive style.

Table 4.4 – Evaluation of pre-mixed frothers for independent control

Pre-Mixed Frother Components				***Molar Ratio***	***Ability for independent control***
1-Hexanol	-	Polypropylene Glycol	-	Hexanol/PO $\frac{1}{0.05}$ $\frac{1}{0.1}$ $\frac{1}{1}$ $\frac{1}{2}$ $\frac{1}{4}$	No
1-Hexanol	-	-	Polyethylene Glycol	Hexanol/EO $\frac{1}{1}$ $\frac{1}{2}$ $\frac{1}{3}$ $\frac{1}{4}$	No
-	1-Butanol	Polypropylene Glycol	-	Butanol/PO $\frac{1}{0.1}$ $\frac{1}{1}$ $\frac{1}{4}$	No
-	1-Butanol	-	Polyethylene Glycol	Butanol/EO $\frac{1}{1}$ $\frac{1}{2}$ $\frac{1}{4}$	No

4.3.3 Base/Additive Style

Figure 4.5 shows the results for 1-Hexanol at various base concentrations with increasing Tetraethylene glycol (TetraEG) as additive. The additive affects E_g at the lowest base concentration but otherwise has little effect on gas holdup. The bubble size remains largely independent of additive save for fluctuations at low additions. The J_{wO} results exhibit an increase with additive at base concentrations < ca. 30 ppm but a decrease at higher base (1-Hexanol) concentrations, the J_{wO} all tending to a common value.

This example approaches the independence sought: 1-Hexanol controls D_{32} and TetraEG controls J_{wO}; however, the reversal in J_{wO} with increasing additive at higher base concentrations is seen as potentially problematic. To try to resolve, the next series considered lower molecular weight candidates.

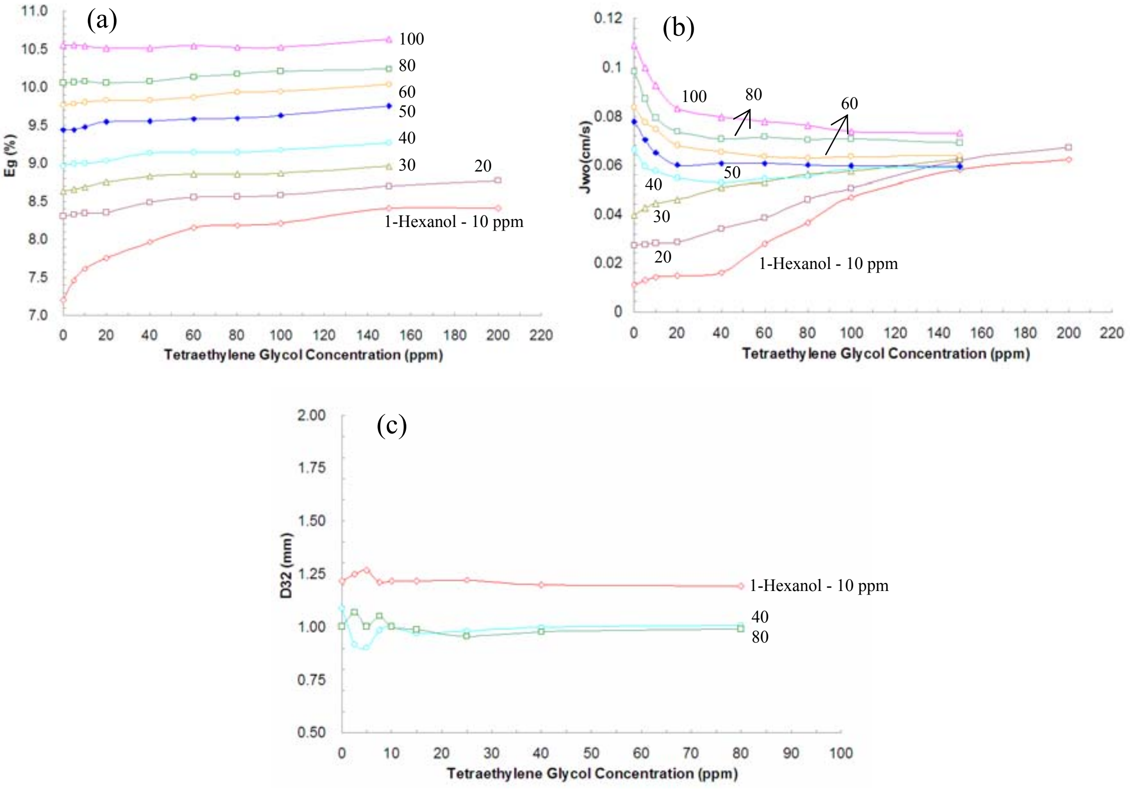
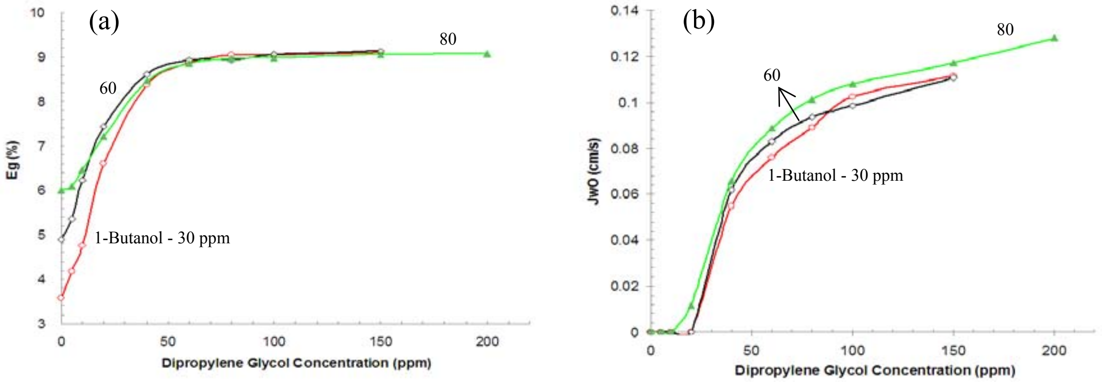


Figure 4.5: Effect of Tetraethylene Glycol (additive) concentration on (a) gas holdup – E_g; (b) water overflow rate – J_{wO}; and (c) bubble size – D_{32}, in the presence of 1-Hexanol (base) at various concentrations

Figure 4.6 shows results for 1-Butanol (base) and Dipropylene glycol (DPG) (additive). Not considered a frother in its own right, 1-Butanol does reduce bubble size and increase gas holdup with sufficient concentration (CCC ~ 60 ppm) but does not produce overflow (J_{wO} = 0) even at concentrations up to 80 ppm (evident for 0 additive case in Figure 4.6). Small additions of DPG increase E_g significantly and above ca. 20 ppm produce overflow with as little as 30 ppm 1-Butanol. Above ca. 50 ppm the effect of DPG subsides. This effect on J_{wO} appears promising but independent control is compromised by the effect on bubble size: the same low additions of DPG that increased J_{wO} caused D_{32} to increase.

The bubble size results prompted frother analysis to determine partitioning between solution and froth. Figure 4.7 shows results for 80 ppm 1-Butanol base: small additions of DPG result in strong partitioning of 1-Butanol to the overflow, or, equivalently, to the froth. For example, with 10 ppm DPG underflow (i.e., solution) concentration is down to 57 ppm (from 80 ppm). This loss from solution brings the concentration below the 1-Butanol CCC (ca. 63 ppm, Table 1) and explains the increase in D_{32} at low additive concentration. The DPG also partitions to the overflow but the magnitude (ratio of concentration in overflow to underflow) is less than for 1-Butanol.



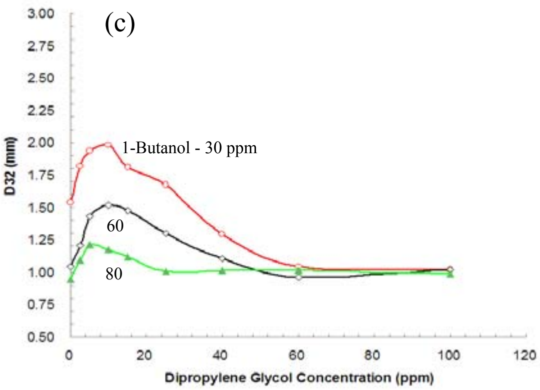


Figure 4.6: Effect of Dipropylene Glycol (additive) concentration on (a) gas holdup – E_g; (b) water overflow rate – J_{wO}; and (c) bubble size – D_{32}, in the presence of 1-Butanol (base) at various concentrations

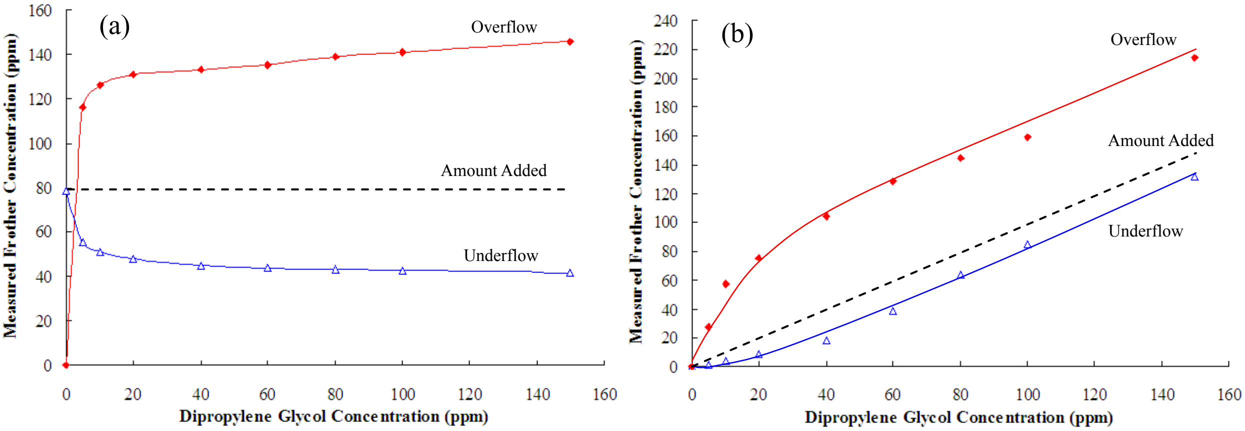


Figure 4.7: Partitioning to overflow and underflow as a function of Dipropylene Glycol (additive) concentration in the presence of 80 ppm 1-Butanol (base): (a) 1-Butanol and (b) Dipropylene Glycol

Trials with 1-Butanol/TPG mixed frother system (Figure 4.8) showed similar trends to the 1-Butanol/DPG system: E_g and J_{wO} exhibit sharp increases for small additions (up to 20 ppm DPG) to reach similar maximum values; and cause an increase in D_{32}. Comparing Figures 4.6 and 4.8, it can be concluded that the increase of number of Propylene Oxide (PO) groups from 2 to 3 does not materially alter hydrodynamic properties (E_g and D_{32}) or froth properties (J_{wO}).

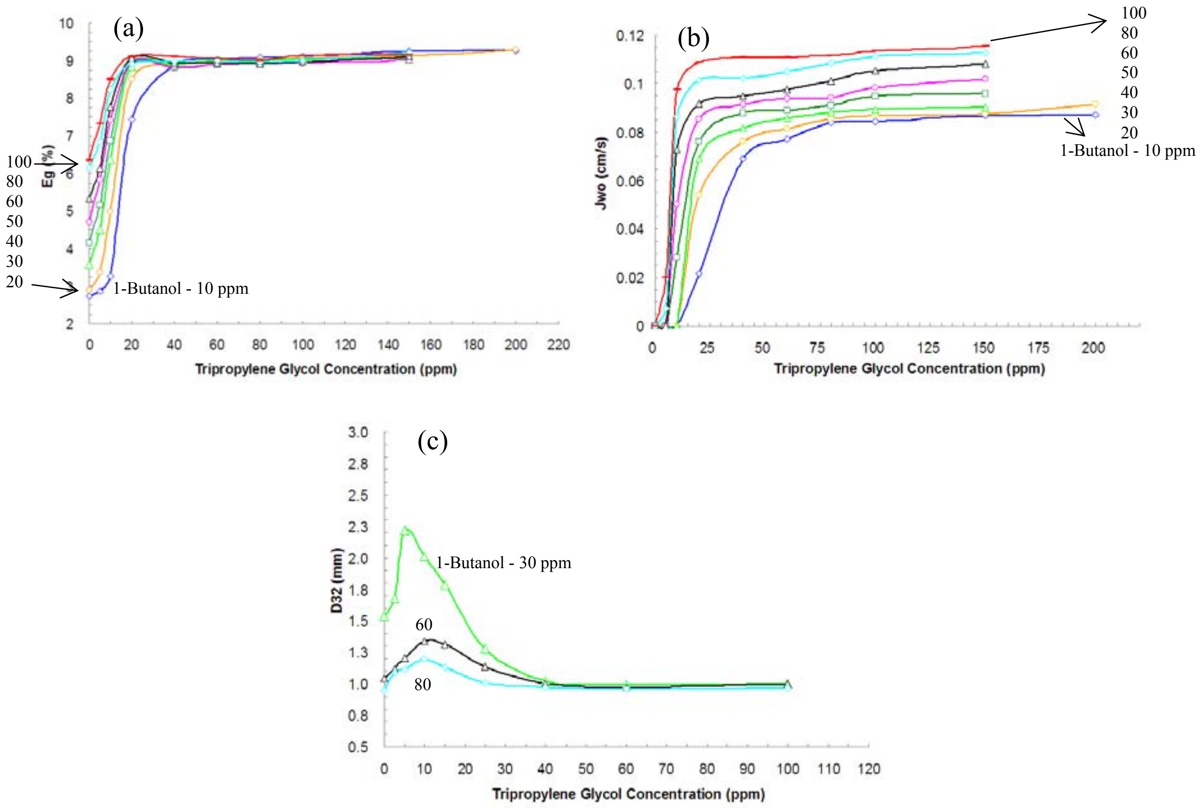


Figure 4.8: Effect of Tripropylene glycol (additive) concentration on (a) gas holdup – E_g; (b) water overflow rate – J_{wO}; and (c) bubble size – D_{32}, in the presence of 1-Butanol (base) of various concentrations

From Figures 4.6 and 4.8 it is apparent that Polypropylene Glycol (i.e., DPG or TPG) is not the appropriate additive because of the negative impact on bubble size. The next series substituted Polyethylene Glycols as the additive to 1-Butanol base.

Increasing number of Ethylene Oxide (EO) groups (i.e., parameter l = 1 to 4 in the structural formula) produced no overflow up to l = 3 even up to 200 ppm (not shown); but for l = 4, i.e., Tetraethylene glycol (TetraEG), overflow was generated and thus this additive was selected.

Figure 4.9 shows for the 1-Butanol/TetraEG base/additive system that E_g and J_{wO}

increased with TetraEG concentration (at least up to ca. 150 ppm) but, in contrast to DPG or TPG as additive, the D_{32} was essentially independent of additive concentration. Figure 4.10 helps explain this lack of effect on D_{32} showing that, compared to DPG and TPG as additives, 1-Butanol partitioning to the froth was much less with TetraEG, the concentration in solution remaining close to 80 ppm (i.e., above CCC), sufficient to maintain bubble size.

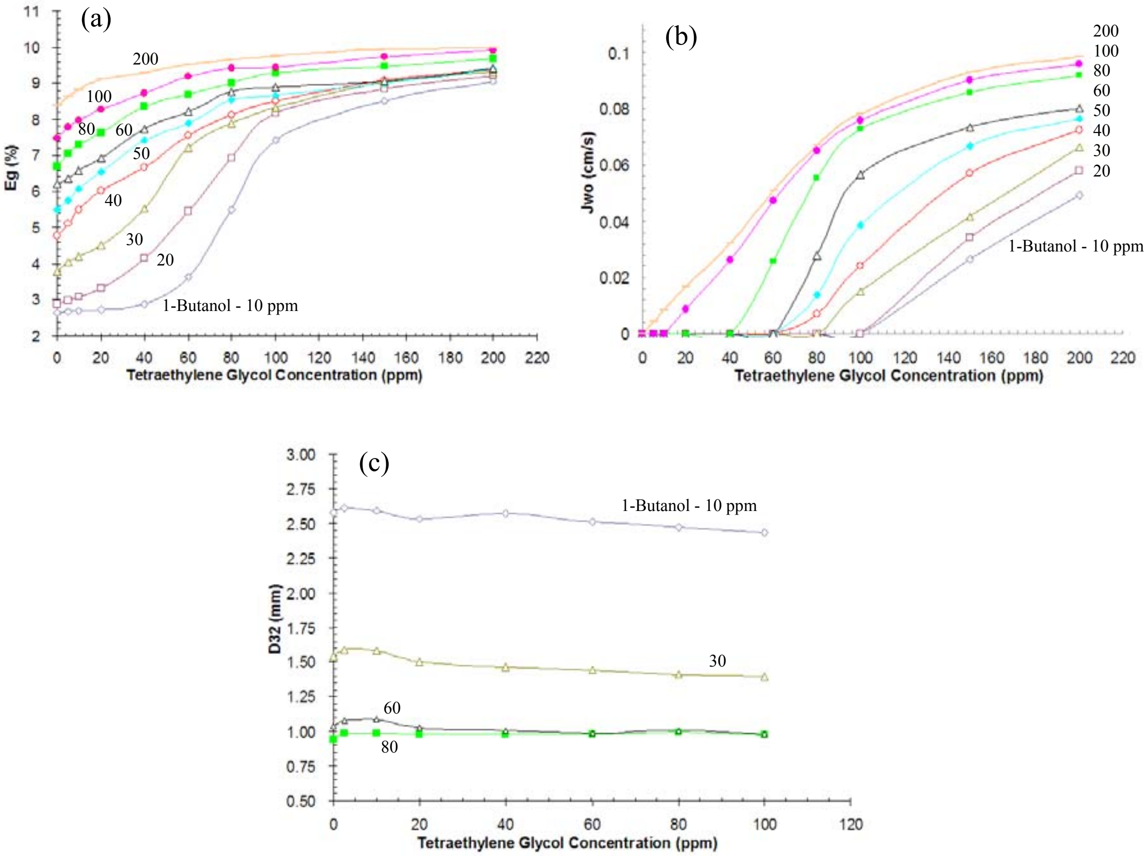


Figure 4.9: Effect of Tetraethylene glycol (additive) concentration on (a) gas holdup – E_g; (b) water overflow rate – J_{wO}; and (c) bubble size – D_{32}, in the presence of 1-Butanol (base) at various concentrations

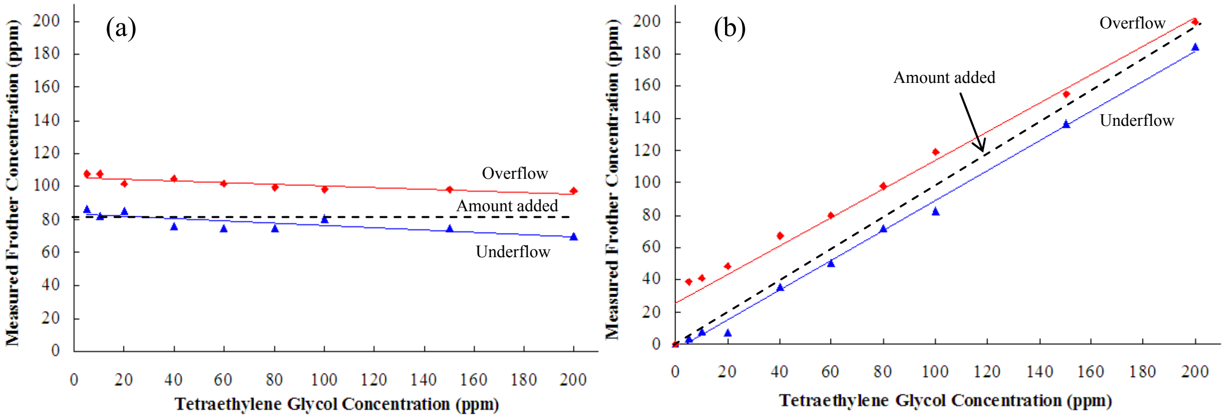


Figure 4.10: Partitioning to overflow and underflow as a function of Tetraethylene Glycol (additive) concentration in the presence of 80 ppm 1-Butanol (base): (a) 1-Butanol and (b) Tetraethylene Glycol

The 1-Butanol/Polyethylene Glycol (PEG) system was explored by increasing the number of EO. Figure 4.11 shows results for 30 ppm 1-Butanol base with additives PEG 300 (l = 6.4) and PEG 400 (l = 8.7) as well as TetraEG. It is evident that increasing EO increases E_g and J_{wO} but, in common with TetraEG, D_{32} does not change.

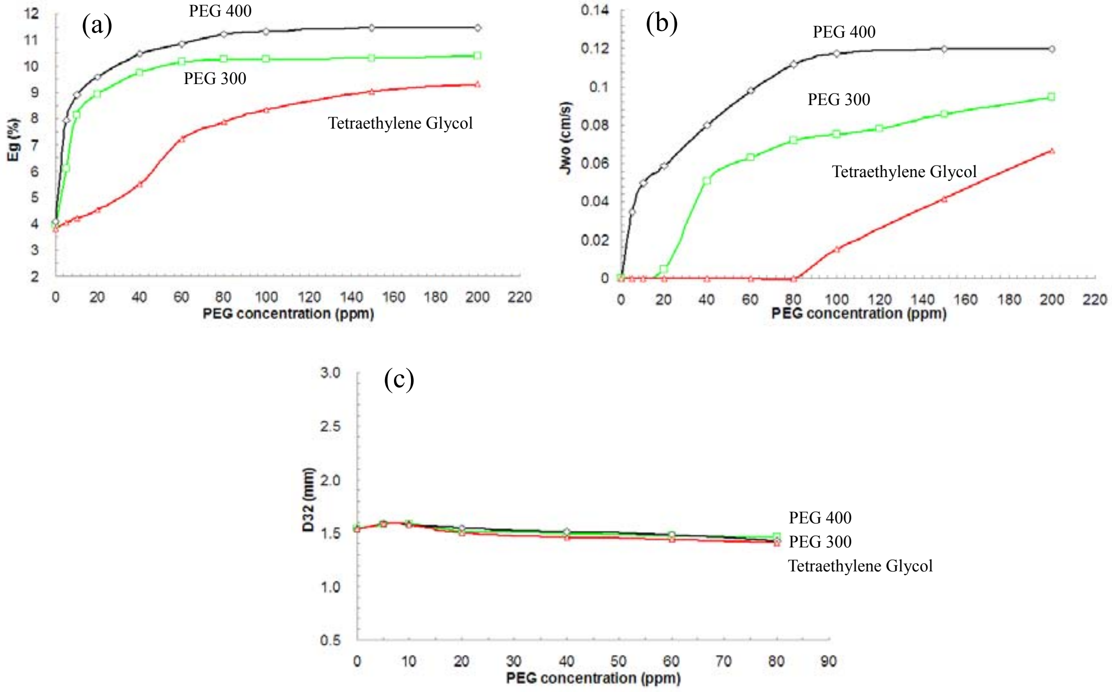


Figure 4.11: Comparison of TetraEG, PEG 300 and PEG 400 (additive) concentration on (a) gas holdup – E_g; (b) water overflow rate – J_{wO}; and (c) bubble size – D_{32}, in the presence of 30 ppm 1-Butanol (base)

As summarized in Table 4.5, among all the tested base/additive dual frother system only 1-Butanol/PEG with EO > = 4 proved effective achieving independent control of the properties of both zones.

Table 4.5 – Evaluation of base/additive frothers for independent control

Base/Additive Frother Type	***Base Frother***		***Additive Frother***		***Ability for independent control***
	Type	Concentration range (ppm)	Type	Concentration range (ppm)	
1-Hexanol/TetraEG	1-Hexanol	10-100	TetraEG	5-150	**No**
1-Butanol/DPG	1-Butanol	30-80	DPG	5-200	**No**
1-Butanol/TPG	1-Butanol	10-100	TPG	5-150	**No**
1-Butanol/MonoEG	1-Butanol	30-100	MonoEG	5-200	**No**
1-Butanol/DEG	1-Butanol	30-100	DEG	5-200	**No**
1-Butanol/TEG	1-Butanol	30-100	TEG	5-200	**No**
1-Butanol/TetraEG	1-Butanol	10-200	TetraEG	5-200	**Yes**
1-Butanol/PEG 300	1-Butanol	30	PEG 300	5-200	**Yes**
1-Butanol/PEG 400	1-Butanol	30	PEG 400	5-200	**Yes**

4.4 Discussion

In flotation, frothers have two main functions: aiding control over hydrodynamic properties of the pulp zone (e.g. bubble size and gas holdup) and aiding control over froth properties (e.g. water overflow rate). To optimize performance, it can be argued, requires independent control of the zone properties. This is difficult to achieve with a single frother since the properties of both zones are concentration-dependent. Hence the pursuit in this chapter of dual frother systems, aiming to find a blend where one component controlled pulp hydrodynamics while the second controlled froth properties.

Motivation for this approach came from an observation by Cappuccitti and Finch [2008]. Creating potential frothers by reacting Alcohols with Ethylene Oxide (EO) to produce Polyethoxylated Alcohols, they observed that increasing the number of EO increased gas holdup (E_g) while froth height remained largely unchanged. This was among the first pieces of evidence that independent manipulation of zone properties could be achieved. Rather than consider reaction products at this stage, however, blends of two frothers were considered. Later, Chapter 6, new frothers will be synthesized.

Commercial frothers derive principally from the Alcohols and the wide variety of Polyglycols. Alcohols are known to reduce bubble size but exhibit poor froth building capability (at least in the absence of floatable particles, as is the situation here). Combinations of Alcohols would not seem suited to our task, therefore, and were not considered. Polyglycols show a wide range of froth stabilizing properties as well as being able to control bubble size. Combinations of Polyglycols could be candidates but blends of Alcohols and Polyglycols were deemed most likely to meet the target of independent control. The literature on blends is limited to Alcohol/Polyglycol which offered support to this being the best starting point.

The next task was the choice of properties to characterize the blends. For froth properties water overflow rate was chosen as in our experience it is more reliable than measures such as froth height [Elmahdy and Finch, 2009; Elmahdy, 2011]. Araya [2010] noted that froths formed from blends often exhibited a wide bubble size range, coarsening towards the top, a feature different from single frothers which gave more homogeneous bubble size that made identifying the base of the froth, and thus measuring froth height, difficult. Increased uncertainty with blends was touched on in this work. In the 80 ppm 1-Butanol/Dipropylene Glycol base/additive case the relative standard deviation (RSD) was 3.8% at DPG concentration 200 ppm, somewhat larger than RSD 1.9% for DPG 200 ppm alone. The influence of blends on increasing uncertainty might be revealing but is outside the current scope.

Employing water overflow rate as the metric is attractive because it is based on a dynamic test which mimics flotation and by the fact that water overflow rate is important in flotation as it controls particle recovery by entrainment. A disadvantage is that overflow rate depends on froth depth. In the tests here froth depth was 5 mm and it could be debated with such a shallow depth that water overflow rate is not entirely a froth property but reflects the amount of water being carried by the bubble swarm into the froth, which may depend on frother type [Nguyen et al., 2003; Moyo et al., 2007; Zhang et al., 2010]. All considered, however, the sensitive response evident here and the excellent precision, we believe, make water overflow rate a suitable choice of froth property.

Bubble size and gas holdup were monitored to track hydrodynamic properties. Gas holdup usually shows an inverse response to bubble size, increasing as bubble size decreases and vice versa. The reason is that bubble rise velocity is dependent on bubble size; as bubbles reduce in size (at least < 2 mm or so) rise velocity decreases [Clift et al., 1978] which increases bubble retention time and thus increases gas holdup. Exploiting the relationship, gas holdup sometimes substitutes for bubble size, being easier to measure (at least in the two-phase air-water system). For most instances in the current experiments this inverse relationship held, but not in all. The relationship is known to break down when a surfactant has an effect on bubble rise velocity other than through bubble size reduction [Rafiei et al., 2011]. Although there is no independent evidence, at this juncture it is postulated that in blends such as the pre-mixed 1-Hexanol and Polypropylene Glycol case (Figure 4.3) the PPG slows the bubble sufficiently to offset the effect of the increase in bubble size. This postulate will be explored in future work.

Less researched, there is also evidence of a positive relationship between gas holdup and water overflow rate. For given conditions, predominantly froth depth, a linear dependence has been reported [Moyo et al., 2007; Gomez et al., 2011]. The present work shows there is a general relationship, water overflow rate increasing with increasing gas holdup, the exception being 1-Hexanol with Tetraethylene Glycol (Figure 4.5). In common with the bubble size-gas holdup relationship, detailed analysis of the gas holdup-water overflow relationship is beyond the scope of the current chapter.

Two ‘styles’ of blend were examined: pre-mixed and base/additive. The pre-mixed style is commonly how blends are introduced in flotation plants [Cappuccitti and Finch, 2008]. It thus invited test work but this was not extensive as pre-mixing is not sensibly different from a single frother as regards its functions. The results bore that sense out.

Most focus was on the base/additive style. A surprise was that the simple notion of Alcohol as base to control bubble size with Polyglycol as additive to manipulate overflow rate proved not simple at all. In one case this was because of undesirable effects on the overflow rate (1-Hexanol/Tetraethylene glycol, Figure 4.5); in another of undesirable effects on bubble size (1-Butanol/Dipropylene glycol, Figure 4.6). The effect of small additions of Dipropylene glycol (DPG) to 1-Butanol was to increase bubble size. This phenomenon has been noted before with 1-Pentanol and PPG 425 [Elmahdy and Finch, 2009]. The origin of the bubble size increase was speculated to be altered coalescence or breakup rates [Elmahdy, 2011]. The findings here point to frother partitioning as the cause: analysis revealed that addition of DPG caused 1-Butanol to partition strongly to the froth, bringing Butanol concentration in solution below its CCC and thus accounting for the increase in bubble size. The mechanism of interaction (synergy) is not known but may be common in surfactant mixtures [Salager, 1999] and is suspected in frother blends [Cappuccitti and Nesset, 2009]. The partitioning of frothers probably influences froth properties too by putting extra frother in the froth (and might be a factor in the uncertainty in froth height determination discussed above). Although not the current interest, the action of frother with surfactants like oleic acid and amines used as flotation collectors may be worth examining through measurement of partitioning.

As noted the search did not prove straightforward, but was eventually successful. The blend 1-Butanol (base) with Polyethylene glycol (additives) with four or more EO groups (Figures 4.9 and 4.11 and Table 4.5) gave the independence sought. Whether these blends represent commercial opportunities remains another question.

4.5 Conclusions

The aim of this work was to establish a dual frother system that provided independent control over the froth property water overflow rate (J_{wO}) and two pulp hydrodynamic properties, Sauter mean bubble size (D_{32}) and gas holdup (E_g). The blends studied were Alcohols with either Polypropylene Glycols (PPG) or Polyethylene Glycols (PEG). The most significant findings were:

1. Pre-mixed frothers, represented as Alcohol/Propylene Oxide and Alcohol/Ethylene Oxide blends, did not give independent control over the two functions.

Using the base/additive approach the following was noted:

2. With 1-Hexanol/TetraEG, J_{wO} converged to roughly the same level as TetraEG concentration was increased, considered a negative effect.

3. With 1-Butanol/DPG and 1-Butanol/TPG, D_{32} increased upon addition of a minor amount of additive, a negative effect. The increase of D_{32} was traced to partitioning of 1-Butanol to the froth which reduced solution concentration below the 1-Butanol CCC.

4. With 1-Butanol/PEG, independent control was demonstrated provided the PEG had four or more Ethylene Oxide groups.

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Connecting Texts between Chapters 4 and 5

Chapter 4 studied dual frother blends with the ambition of achieving independent control over the two frother functions. During the work it was noted that some frother blends resulted in an unexpected increase in bubble size. Frother partitioning to froth was suspected which required development of analytical methods. This is undertaken in Chapter 5 where in addition to HLPC a novel method based on a combination of NMR and TOC is developed.

Chapter 5 – Frother Partitioning in Dual-Frother Systems: Development of Analytical Techniques

Abstract

Dual frother blends are becoming popular in flotation practice. There is no work showing how frothers in the blend partition between the pulp and froth zones. In this paper two methods, high pressure liquid chromatography (HPLC) and a novel proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) associated with total organic carbon analysis (TOC), are developed to determine partitioning in Alcohol/Polyglycol blends. In two-phase air-water tests using a bubble column partitioning with three blends is examined. Two examples show strong partitioning of Alcohol which corresponds to reported cases of these blends giving an increase in bubble size.

5.1 Introduction

The significance of frother in controlling flotation efficiency has long been recognized [Harris, 1976; Ahmed and Jameson, 1985; Dobby and Finch, 1986; Yoon and Luttrell, 1986; Fuerstenau, 1999]. The main roles of frother are two-fold: to help disperse air into fine bubbles to promote particle collection; and to stabilize the froth phase to enable the collected particles to overflow [Zieminski et al., 1967; Klimpel and Isherwood, 1991; Laskowski, 1998].

There are two types (classes or families) of frother commonly used in flotation practice today, Alcohols and Polyglycols [Klimpel and Isherwood, 1991; Laskowski, 1998]. Alcohol frothers are usually restricted to 5 – 7 carbons either straight or branch chained; MIBC is the best-known frother in this group. Polyglycol frothers are a large class with varying structure and molecular weight; Flottec 150 (F150) and Dowfroth 250 (DF250) are among the best-known commercial examples in this group.

As general guidelines, Alcohol frothers tend to be more effective for selective fine particle recovery while Polyglycol frothers are more effective for selective coarse particle flotation [Klimpel and Isherwood, 1991]. It seems that the optimal for high recovery with good selectivity would be a blend of the two frother classes. Another argument for blending is to achieve independent control over the two prime roles (or functions), air dispersion and froth stabilization [Elmahdy and Finch, 2009]. Frother blends are becoming popular in flotation practice [Cappuccitti and Finch, 2008].

Recent frother characterization methods have stressed the need to capture both functions: air dispersion, e.g. by measuring bubble size; and froth stabilization, e.g. by measuring equilibrium froth height [Laskowski, 2003; Cappuccitti and Finch, 2008]. There has been some characterization of Alcohol/Polyglycol blends [Kumar et al., 1986; Laskowski et al., 2003; Tan et al., 2005; Elmahdy and Finch, 2009]. Tan et al. [2005] reported a synergistic effect on froth properties: froth height in the blend was greater than the sum of froth heights by the frothers individually. Elmahdy and Finch [2009] also observed this froth-enhancing synergy and reported another, negative synergy, namely that bubble size could be larger in the blends than for the frothers individually.

Accompanying the characterization effort has been development of frother analysis procedures. These include: gas chromatography [Tsatouhas et al., 2005]; total organic carbon [Hadler et al., 2005, Zhang et al, 2010]; calibrations of bubble size and gas hold-up vs. frother concentration [Weber et al., 2003]; and colorimetry [Gélinas and Finch, 2005; Zangooi et al., 2010]. One application is to determine how frother distributes (partitions) between pulp and froth.

Gélinas and Finch [2005; 2007] using colorimetry were among the first to measure partitioning. They found relatively little partitioning of MIBC at one plant but significant partitioning of F150 at a second, detecting up to 100 ppm in the overflow (i.e. froth) compared to ca. 1 ppm in the pulp. The observation explained the F150 enrichment detected in downstream banks which made operation difficult. Zhang et al. [2010] using total organic carbon analysis (TOC) confirmed this stronger partitioning of F150 compared to MIBC through lab-scale two-phase (air-water) tests.

There has been no measurement of partitioning in the case of blends beyond one case where an Alcohol contaminant was tracked along with a Polyglycol frother by adapting the colorimetric technique [Gélinas and Finch, 2007]. Such a study might help interpret the synergistic effects noted above. Partitioning reflects the adsorption of frother on bubbles and how this is influenced in blends is not known.

Analysis of blends poses a challenge. In this study we have developed techniques based on HPLC (high pressure liquid chromatography), and a novel combination of ^{1}H-NMR (proton nuclear magnetic resonance spectroscopy) and TOC. The purpose of this chapter is to introduce the analysis methodology and use to determine frother partitioning in blends of Alcohol and Polyglycol frothers.

5.2 Experimental

5.2.1 Apparatus and Operation

A bubble column, measuring 350 cm x 10 cm diameter (volume ca. 28 L) instrumented for the project was used. A cylindrical porous sparger (6 cm high x 2.5 cm diameter) with a 5 μm nominal porosity was positioned vertically at the base of the column to disperse air. Operation was continuous with the feed (frother solution) rate controlled by a peristaltic pump (Cole Palmer model 7520-25) and overflow and underflow water recycled to the feed tank to close the loop. A calibrated mass flow meter (MKS instruments model M100B53CS18V) was used to maintain superficial air flow velocity (volumetric air rate divided by column cross-sectional area) at 0.5 cm/s. Froth height was maintained manually at 0.5 cm by adjusting the feed pump speed. Samples of underflow and overflow were taken to measure flow rate and frother concentration when steady state was reached, as established by steady pressure readings; all unused samples were returned to the feed tank. The water was Montréal tap and the temperature was equilibrated to room temperature (20~22°C).

5.2.2 Frother Blends

The blends were base/additive style with three selected to represent particular cases based on Chapter 4, two blends giving an increase in bubble size (1-Butanol/Dipropylene Glycol and 1-Pentanol/F150) and one that did not give a change in bubble size (1-Butanol/Tetraethylene Glycol). The two 1-Butanol base blends were analyzed by HPLC, and the third blend was analyzed by the combination of NMR and TOC. The frothers, with their HLB (hydrophile-lipophile balance) and CCC (critical coalescence concentration, i.e. concentration giving minimum bubble), are listed in Table 5.1. The commercial frother F150 was obtained from Flottec with the remainder purchased from Sigma-Aldrich. Purity was 99% or higher as verified by the ^{1}H-NMR spectrum. The blends were prepared by mixing a fixed concentration of the Alcohol at a concentration above its CCC with incremental additions of the Polyglycol.

Table 5.1 – Frothers tested with some properties

Frother Family	Frother Type	Calculated HLB (Davies method)	CCC95* (ppm)	Molecular Weight (g/mol)	Chemical Formula
Alcohols	1-Butanol	7	63.2	74	$CH_3CH_2CH_2CH_2OH$
	1-Pentanol	6.53	24.5	88	$CH_3CH_2CH_2CH_2CH_2OH$
Polyglycols	Tetraethylene Glycol	12.12	-	202	$H(C_2H_4O)_4OH$
	Dipropylene Glycol	9.25	53.5	134	$H(C_3H_6O)_2OH$
	F150**	8.625	6.1	425	$H(C_3H_6O)_7OH$

* Data from Zhang et al., 2012a

** Also known as PPG 425

5.2.3 Frother Analysis

5.2.3.1 HPLC

The instrument was HP model series 1050 with a Hypersil ODS column (series 93108-8, particle size 5 µm, 150 x 4.60 mm) and a Refractive Index (RI) detector (HP model series 1047A). The mobile phase was deionized water (ca. 18 M-Ohm) and flow rate was 1.5 mL/min. Samples were filtered (2.5 µm syringe filter) and transferred to 2 mL vials. The injection volume was 250 uL and running time for each sample was 15 minutes. Usually three injections were completed for each sample and the mean calculated. The separation was carried out at room temperature, 22 - 24°C; and the temperature control of the RI detector was set at 30°C. After recording 10 to 15 chromatograms, the column was rinsed with Methanol at a flow rate of 2 mL/min to elute the adsorbed substances.

5.2.3.2 NMR Spectroscopy

To perform NMR, the frothers were extracted into deuterated chloroform (99.96 atom%, from Sigma Aldrich) by shaking vigorously for five minutes in a 125 mL separatory funnel. The volume ratio of sample solution to deuterated chloroform was 10:1. Two successive extractions were performed to ensure all frother was extracted. The chloroform (with the dissolved samples) was removed and transferred to a high quality 5 mm NMR tube (Wilmad 535, limit 600 MHz frequency, L 7 in.) for locking and shimming. The NMR tube which was held in a plastic spinner was then placed into the magnet. The ^{1}H-NMR spectra were recorded on a 600 MHz spectrometer (Bruker AVANCE-600) with temperature controlled at 298 K. Data acquisition and integration were performed using the commercial software MestRe-C.

In the blend the two frothers are identified by their characteristic peak in the spectra. Advantage is taken of the fact that the ratio of integral areas of the two characteristic peaks is dependent on the molar ratio of the two frothers. Once the molar ratio of the frothers in the blend is given by NMR, the individual frother concentration is determined from the total organic concentration (TOC) knowing the two frothers are the only organics present.

5.2.3.3 TOC

The technique has proven reliable after allowing for background TOC in tap water [Zhang et al., 2010]. The instrument was a Dohrmanns DC 80 (TELEDYNE Instruments Company, U.S.). The detectable concentration range for organic carbon is 0~1000 ppm and each result was the mean of at least three repeats.

5.3 Results

5.3.1 HPLC

5.3.1.1 Calibration

The blends analyzed were 1-Butanol/Tetraethylene Glycol, and 1-Butanol/Dipropylene Glycol. Figure 5.1 shows the chromatogram for the two blends at 50 ppm for each component. The two frother components are readily detected with no interfering signals (the noise at the beginning is ascribed to small content of inorganic ions in the aqueous solution, which interact with the column but do not affect accuracy).

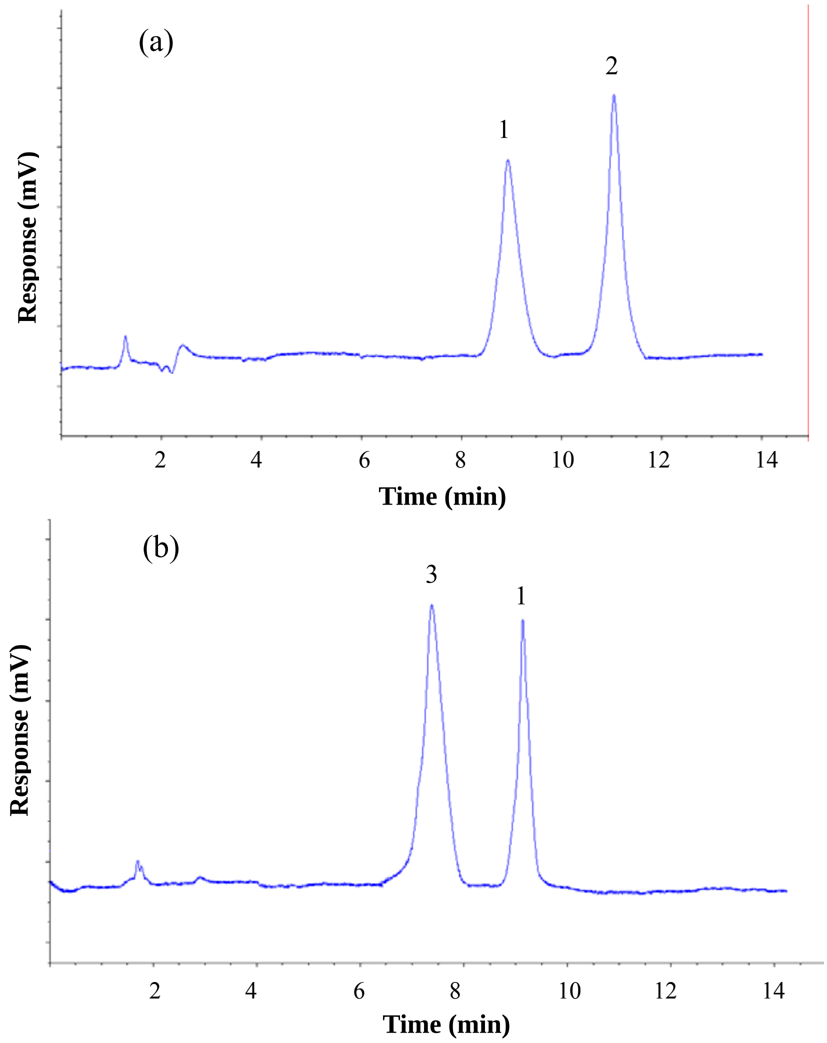


Figure 5.1: Chromatogram of blend of: (a) 50 ppm 1-Butanol (peak ‘1’) and 50 ppm Tetraethylene Glycol (peak ‘2’); (b) 50 ppm 1-Butanol (peak ‘1’) and 50 ppm Dipropylene Glycol (peak ‘3’). HPLC conditions: column: Hypersil ODS (series number: 93108-8, particle size 5 µm, 150 x 4.60 mm); injections: 250 uL; mobile phase: deionized water; flow rate: 1.5 mL/min; detection: refractive index

To calibrate, the area under the peak was used. The calibration for 1-Butanol and Tetraethylene Glycol is shown in Figure 5.2. Linear calibration for both components is evident with correlation coefficients greater than 0.99. Calibration for the 1-Butanol and Dipropylene Glycol blend was equally successful (see Appendix).

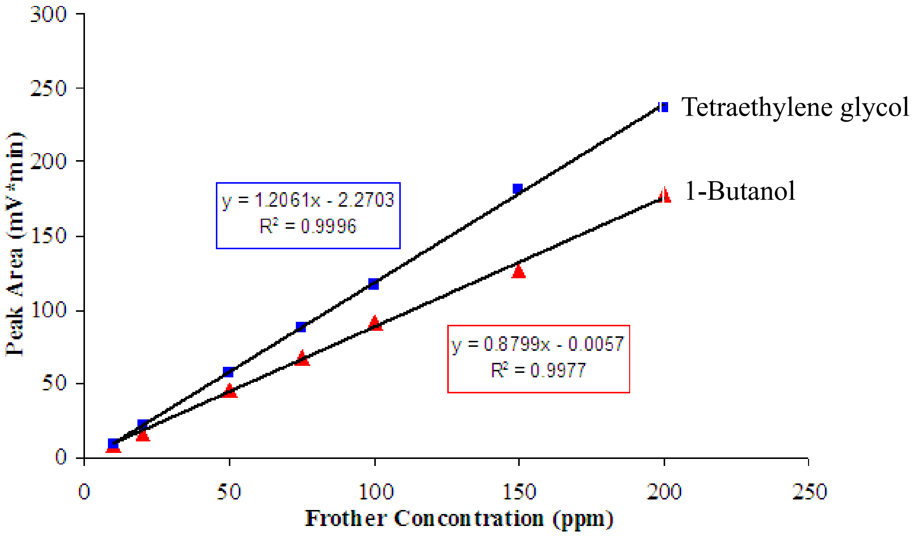
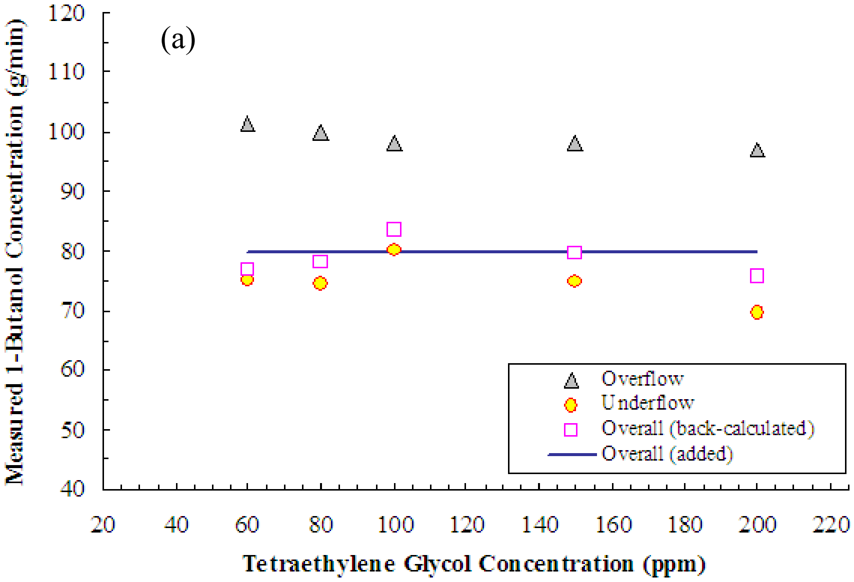


Figure 5.2: Calibration plot of 1-Butanol and Tetraethylene Glycol in the blend

5.3.1.2 Validation

Figure 5.3 establishes the validity of the HPLC technique showing that the back-calculated feed (‘measured’ overall) frother concentration compares well to the known added feed (overall) concentration. Reliability is established by noting that the range in relative standard deviation (RSD) is from 0.2 to 5%.



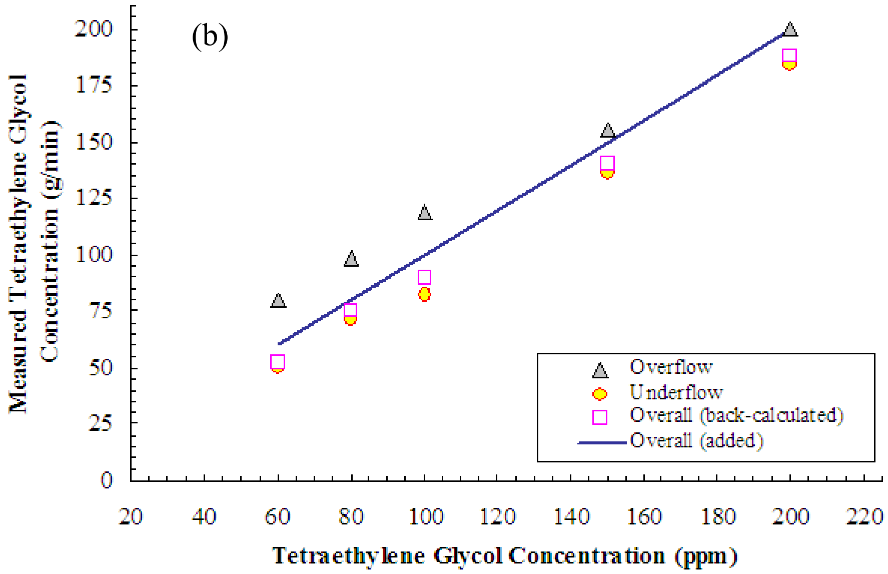


Figure 5.3: Verification of HPLC technique: Mass balance on frother shows back-calculated feed (overall) concentration compares well with added overall concentration: (a) 1-Butanol; (b) Tetraethylene Glycol

5.3.1.3 Partitioning: 1-Butanol/Tetraethylene Glycol & 1-Butanol/Dipropylene Glycol

Ten increments of additive (Polyglycol) up to 200 ppm were made and at each blend samples of overflow and underflow were taken for analysis. An example chromatogram is shown in Figure 5.4 at 80 ppm 1-Butanol with 5 ppm (a) and 150 ppm (b) Tetraethylene Glycol. The concentration results corresponding to Figure 5.4 are given in Table 5.2. Note enrichment (partitioning) of both of Tetraethylene Glycol and 1-Butanol in the overflow compared to underflow.

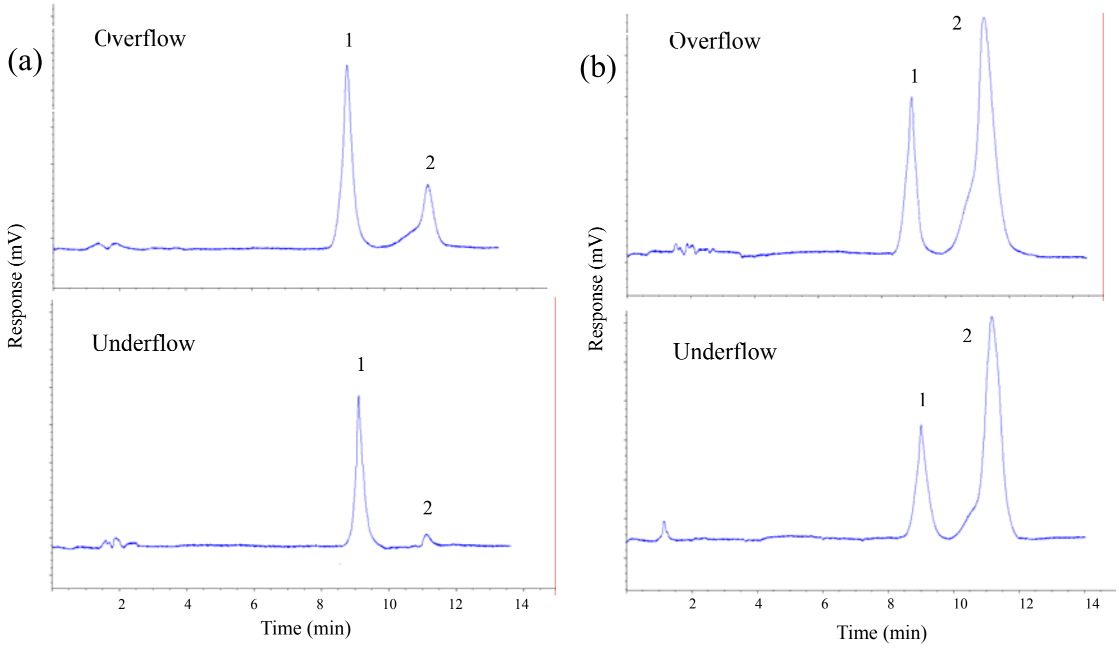


Figure 5.4: Chromatogram of overflow and underflow for: (a) 80 ppm 1-Butanol (peak 1) and 5 ppm Tetraethylene Glycol (peak 2); (b) 80 ppm 1-Butanol (peak 1) and 150 ppm Tetraethylene Glycol (peak 2)

Table 5.2 – Example frother partitioning using HPLC analysis

Frother system concentration (ppm)	**Stream**	**Frother component**	**HPLC chromatogram peak area (mV*min)**	**Estimated frother concentration (ppm)**
80 ppm 1-Butanol & 5 ppm Tetraethylene Glycol	Overflow	Tetraethylene Glycol	44.1	38.4
		1-Butanol	94.8	107.7
	Underflow	Techaethylene Glycol	2.3	3.8
		1-Butanol	75.9	86.2
80 ppm 1-Butanol & 150 ppm Tetraethylene Glycol	Overflow	Tetraethylene Glycol	185.3	155.5
		1-Butanol	86.3	98.1
	Underflow	Tetaaethylene Glycol	162.4	136.5
		1-Butanol	65.6	74.6

Figure 5.5 shows the frother partitioning to overflow and underflow: the overflow concentration is consistently higher than the underflow concentration for both frothers.

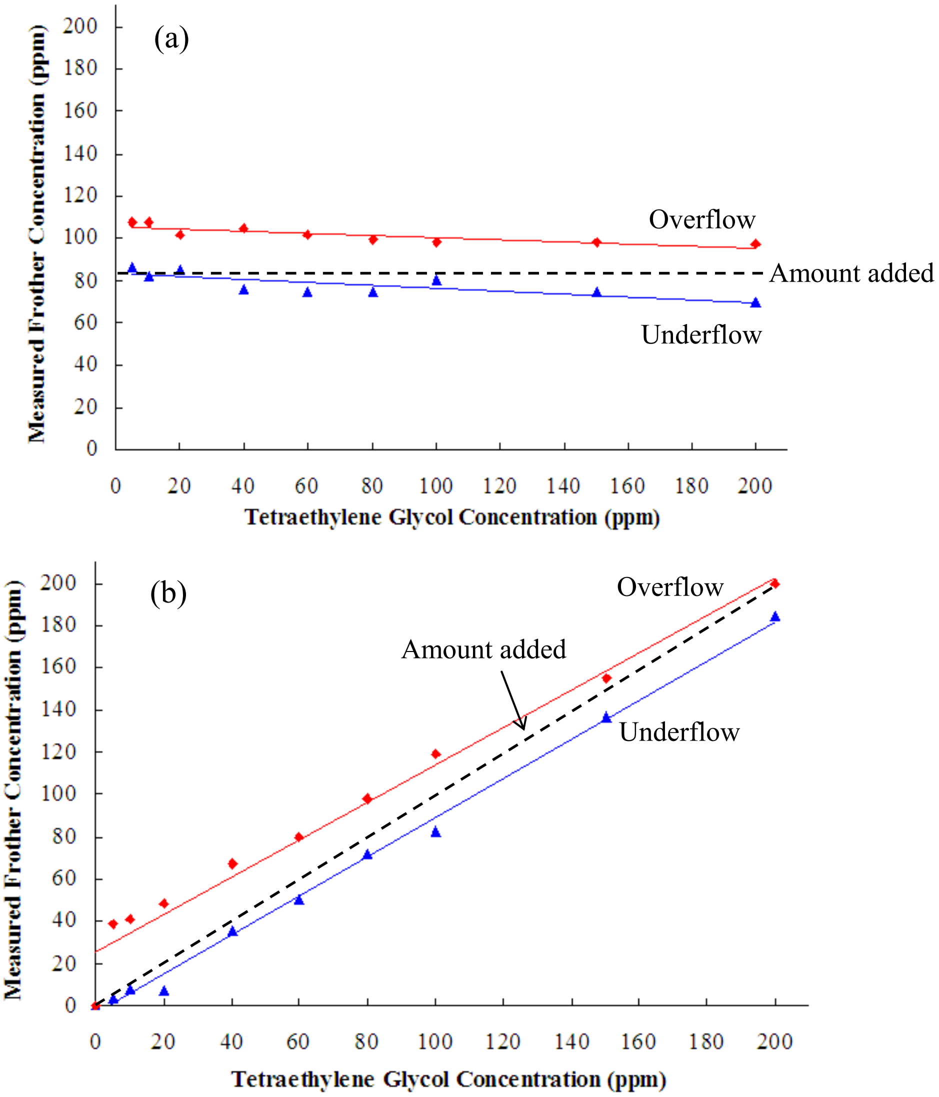


Figure 5.5: Frother in overflow and underflow as a function of Tetraethylene Glycol (additive) concentration in the presence of 80 ppm 1-Butanol: (a) 1-Butanol and (b) Tetraethylene Glycol

The partitioning results for 1-Butanol/Dipropylene Glycol are shown in Figure 5.6. It reveals more significant partitioning of both components to the overflow compared to the 1-Butanol/Tetraethylene Glycol blend. For example, at 5 ppm addition, Dipropylene Glycol concentration in the overflow is above 20 ppm and 1-Butanol concentration increases from 80 up to 120 ppm with correspondingly decrease in the underflow from 80 to 55 ppm.

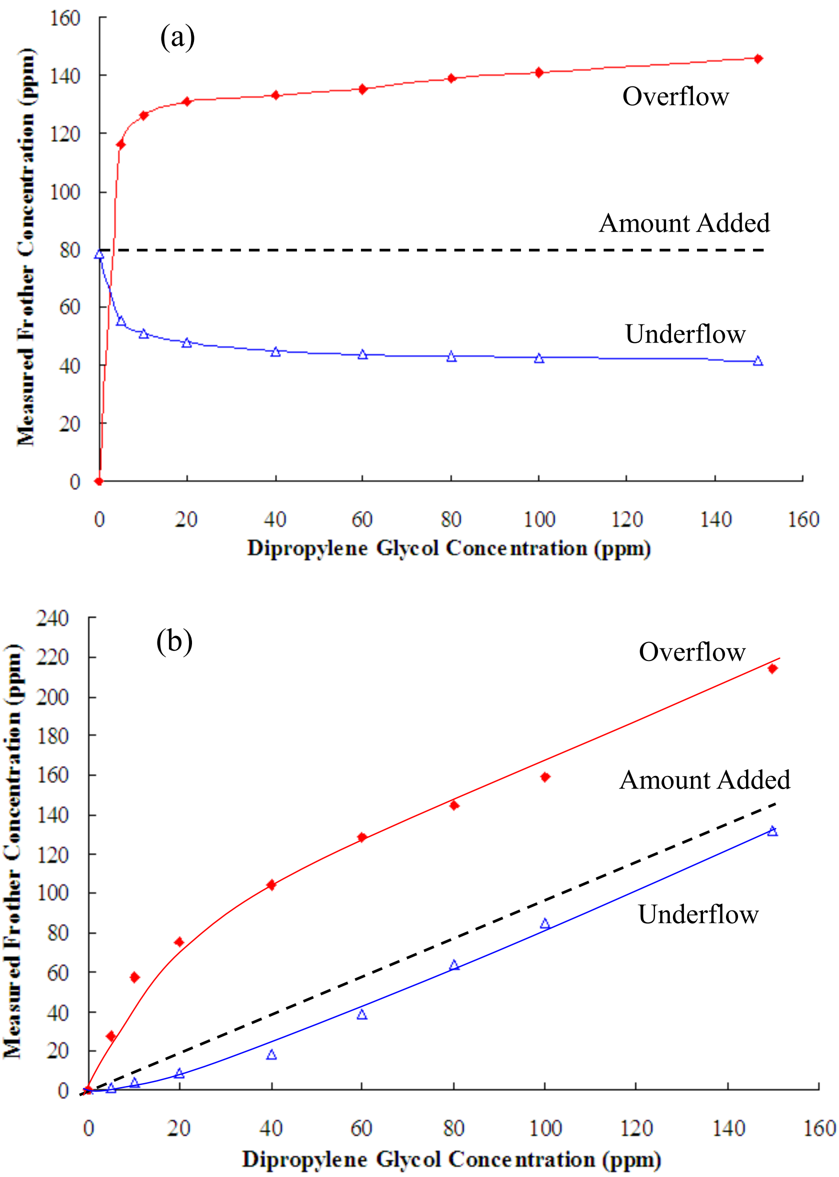


Figure 5.6: Frother concentration in overflow and underflow as a function of Dipropylene Glycol (additive) concentration in the presence of 80 ppm 1-Butanol: (a) 1-Butanol and (b) Dipropylene Glycol

5.3.2 NMR/TOC

5.3.2.1 Method and Verification

The technique is illustrated using the 1-Butanol/Tetraethylene Glycol blend which affords verification by comparing with the partitioning results from HPLC. The ^{1}H-NMR spectra for the components singly and in the blend are shown in Figure 5.7.

Noting there are no signals from Tetraethylene Glycol < 2.5 ppm chemical shift (δ) the methyl group proton (at ca. $\delta = 0.8$ ppm) is used as characteristic of 1-Butanol; likewise, noting no overlap with 1-Butanol signals on the range of ca. $\delta = 3.55 – 3.65$ ppm, the merged signal of the Ethylene Oxide (EO) groups associated with the terminal hydroxyl was used as the characteristic peak of Tetraethylene Glycol.

Figure 5.8 shows NMR spectra for 80 ppm 1-Butanol and 5 ppm Tetraethylene Glycol. The mole ratio was determined from the ratio of the peak integration area and from the TOC result the mole ratio was converted to actual molar concentration then to ppm. Table 3 summarizes data from NMR and TOC, and the corresponding results for frother partitioning. Figure 5.9 gives the partitioning result for the full range of additive (Tertaethylene Glycol) concentration and the corresponding results from HPLC. The results for the two analysis techniques compare well, differences between the two range from < 1% at high concentration to 10% at low concentration (5 ppm Tetraethylene Glycol).

The comparison verifies the novel NMR/TOC analysis technique. A second verification is from the mass balance, as used to verify the HPLC technique. Figure 5.10 shows the back-calculated feed concentration is in good agreement with the added concentration. Precision was poorest for the first point (RSD 4.8%) while the rest remained within 0.05 to 2.8% RSD indicating the NMR/TOC technique is reliable.

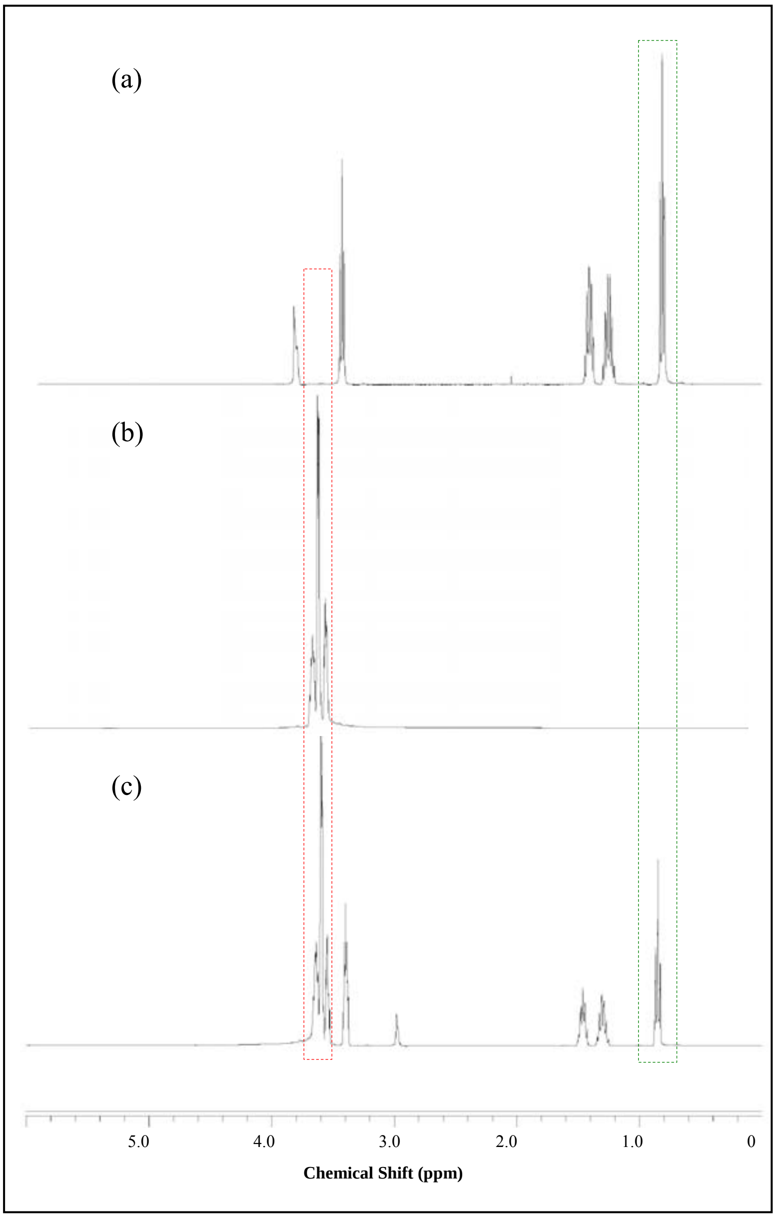


Figure 5.7: ^{1}H-NMR spectra of (a) 1-Butanol; (b) Tetraethylene Glycol and (c) the mixture of 1-Butanol and Tetraethylene Glycol (molar ratio 1:1)

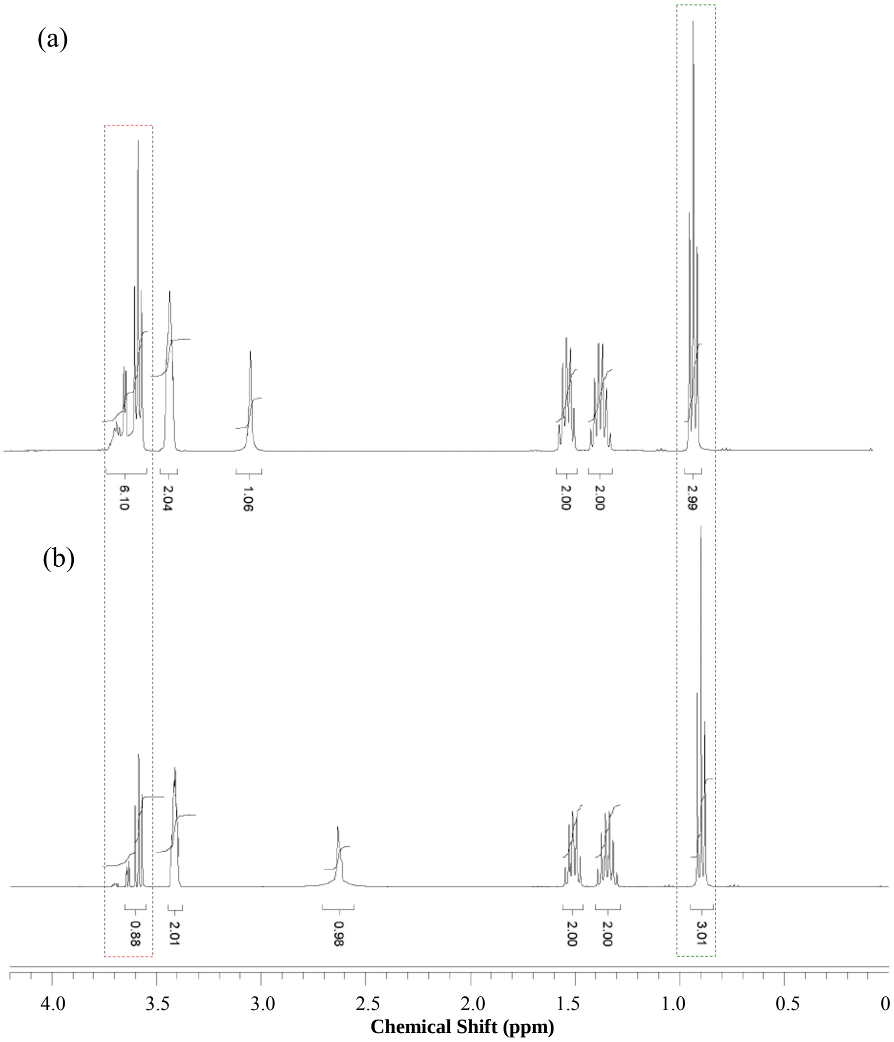


Figure 5.8: An example ^{1}H-NMR spectra of the mixed frothers in (a) overflow and (b) underflow, at the system concentration of 80 ppm 1-Butanol (base) and 5 ppm Tetraaethylene Glycol (additive)

Table 5.3 – Example frother partitioning using NMR/TOC technique for 80 ppm 1-Butanol (base) and 5 ppm Techaethylene Glycol (additive)

Stream	**TOC measurement (ppm)**	**Frother component**	**Integral of characteristic peak**	**Estimated frother concentration (ppm)**
Overflow	108.2	Tetraethylene Glycol	6.10	35.2
		1-Butanol	2.99	103.7
Underflow	72.8	Tetraethylene Glycol	0.88	3.5
		1-Butanol	3.01	73.4

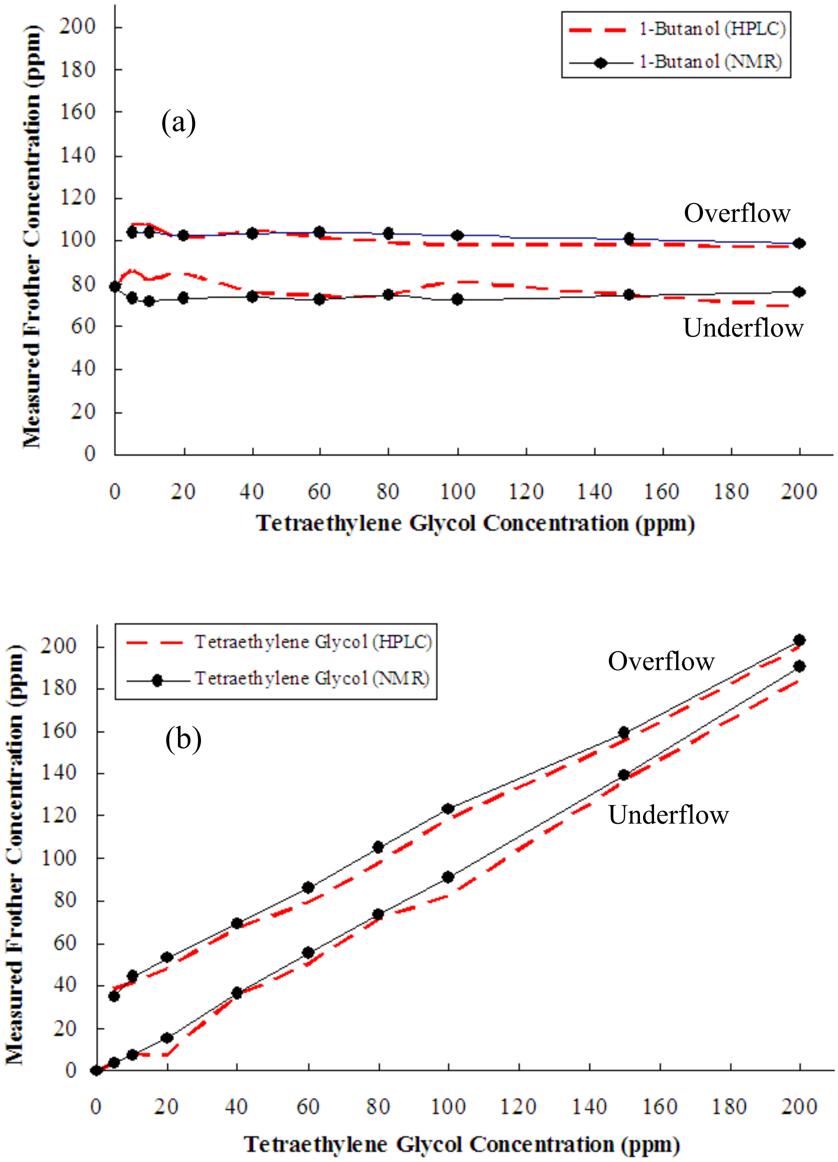


Figure 5.9: Verification of NMR/TOC technique: comparison of partitioning results with HPLC techniques: concentration in overflow and underflow as a function of Tetraethylene Glycol addition in presence of 80 ppm 1-Butanol: (a) 1-Butanol and (b) Tetraethylene Glycol

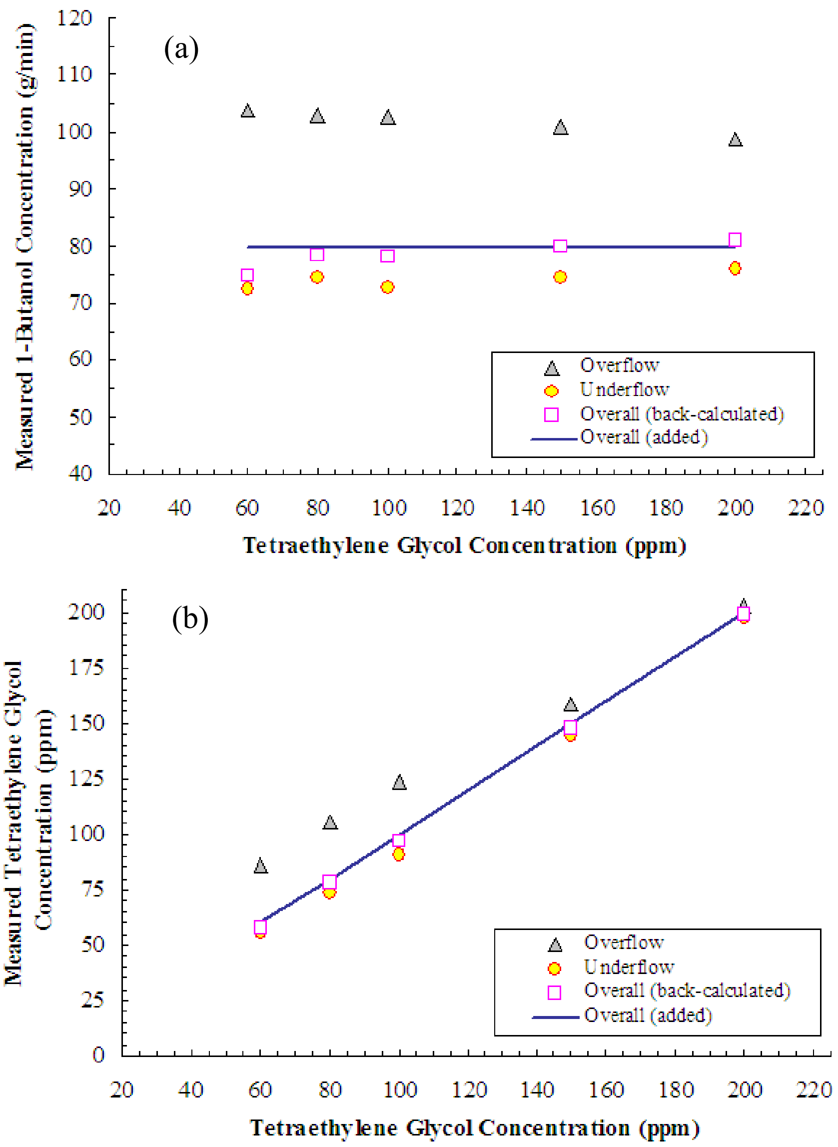


Figure 5.10: Verification of NMR/TOC technique: mass balance on frother showing back-calculated feed (overall) concentration compares well with added overall concentration: (a) 1-Butanol; (b) Tetraethylene Glycol

5.3.2.2 Partitioning: 1-Pentanol/F150

The selection of the non-overlapping characteristic peaks for these two frothers is illustrated in Figure 5.11 where the signals at δ = 0.9 and 1.1 ppm represent the protons in the methyl group of 1-Pentanol and F150, respectively.

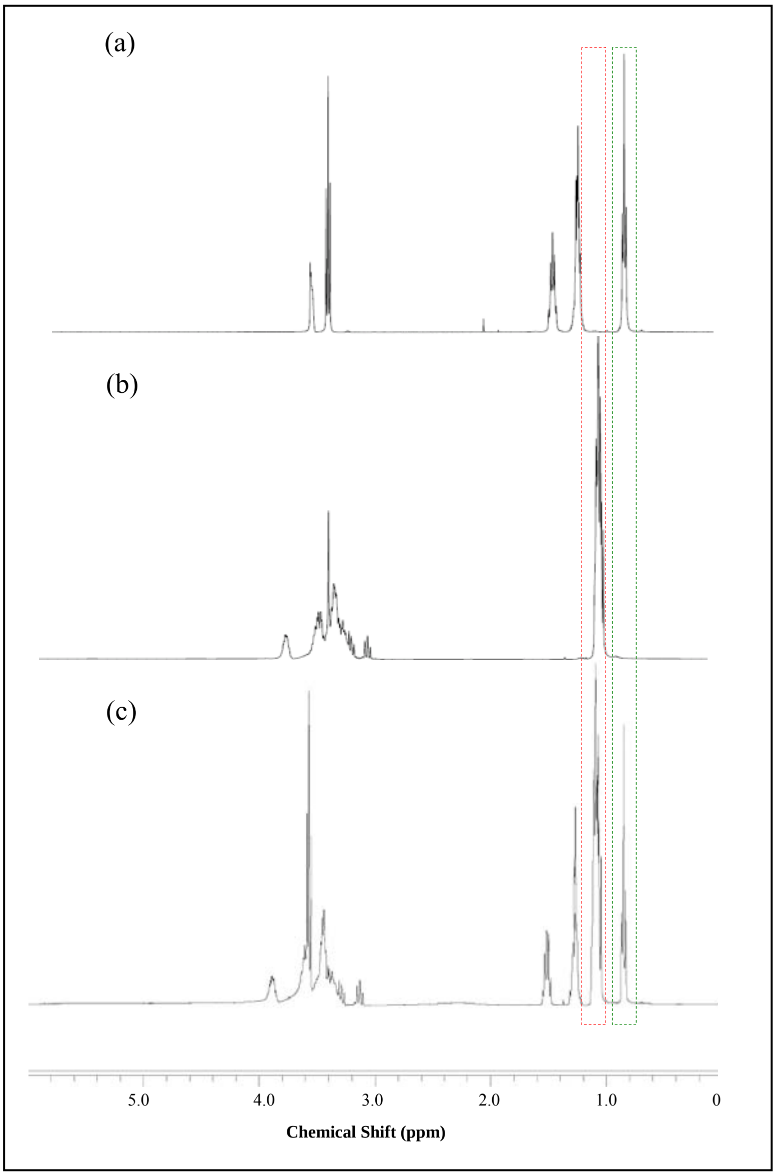


Figure 5.11: ^{1}H-NMR spectra of (a) 1-Pentanol; (b) F150 and (c) the mixture of 1-Pentanol and F150 (molar ratio 1:1)

Table 5.4 gives an example calculation for a particular blend, revealing strong partitioning of both frothers, especially the F150 where overflow concentration increases to ca. 30 ppm for only 5 ppm added.

Table 5.4 – Example frother partitioning using NMR/TOC: 40 ppm 1-Pentanol (base) and 5 ppm F150 (additive)

Stream	TOC measurements (ppm)	Frother component	Integral of characteristic peak	Estimated frother concentration (ppm)
Overflow	59.5	F150	8.43	29.1
		1-Pentanol	3.00	62.1
Underflow	22.4	F150	0.59	1.02
		1-Pentanol	3.01	31.9

Figure 5.12 shows the partitioning results for the range of additive (F150) concentration for 40 ppm 1-Pentanol (base) concentration. The trends indicate strong partitioning to the overflow of with, for example, 1-Pentanol concentration dropping to ca. 25 ppm, i.e. below the 1-Pentanol CCC, with small additions of F150.

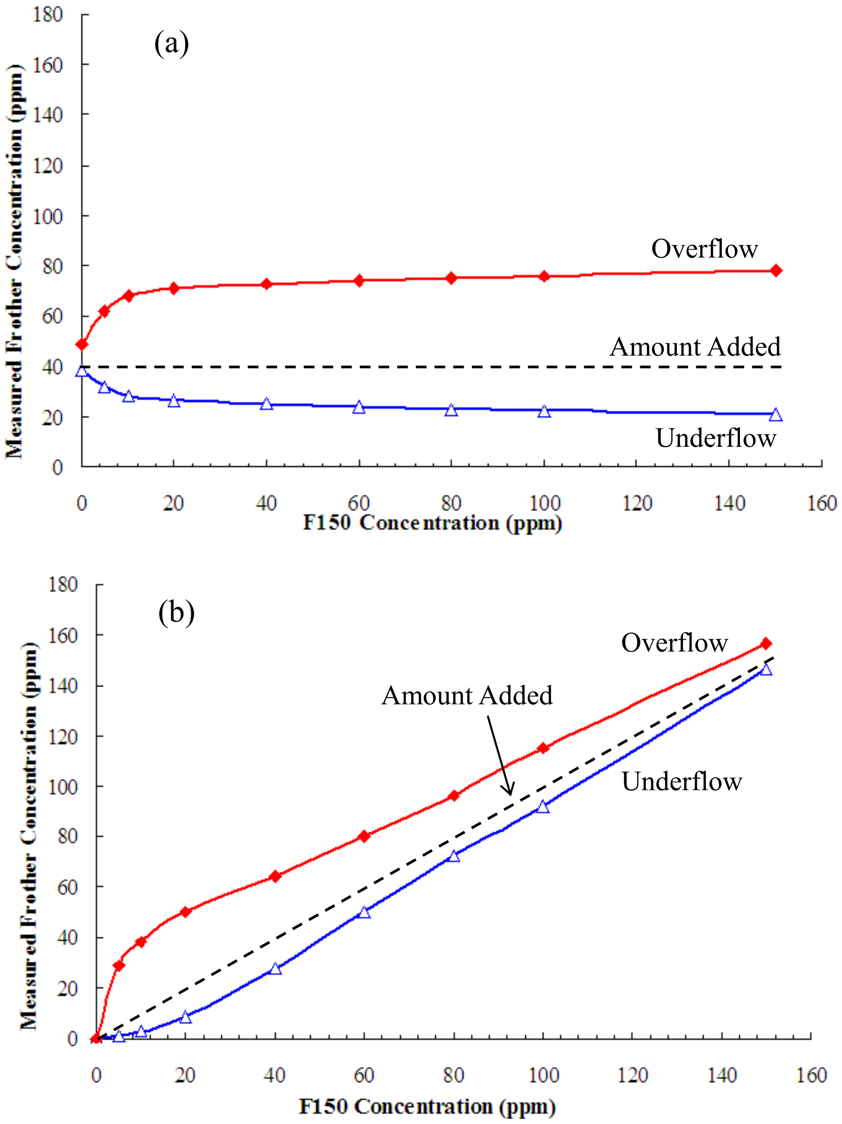


Figure 5.12: Frother concentration in overflow and underflow as a function of F150 (additive) concentration in the presence of 40 ppm 1-Pentanol: (a) 1-Pentanol and (b) F150

5.4 Discussion

Research into and application of frother blends demand methods to analyze the component frothers. This need was emphasized when determining the properties of dual frother blends some unexpected findings were encountered, notably increased bubble size in the case of 1-Butanol/Dipropylene Glycol [Zhang et al., 2012b] and 1-Pentanol/F150 [Elmahdy and Finch, 2009]. Some research was conducted to assess if this increase in bubble size was due to changes in bubble coalescence or breakup [Elmahdy, 2011] but another possibility was partitioning of one or both frothers to the froth resulting in reduced concentration in solution which could be sufficient to increase bubble size.

Partitioning refers to increased concentration in the froth (or overflow) compared to the solution (or underflow). Frothers by their aphipathic nature tend to concentrate at the air-water interface (bubble surface) and thus are transferred to the froth. In continuous tests, as here using the bubble column setup, partitioning can be measured by analyzing samples of the overflow and underflow. Partitioning has been measured for single frothers, F150 for example showing strong partitioning (i.e. high concentration in overflow relative to underflow). To follow partitioning in dual frother blends, the task in this chapter, required devising analytical methods capable of simultaneous determination of concentration of both frothers.

HPLC was used for two blends, 1-Butanol/Tetraethylene Glycol and 1-Butanol/Dipropylene Glycol. The two components were readily discerned in the chromatogram and from the linear calibrations concentrations were determined. The technique was validated by showing the mass balance ‘closed’; i.e., the feed concentration back-calculated from the products was in agreement with the known, added concentration. Partitioning was demonstrated by comparing the overflow and underflow concentrations with the added concentration. The 1-Butanol/Dipropylene Glycol blend showed the Butanol was strongly partitioned by small additions of Polyglycol, more so than for Butanol in the 1-Butanol/Tetraethylene Glycol blend. This corresponds to the noted effect for the former blend that showed an increase in bubble size upon small additions of Polyglycol while the latter did not [Zhang et al., 2012b]. Specifically, the 1-Butanol concentration in the 1-Butanol/Dipropylene Glycol blend was reduced from 80 ppm to < 60 ppm, i.e. below its CCC, for which the small addition of Polyglycol remaining in solution could not compensate and thus the increase in bubble size can be explained.

The results also show partitioning of the Polyglycol. The Tertaethylene Glycol initially appears to partition more than the Dipropylene Glycol, the first 5 ppm incremental addition producing nearly 40 ppm in the overflow compared to ca. 20 ppm, respectively. By the last increment, however, it is apparent that the Dipropylene Glycol partitions more than the Tetraethylene Glycol.

HPLC is probably capable of analyzing the third blend, 1-Pentanol/F150, but the columns available proved unsuited because of the longer chain (7 PO groups) of the F150. It is also the case that certain combinations can prove troublesome in HPLC due to overlapping peaks, thus there is an incentive for an alternative technique.

We had used NMR previously in characterizing frothers, determining the H-ratio as an alternative to HLB, for example, and identifying the family in the case of some commercial frothers [Zhang et al., 2012c]. Although not commonly used for such simple molecules at such low concentrations the availability of the 600 MHz instrument does make quantitative analysis a possibility [Kalinoski, 1996]. The two components, 1-Pentanol and F150, gave readily resolved characteristic peaks. Advantage was then taken of the fact that the ratio of the integral area of the characteristic peaks (relative peak area) is dependent on the relative concentration of the two components. It was then left to determine the total organic content, knowing the two frothers were the only organics added, to determine their individual concentration from the relative peak area. The combination NMR/TOC technique was validated by showing good agreement with the HPLC result for the blend 1-Butanol/Tetraethylene Glycol and by again demonstrating that the mass balance closed.

The NMR/TOC technique revealed strong partitioning of 1-Pentanol to the overflow, small additions of F150 bringing the solution (underflow) 1-Pentanol concentration below its CCC for which the small addition of F150 could not compensate hence correlating with the increase in bubble size noted by Elmahdy and Finch [2009].

Strong partitioning seems a compelling explanation for observed increases in bubble size with some dual frother blends. In concert with speculations based on effects on coalescence or breakup [Elmahdy, 2011], however, the mechanism causing strong partitioning is not apparent. Enhanced partitioning is known in other cases of surfactant blends, but no mechanism was proposed [Salager, 1999]. The data here suggest that the more hydrophobic PO-based Polyglycols produce the phenomenon when added to Alcohols rather than the more hydrophilic EO-based frothers. How this is linked to an apparent increase in Alcohol adsorption on the bubble is not clear. There could be H-bonding between O of the PO and the OH of the Alcohols resulting in a more surface active species. This would imply that both frothers partition similarly, for which there seems some evidence (in Figures 5.6 and 5.12 both frothers initially partition strongly) but then Tertaethylene Glycol seems to partition strongly, independent of the 1-Butanol (Figure 5.5). Arguing against bonding is the fact that the NMR spectra gave no such hint although for H-bonds this can be subtle [Zhou, et al., 2009]; and arguing against increase in surface activity is the fact that surface tension failed to support this in the case of 1-Pentanol/F150 [Elmahdy, 2011].

Further speculation on the mechanism of partitioning is not warranted by the limited data presented. What we have shown is that dual frother systems can be analyzed not only by HPLC as anticipated but also by a novel NMR/TOC combination. Together these analytical methods provide great flexibility in the analysis of frother blends which as illustrated here has helped interpret bubble size effects of possible importance in flotation systems.

5.5 Conclusions

Two techniques were developed to analyze individual frother concentration in dual frother blends, one using HPLC and a second using a novel NMR/TOC combination. The methods were used to determine frother partitioning between underflow and overflow in continuous testing in a bubble column. Strong partitioning to the overflow of 1-Butanol and 1-Pentanol was shown in blends with Dipropylene Glycol and F150, respectively, but little partitioning for 1-Butanol blended with Tetraethylene Glycol. These findings offer an explanation of the increase in bubble size reported in the former two cases. Together HPLC and NMR/TOC offer a flexible way to analyze frother blends to help interpret their action in flotation systems.

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Connecting Texts between Chapters 5 and 6

There have been two directions to develop new frothers in recent years. One is to modify known frothers based on evaluation of the frother molecular structure − function relationship, as introduced in Chapters 3, 4 and 5. The second is to synthesize new frothers. Following the structure-function theme, Chapter 6 addresses synthesizing new frothers from combination of alkyl, PO and EO groups designed to try to achieve target hydrodynamic and froth stability properties.

Chapter 6 - Synthesis and Characterization of New Polyglycol-Based Frothers: A Structure–Function Study

Abstract

In this chapter we describe the synthesis of a new homologous series of linear Polyglycol-based frothers that consist of Ethylene Oxide (EO) and hydroxyl as hydrophilic groups and Propylene Oxide (PO) and alkyl chains as hydrophobic groups. The synthesized frothers were of two types: Alkyl-Ethoxy-Propoxylate (abbrev. $C_nEO_lPO_m$) and Alkyl-Propoxy-Ethoxylate ($C_nPO_mEO_l$) giving: (a) different number of groups and chain length, and (b) different locations of the groups. The identities were confirmed by proton nuclear magnetic resonance (NMR) spectroscopy and total organic carbon (TOC) analysis.

The characterization of the products was carried out in a bubble column. At steady state, bubble size, gas holdup and water overflow rate were measured as a function of frother concentration. The results indicate that increasing number of PO groups led to significant decrease in bubble size, and increase in gas holdup and water overflow rate. Increasing the alkyl chain length, gave similar but less pronounced trends. There was no impact of increasing the number of EO groups on bubble size but there was an in increase in gas holdup and water overflow rate. Changing the location of the PO and EO group had a significant effect on all three parameters.

6.1 Introduction

Frothers are heteropolar surfactants, i.e., comprise polar and non-polar groups, which are used to promote flotation performance through control of hydrodynamic and froth properties [Zieminski et al., 1967; Klimpel and Isherwood, 1991; Laskowski, 1998;

Cappuccitti and Finch, 2007]. The most commonly used frothers fall in two main categories: Aliphatic Alcohols ($C_nH_{2n+1}OH$) and Polyglycols ($C_nH_{2n+1}(OC_3H_6)_mOH$ or $C_nH_{2n+1}(OC_2H_4)_lOH$) [Klimpel and Isherwood, 1991; Laskowski, 1998]. These compounds can be represented by the general formula: $R(X)_nOH$ where R is H or alkyl (C_nH_{2n+1}), and X is Propylene Oxide (PO, OC_3H_6) or Ethylene Oxide (EO, OC_2H_4). The choice of frother has important implications in flotation performance [Laskowski, 2003; Cappuccitti and Finch, 2007; Finch, 2010]; however, there is no accepted selection procedure other than empirical testing.

The action of frother derives ultimately from the structure. Zhang et al. [2012] showed bubble size reduction as measured by CCC (critical coalescence concentration) could be related to structure as quantified by HLB (hydrophile-lipophile balance). The hydrophilic groups are O, OH and EO and the lipophilic (hydrophobic) groups are alkyl and PO. Moyo et al. [2007] linked water overflow rate to the length of alkyl chain and, along with Zhang et al. [2010], noted that PO-based Polyglycols gave higher water recovery than Alcohols. Laskowski [2003] made broadly similar observations.

There have been periodic attempts to create new frother chemistries in the anticipation of tailored flotation properties. Klimpel and Isherwood [1991] reacted Propylene Oxide with Aliphatic Alcohols, resulting in such formulations as Hexanol$(PO)_2$, Pentanol$(PO)_2$ and MIBC$(PO)_2$. The frothers in this family extended the coarse particle size range of flotation, but at the expense of recovering less fine material. Harris and Jia [2000] added a sulphur atom to Polyalkoxylated compounds of various configurations. They showed that these frothers increased copper and molybdenum recovery in flotation of porphyry ores. Cappuccitti and Finch [2007] reacted Aliphatic Alcohols C_1 (Methanol) to C_4 (Butanol) with between 0.2 to 5 moles of EO. These frothers demonstrated that the hydrodynamic and froth properties depended on the number of EO groups. Testing identified Ethoxylated Butanols as potential equivalents to MIBC. By changing the number of EO groups products could be made slightly weaker (EO = 1.5) or stronger (EO = 3) than MIBC but the new chemistry could not provide hydrodynamic/froth characteristics similar to PO-based Polyglycols.

As noted, new chemistries tend to be reaction products of Alcohols and Polyglycols, either Alkyl-Ethoxylates (abbrev. C_nEO_l) or Alkyl-Propoxylates (C_nPO_m). This recognizes that frother molecules with two functional groups located at appropriate positions in the molecular architecture may offer advantages over mono-functional frothers. An extension of this thinking is to synthesize compounds consisting of three functional groups with various sequences of hydrophilic and hydrophobic groups.

The purpose of this chapter is to synthesize new frothers comprising three functional groups occupying different positions, specifically linear-structured Alkyl-Ethoxy-Propoxylates ($C_nEO_lPO_m$) and Alkyl-Propoxy-Ethoxylates ($C_nPO_mEO_l$) and determine the effect on flotation-related properties by measuring bubble size, gas holdup and water overflow rate.

6.2 Experimental

6.2.1 Synthesis

6.2.1.1 Materials

The reagents used are listed in Table 6.1. The Polyglycols and their Ethers, Alcohols, 1,2-Diiodoethane and sodium hydride were analytical grade all from Aldrich-Sigma Chemical Co. (Canada, Ltd) and used without further purification. The solvent tetrahydrofuran (THF) was obtained from commercial source with high purity (>99.9%). The dialysis membrane (16 mm x 10 mm) with 100-500Da. MWCO was purchased from Spectrum Laboratories Inc. The solvent deuterium oxide for NMR experiments was 99.994 atom% D from Aldrich-Sigma Co. (Canada, Ltd). All glassware and vessels were cleaned and oven-dried prior to use.

Table 6.1 − Reagents used in synthesis

Reagent ID	*Name*	*Component/Abbreviation (Purity)*
1	Dipropylene Glycol	$H(OC_3H_6)_2OH$ (≥99%)
2	Tripropylene Glycol	$H(OC_3H_6)_3OH$ (≥97%)
3	Tripropylene Glycol Monopropyl Ether	$C_3H_7(OC_3H_6)_3OH$ (≥97%)
4	Ethylene Glycol	$H(OC_2H_4)OH$ (≥99.8%)
5	Ethylene Glycol Monopropyl Ether	$C_3H_7(OC_2H_4)OH$ (≥99.4%)
6	1-Propanol	C_3H_7OH (≥99.7%)
7	1-Pentanol	$C_5H_{11}OH$ (≥99.5%)
8	1,2-Diiodoethane	ICH_2CH_2I (≥99%)
9	Sodium hydride	NaH (≥95%)
10	Tetrahydrofuran (solvent)	THF (≥99.9%)

6.2.1.2 Preparation and Purification

We synthesized five nonionic linear Polyglycol-based frothers with varying numbers of repeating units in each group (PO, EO and Alkyl) and position of EO and PO groups by stepwise substitution. The chemical components, formulae and names are listed in Table 6.2.

Table 6.2 − The chemical components, families, formulae and names of the synthesized frothers

Frother ID	***Frother type***	***Alkyl (C_nH_{2n+1})***	***PO (OC_3H_6)***	***EO (OC_2H_4)***	**Chemical formula**	**Chemical name**	**Abbrev.**
		n	**m**	**l**			
1	Alkyl-Ethoxy-Propoxylate	3	2	1	$C_3H_7(EO)(PO)_2OH$	Dipropoxy Monoethoxy Propanol	DPMEPro
2		3	3	1	$C_3H_7(EO)(PO)_3OH$	Tripropoxy Monoethoxy Propanol	TPMEPro
3		5	3	1	$C_5H_{11}(EO)(PO)_3OH$	Tripropoxy Monoethoxy Pentanol	TPMEPen
4		3	3	2	$C_3H_7(EO)_2(PO)_3OH$	Tripropoxy Diethoxy Propanol	TPDEPro
5	Alkyl-Propoxy-Ethoxylate	3	3	2	$C_3H_7(PO)_3(EO)_2OH$	Diethoxy Tripropoxy Propanol	DETPPro

To illustrate the procedure it is described in detail for Dipropoxy Monoethoxy Propanol (DPMEPro). The product was synthesized by the three-step reaction shown in Figure 6.1a. In the first step, Sodium Dipropylene Glycol was prepared by reacting Dipropylene Glycol and sodium hydride in the solvent Tetrahydrofuran (THF). Sodium hydride (4.8 g, 0.12 mol) was dissolved in 20 mL of THF in a flame-dried round-bottom flask (three-neck, 100 mL) agitated by a magnetic stirring bar. Dipropylene Glycol (16.08 g, 0.12 mol) was then added into the flask dropwise. The solution was stirred and cooled in an ice-cooled water bath during the addition of Dipropylene Glycol for 2 hours, maintaining the temperature at 0^{o} C. In step 2, 1-Propanol (7.2 g, 0.12 mol) was dissolved in 20 mL of THF and sodium hydride (4.80 g, 0.12 mol) was added and stirred in another round-bottom three-neck flask , 250 mL) also held in an ice-cooled water bath to maintain 0^{o} C for 2 hours. At the end of the 2 hours 1,2-Diiodoethane (31 g, 0.11 mol) in a solution of THF was gradually introduced to react with the newly generated sodium propan-1-olate. During the introduction, the vessel was relocated to a heating bath with a consistent temperature of 60^{o} C under continuous reflux and stirring conditions for 2 hours. After step 2, the Sodium Dipropylene Glycol (from step 1) was taken via a syringe from the 100 mL flask and transferred to the solution (1-(2-iodoethoxy)propane) dropwise with continuously stirring. The solution rapidly became viscous. After addition was completed, stirring and refluxing were continued at 60^{o} C for another 2 hours.

In the product purification stage, first solvent was evaporated under vacuum on a rotary evaporator for 2 hours. The product was then filtered and dialyzed against 4L deionized (ca. 18 M-Ohm) water for at least 48 hours in a dialysis membrane tube (100-500Da MWCO). Subsequently the product was dried and concentrated under vacuum in rotovap for 4 hours then in a vacuum oven (50^{o} C) for 12 hours or overnight. The last purification step was by column chromatography (silica gel, $CHCL_3$/Methanol, 5:1 (v/v)) to yield the purified off-white solid compound.

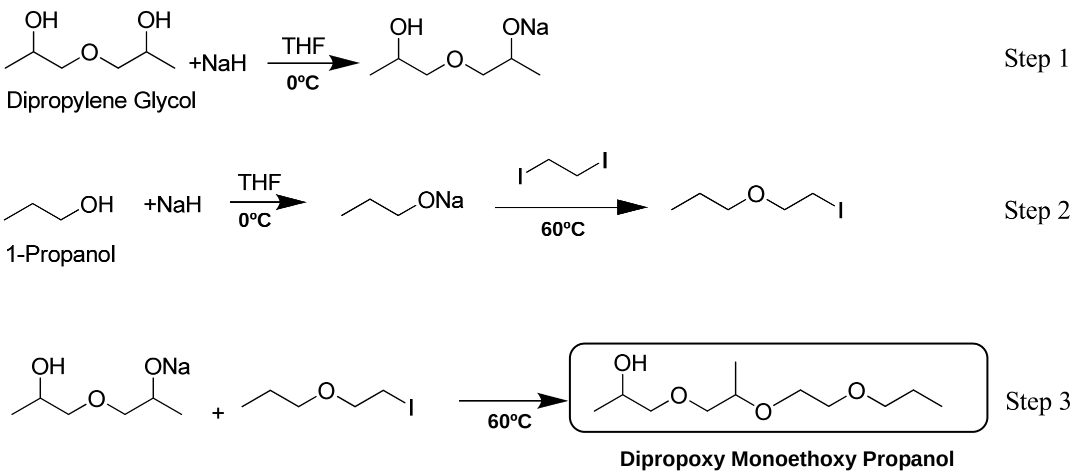


Figure 6.1a: Synthetic route of Dipropoxy Monoethoxy Propanol (DPMEPro)

The other compounds were synthesized using a similar strategy as for DEMEPro using the appropriate combinations of reactants. For instance, TPMEPro was prepared using Tripropylene Glycol; TPMEPen was prepared using Tripropylene Glycol and 1-Pentanol; TPDEPro was prepared using Tripropylene Glycol and Ethylene Glycol Monopropyl Ether; and DETPPro was synthesized using Tripropylene Glycol Monopropyl Ether and Ethylene Glycol; this last reaction is shown in Figure 6.1b.

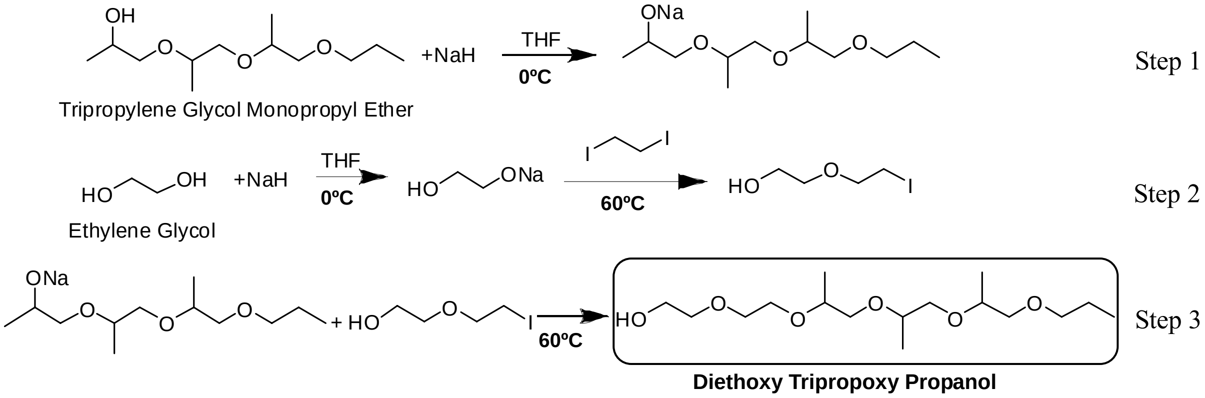


Figure 6.1b: Synthetic route of Diethoxy Tripropoxy Propanol (DETPPro)

6.2.1.3 Product Verification

Proton NMR spectrometry and total organic carbon (TOC) analysis were used for product verification. Each product (i.e. 20 mg) was dissolved by sufficient deuterium oxide (solvent D_2O, 0.7 mL) in a high quality 5 mm NMR (Wilmad 528, limit 500 MHz frequency, L 7 in.) tube to obtaining the NMR spectrum. The ^{1}H NMR spectra were recorded on a 400 MHz spectrometer (Bruker AVANCE-400) at a frequency of 400.27 MHz for protons, with temperature controlled at 298 K. Data acquisition and integration were performed using the commercial software MestRe-C. To perform TOC analysis (Dohrmanns DC 80, TELEDYNE Instruments) appropriate amounts of product were weighed and diluted in deionized water (ca. 18 M-Ohm) over the concentration range 5 to 200 ppm. For each sample total organic carbon concentration was measured with allowance for any organics in the water, and compared to the calculated concentration in accordance with the anticipated molecular formula.

6.2.2 Frother Characterization

A bubble column (Figure 6.2), 350 cm x 10 cm diameter (volume 28 L), was mounted for the project. A stainless cylindrical porous sparger (6 cm high x 2.5 cm diameter) with a 5 micron nominal porosity was positioned vertically at the base of the column to disperse air. The sparger was selected to ensure significant bubble size and gas holdup changes for all frother products. Operation was continuous with the feed (frother solution) controlled by a peristaltic pump (Cole Palmer model 7520-25) with overflow and underflow (recycled to the feed tank to close the loop. A calibrated mass flow meter (MKS instruments model M100B53CS18V) was used to maintain the superficial air flow velocity (J_g) at 0.5 cm/s. A differential pressure transmitter (Bailey model PTSDDD) was tapped between 260 cm and 329.5 cm above the sparger to determine gas holdup (E_g). As a backup gas holdup measurement, three 2.5 cm wide stainless ring electrodes separated by acrylic sections 7.5 cm wide (Figure 6.2) were mounted at the mid-section of the column to estimate gas holdup from conductivity using Maxwell's model [Tavera et al., 2001] (The gas holdup measured by the two techniques were comparable – a typical comparison is given in Appendix). Bubble size measurements (D_b) were made using the McGill Bubble Size Analyzer (MBSA).

To operate, underflow rate was fixed at 1600 g/min and froth height was maintained at 0.5 cm by manipulating the pump speed (i.e., feed rate). Samples were collected from the overflow over known periods of time to measure the flow rate when the system was at steady state. Each measurement was repeated two times and a mean value was recorded (if the standard error exceeded 5% a third, or fourth repeat was performed). The mass rate (g/min) was converted to volume rate and divided by the column cross-sectional area to give the water superficial overflow rate (J_{wO}, cm/s). All samples were returned to the feed tank.

The test work was performed in the two-phase, air-water system. The water source was Montréal tap and the temperature was equilibrated to room temperature (20~22°C). A temperature sensor (Thermopar type K) was used to record temperature to correct the superficial air flow rate and conductivity values to the standard temperature of 25°C.

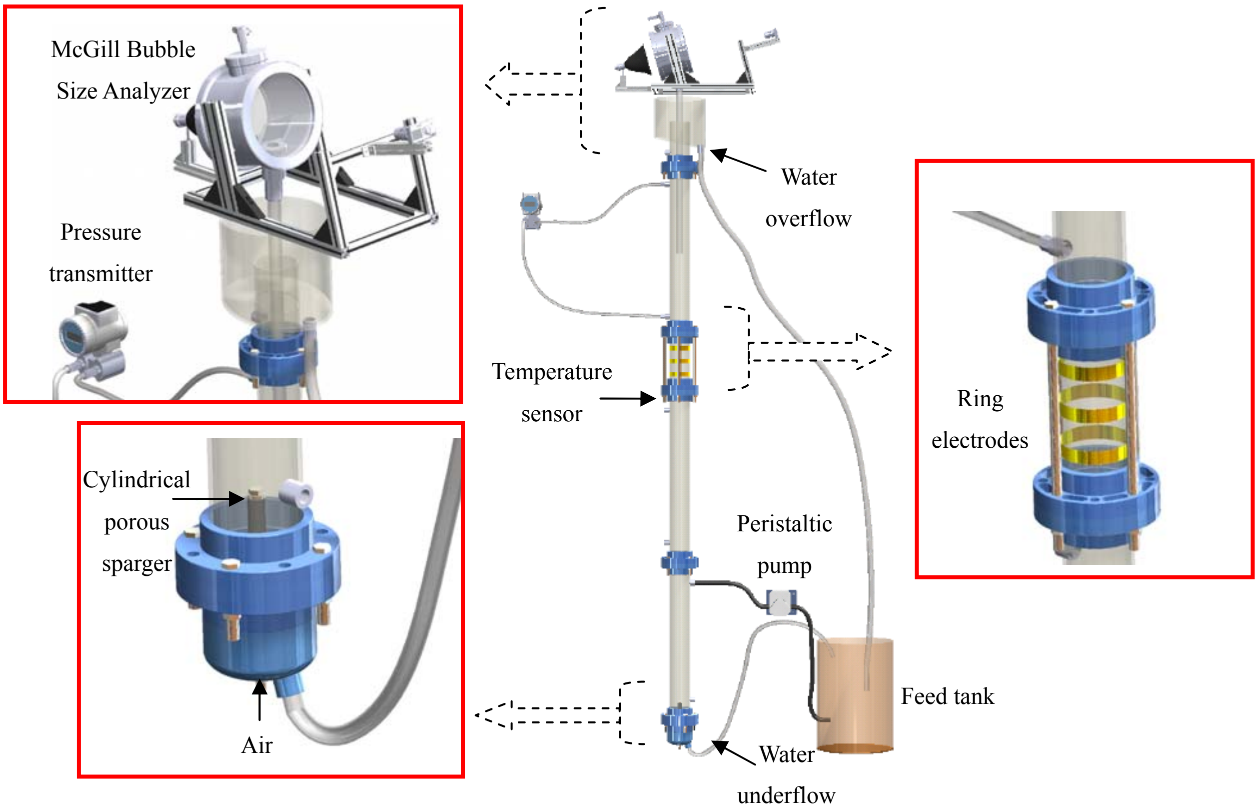


Figure 6.2: The experimental set-up of column operated continuously in closed loop with accessories and measurements, E_g, D_b and J_{wO}, indicated

6.3 Results

6.3.1 Verification of Synthesized Compounds

The ^1H NMR spectra for the five synthesized frothers shown in Figure 6.3 confirm the target chemical structure. Taking DPMEPro (Figure 6.3a) as an example, the signals from $\delta = 3.3$ to 4.0 ppm are assigned to methylene and methine protons of the PO, EO and alkyl groups (i.e., the first methylene conjoint with the O) and the terminal OH group. The signal at $\delta = 1.55$ ppm is assigned to the methylene of the alkyl group conjoint with the terminal methyl. The other signals at $\delta = 1.35$, 1.2 and 0.85 ppm are attributed to the methyl protons of the two PO and alkyl groups, respectively. The synthesis was carried out in triplicate, and the NMR spectrum results were consistent among the runs.

For the other four compounds: Compared with Figure 6.3a, in Figure 6.3b the signal at $\delta = 1.35$ ppm is assigned to protons of two methyls in different PO groups; in Figure 6.3c the two methyls in PO groups and the two methylenes which adjoin the terminal methyl in the alkyl group are indicated at $\delta = 1.35$ ppm; compared with Figure 6.3b, in Figure 6.2d, two more methylenes from the EO group are identified in the range $\delta = 3.3$ to 4.0 ppm; and compared with Figure 6.3d, in Figure 6.3e the three methyls from PO groups are located at $\delta = 1.35$ ppm while the signal at $\delta = 1.35$ ppm disappears due to the switched sequence of EO and PO groups.

Since the signals associated with methyl units represented in alkyl and PO groups were observed in the spectra, the integration (shown in Figure 6.3) of these characteristic peaks can be used to calculate the chemical composition. The average composition of EO groups then can be estimated from the overlapped signals in the range $\delta = 3.3$ to 4.0 ppm. Comparison of the average composition of alkyl chain, PO and EO units, with the derivation from the molecular formula shows good agreement (Table 6.3).

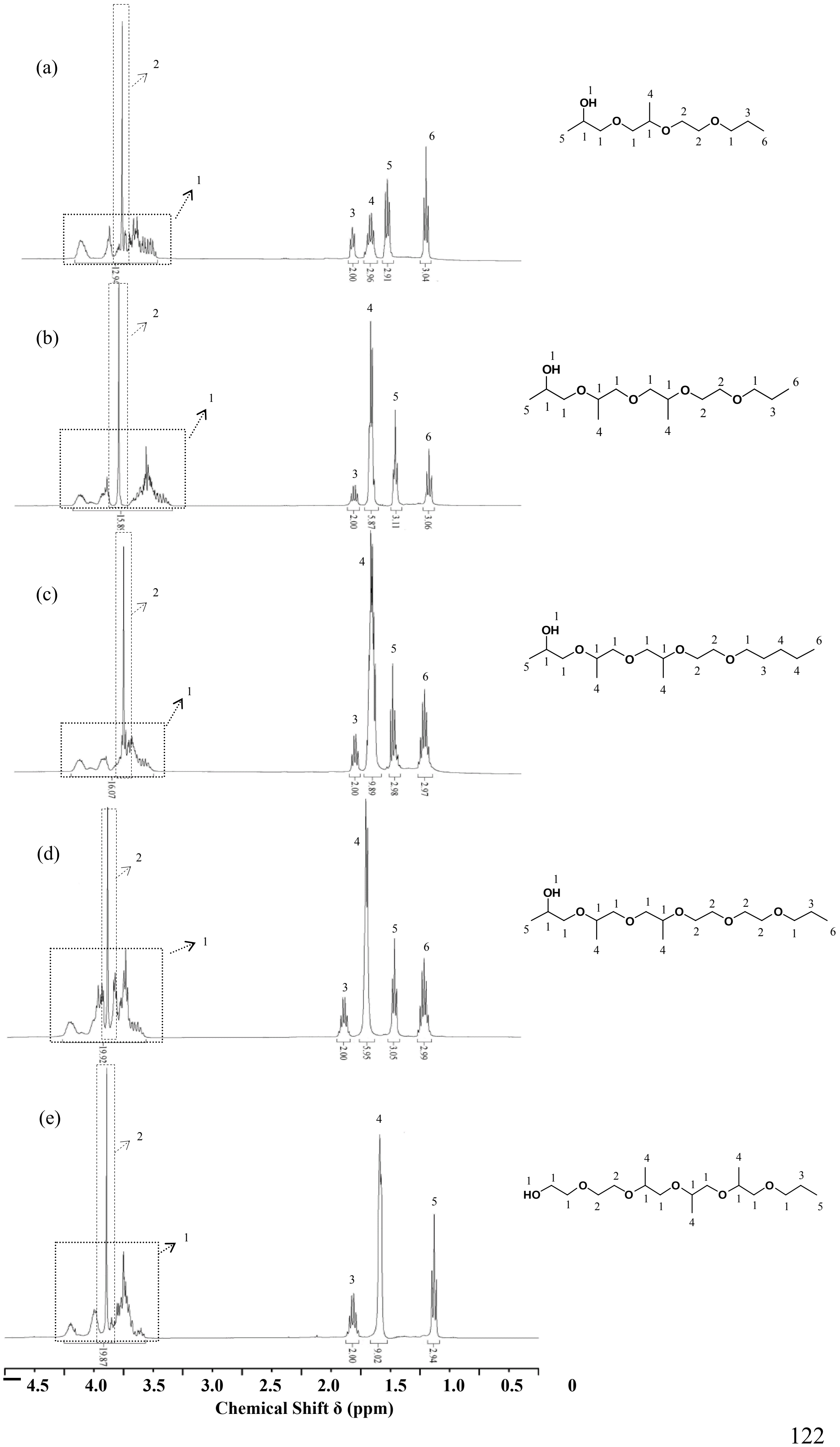

(a)
(b)
(c)
(d)
(e)
1
2
3
4
5
6
OH
HO
O
12.94
2.00
2.96
2.91
3.04
15.8
2.00
5.87
3.11
3.06
16.07
2.00
9.89
2.98
2.97
19.92
2.00
5.95
3.05
2.99
19.87
2.00
9.02
2.94
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift δ (ppm)

Figure 6.3: ^{1}H NMR spectra of (a)DPMEPro; (b)TPMEPro; (c)TPMEPen; (d)TPDEPro and (e)DETPPro

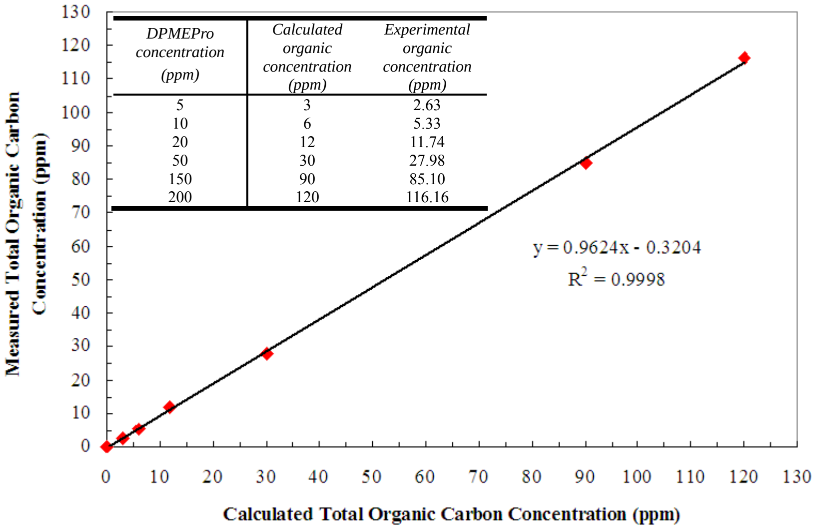
Table 6.3 − The average number of alkyl, PO and EO units in the synthesized compounds form the formulae and as determined by ^{1}H NMR*

Compounds name	*Average alkyl chain*[a]		*Average PO units*		*Average EO units*	
	Stated (in molecular formula)	Determined (by NMR)	Stated (in molecular formula)	Determined (by NMR)	Stated (in molecular formula)	Determined (by NMR)
DPMEPro	3	2.9	2	1.9	1	1.1
TPMEPro	3	2.9	3	2.9	1	0.9
TPMEPen	5	4.8	3	2.8	1	0.8
TPDEPro	3	2.8	3	2.9	2	1.9
DETPPro	3	2.9	3	2.9	2	2.1

* The relative number of compositions was determined through comparison of integrated intensities for resonance signals. The protons (i.e. 2) of methylene (δ = 1.5-1.6 ppm, in alkyl chain) adjoin the terminal methyl group was assigned as the reference signal.

[a] Carbon units.

As shown in Figure 6.4, there was good agreement between the calculated total organic carbon concentrations and the TOC experimental values over the range of 5 to 200 ppm DPMEPro which confirmed the high purity of the synthesized compound (slope = 0.9624 and R^2 = 0.9998 at N = 6). Similarly the TOC results for other four synthesized compounds indicated high purity (TPMEPro – slope = 0.9532 and R^2 = 0.9998 at N = 7; TPMEPen – slope = 0.9612 and R^2 = 0.9995 at N = 7; TPDEPro – slope = 0.9569 and R^2 = 0.9999 at N = 7; DETPPro – slope = 0.9444 and R^2 = 0.9997 at N = 7).



DPMEPro concentration (ppm)	*Calculated organic concentration (ppm)*	*Experimental organic concentration (ppm)*
5	3	2.63
10	6	5.33
20	12	11.74
50	30	27.98
150	90	85.10
200	120	116.16

Figure 6.4: Calculated total organic carbon concentration of DPMEPro compares well with measured concentration by TOC analysis

6.3.2 Frother Characterization

Bubble size (D_{32}), gas holdup (E_g) and water overflow rate (J_{wO}) form the basis of assessment of the flotation-related properties of the new compounds. The compounds are compared on the basis of molar concentration. The validation and reliability of the measurements of flotation related properties have been reported in Chapter 4.

6.3.2.1 Influence of PO Number

The two compounds, DPMEPro (m = 2) and TPMEPro (m = 3) represent frothers with different number of PO in the structure. It is observed from Figure 6.5 that the larger PO number corresponds to higher gas holdup and water overflow rate and lower bubble size.

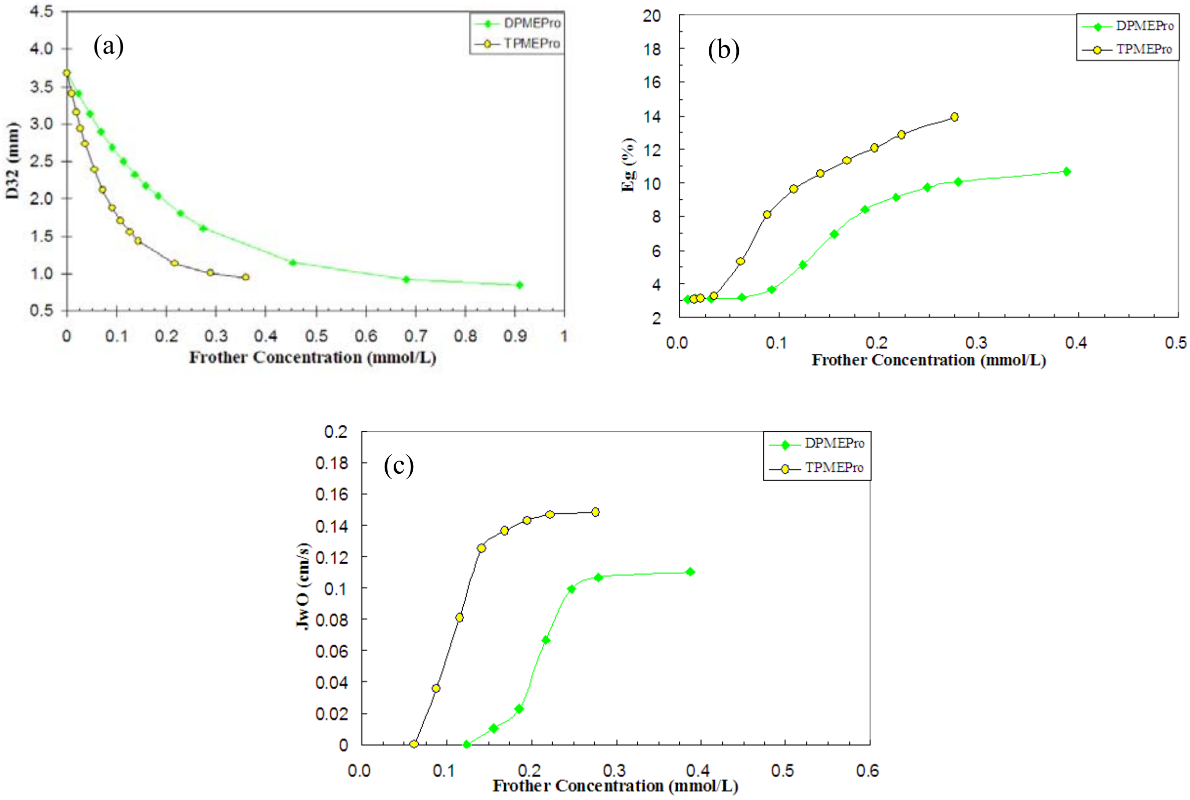


Figure 6.5: Effect of DPMEPro and TPMEPro concentration on (a) bubble size – D_{32}; (b) gas holdup – E_g; and (c) water overflow rate – J_{wO}

6.3.2.2 Influence of Chain Length of Alkyl Group

Figure 6.6 shows results for the two compounds TPMEPro (n = 3) and TPMEPen (n = 5) with different length of alkyl chain. As seen, when chain length is increased gas holdup and water overflow rate increased and bubble size decreased. Compared with altering the number of PO groups (Figure 6.5), the change in properties is less when varying the chain length of the alkyl group.

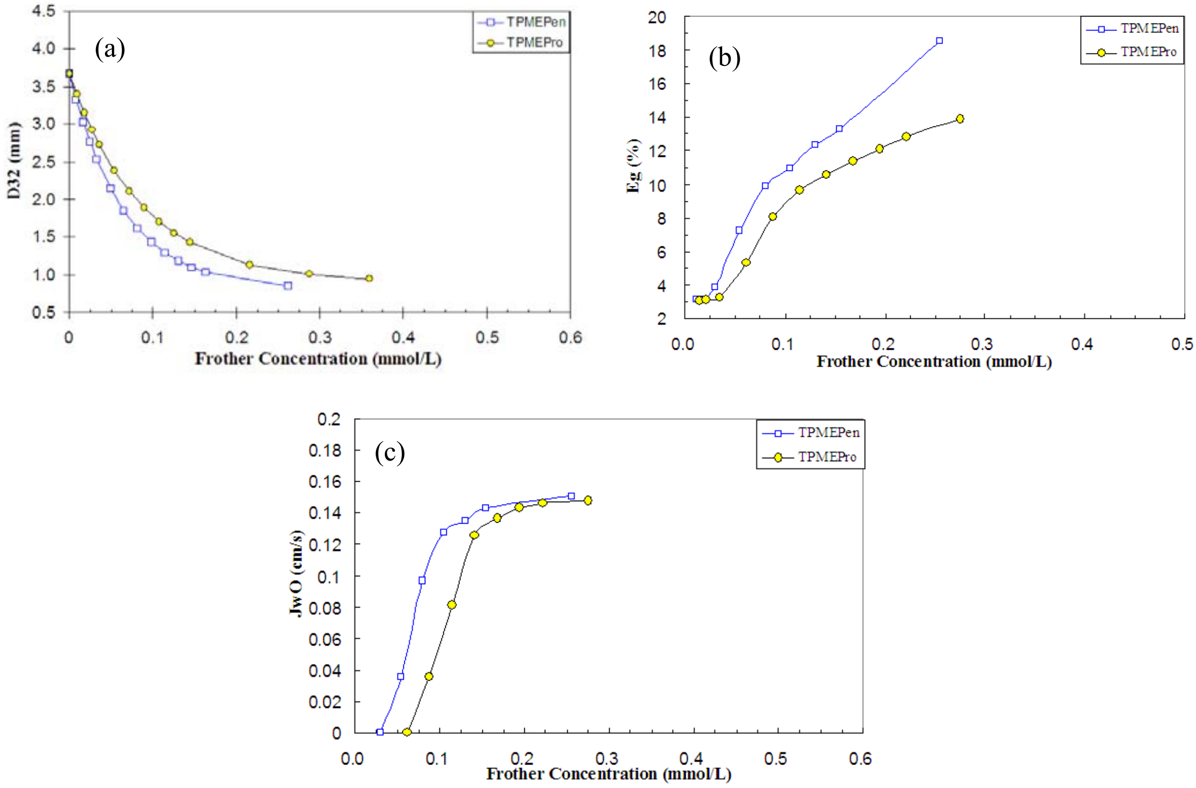


Figure 6.6: Effect of TPMEPro and TPMEPen concentration on (a) bubble size – D_{32}; (b) gas holdup – E_g; and (c) water overflow rate – J_{wO}

6.3.2.3 Influence of EO Number

The effect of the number of EO groups (Figure 6.7) shows an increase in gas holdup and water overflow rate, but a virtually constant bubble size.

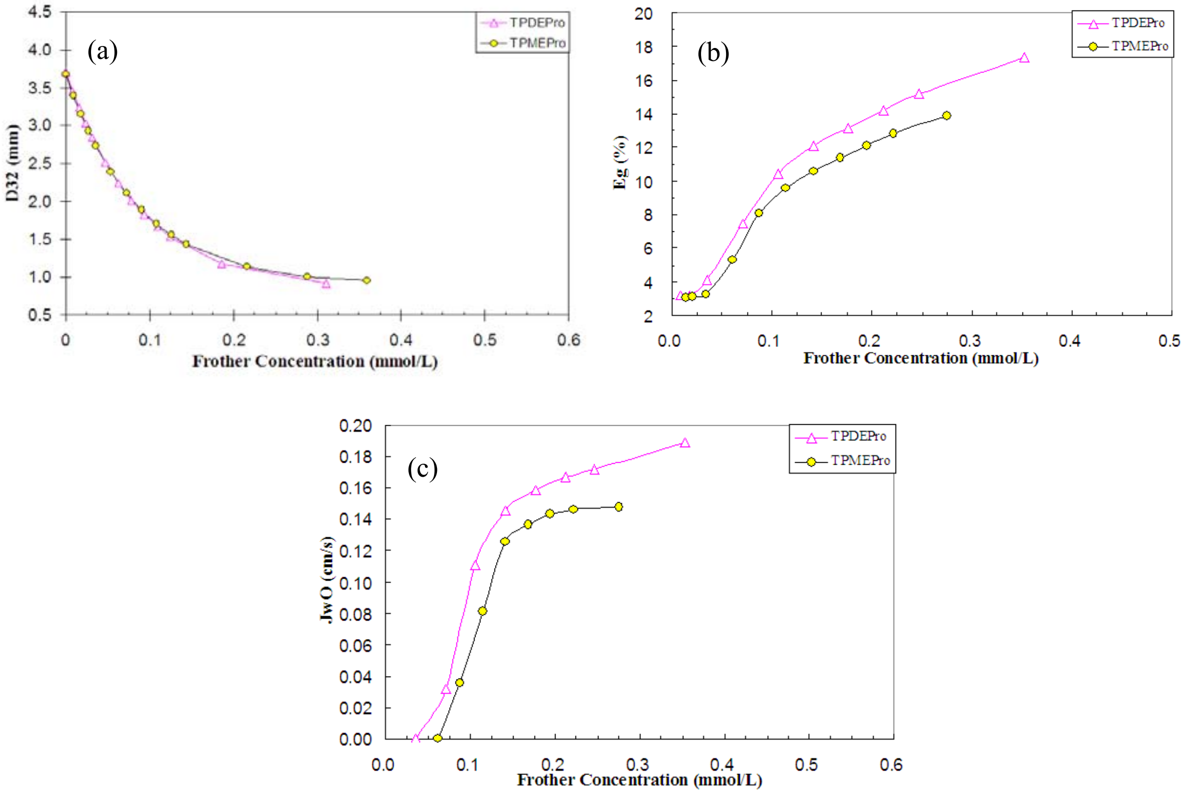


Figure 6.7: Effect of TPMEPro and TPDEPro concentration on (a) bubble size – D_{32}; (b) gas holdup – E_g; and (c) water overflow rate – J_{wO}

6.3.2.4 Influence of Position of PO and EO

Figure 6.8 suggests that switching the sequence from $[EO]_2[PO]_3$ (i.e., TPDEPro) to $[PO]_3[EO]_2$ (i.e., DETPPro) that the latter compound (DETPPro) is more effective in increasing gas holdup and water overflow rate and decreasing bubble size than the former compound (TPDEPro).

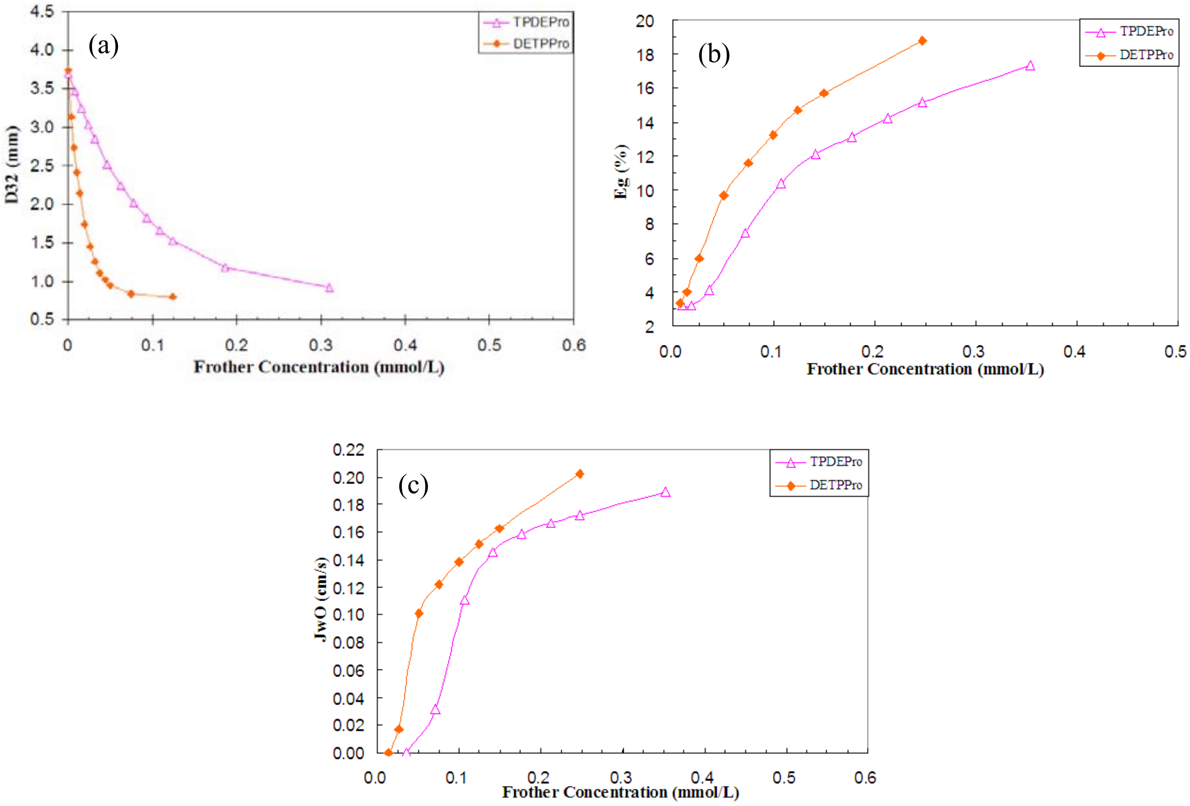


Figure 6.8: Effect of TPDEPro and DETPPro concentration on (a) bubble size – D_{32}; (b) gas holdup – E_g; and (c) water overflow rate – J_{wO}

Table 6.4 compares the new frothers with some common commercial frothers on the basis of CCC95 and minimum bubble size, D_L, and E_g and J_{wO} estimated at the CCC95. The results show that the new compounds have more influence on gas holdup and water overflow rate than the commercial frothers, even compared to F150 one of the strongest froth stabilizing commercial frothers. The disadvantage is the generally higher CCC of the synthesized compounds, the exception being DETPPro.

Table 6.4 − Effect of compounds on flotation-related parameters compared with several commercial frothers

Compounds	*Chemical formula*	*HLB*	Alkyl (C_nH_{2n+1})	PO $(OC_3H_6)_m$	EO $(OC_2H_4)_l$	*CCC95 (mmol/L)*	D_L *(mm)*	E_g* *(%)*	J_{wO}* *(cm/s)*
			n	m	l				
DPMEPro	$C_3H_7(EO)(PO)_2OH$	7.51	3	2	1	0.64	0.81	10.7	0.11
TPMEPro	$C_3H_7(EO)(PO)_3OH$	7.36	3	3	1	0.26	0.91	13.7	0.15
TPMEPen	$C_5H_{11}(EO)(PO)_3OH$	6.41	5	3	1	0.19	0.80	15.0	0.145
TPDEPro	$C_3H_7(EO)_2(PO)_3OH$	7.69	3	3	2	0.26	0.84	15.5	0.175
DETPPro	$C_3H_7(PO)_3(EO)_2OH$	7.69	3	3	2	0.04	0.80	10.0	0.10
Referenced commercial frothers									
MIBC[1]	$C_6H_{14}O$	6.05	6	-	-	0.11	0.99	6.9	0.0075
F150[2]	$H(PO)_7OH$	9.75	-	7	-	0.014	0.76	4.9	0.028
DF250[3]	$CH_3(PO)_4OH$	7.83	1	4	-	0.038	0.85	6.5	0.037
NasFroth 240[4]	$C_4H_9(EO)_3OH$	7.99	4	-	3	0.11	1.0	9.5	0.031

* the corresponding value at the concentration of its own CCC95.

[1] provided by Aldrich-Sigma Co. (Canada, Ltd).

[2] Provided by Flottec.

[3] Provided by Dow Chemical.

[4] Provided by Nasaco.

6.4 Discussion

Reagent optimization is a continuing ambition of flotation research. It entails modification of existing structures or designing new ones to provide improved performance than currently marketed reagents. Most work has been on collectors followed by modifiers with relatively little on frothers [Cytec, 2002]. This means the choice of a frother is limited, typically restricted to Alcohols and Polyglycols. The situation is changing, from the pioneering days of Klimpel and Hansen [1988], Klimpel and Isherwood [1991] and Klimpel [1995] and to the wide range of frothers provided by, for example, Flottec [Cappuccitti, 2011]. Frothers along with air are the common operational variables used to control flotation plants so a focus on frothers is overdue.

The search for new frother chemistries might become less daunting if a frother structure-property relationships approach is used. The structure represents the type, number and position of functional groups in the molecular architecture. The property refers to parameters such as bubble size, gas holdup and water overflow rate which relate to flotation performance.

The first investigation into frother structure-property relationships was by Laskowski and coworkers [1998; 2003]. They investigated the n-Alcohol homologous series by increasing length of alkyl chain and the commercial Polypropylene Glycol Alkyl Ether (PPGAE) homologous series (e.g. DF200, DF250 and DF1012) by varying the number of Propylene Oxide (PO) groups. The results indicated that with the increasing either the length of alkyl chain or number of PO groups, the ability of these compounds to reduce bubble size and create froth improved. By exploring a new homologous series of Ethoxylated Alcohols by altering the number of Ethylene Oxide (EO) groups, Cuppuccitti and Finch [2008] found that by changing the number of EO group products could be made slightly weaker or stronger than MIBC but they could not provide characteristics similar to Polyglycol frothers like PPG or PPGAE. The literature, therefore, does imply some potential benefits of designing new frother compounds for improved flotation performance.

The ultimate goal is to create a general guideline through frother structure-property relationships for designing formulations which can be used to fine-tune properties for a given application. As a start, a new series of compounds, four linear Alkyl-Ethoxy-Propoxylates and one linear Alkyl-Propoxy-Ethoxylate were synthesized with structural variation ranging from 3 to 5 alkyl, 2 to 3 PO, 1 to 2 EO groups and as well as switching the sequence of PO and EO.

The structural characterization of the compounds was made through interpretation of ^{1}H NMR spectra. The average number of each group in the compound was estimated by calculating the integrated area of the proton signals and the ratio of methylene and/or methyl units which represent each chemical group in the molecule. Figure 6.3 and Table 6.3 show the five compounds were identified, the structures confirmed, and the average number of each group estimated by ^{1}H NMR was in accordance with the number derived from the molecular formula.

Total organic carbon (TOC) is an effective straightforward analysis that can accurately quantify the weight fraction of organic carbon in a sample. Since only one organic compound was present and the corresponding formula had been identified, the measured TOC match with the calculated TOC from the formula indicated high purity of the compound.

The approach for characterizing the frothers considered three parameters: bubble size, gas holdup and water overflow rate. As shown in Figure 6.5, increasing the number of PO (m = 2→3) had a significant effect on all three. Compared with PO number, increasing the length of the alkyl chain (n = 3→5), showed the same but less significant trends. For instance, as shown in Table 6.4, the CCC95 for TPMEPro (m = 3; n = 3) is 0.26 mmol/L, which is 2.5 times less than DPMEPro (m = 2) but only 1.4 times more than TPMEPen (n = 5). Comparing the effect of number of PO and number of carbons in the alkyl group an interpretation might be forthcoming from the HLB of the compounds. The HLB number of Propylene Oxide (PO) is -0.15 and is -0.475 for every segment (-CH-, $-CH_2-$ and $–CH_3-$) in the alkyl chain, therefore the HLB number decreases less upon increasing the number of PO by 1 (-0.15*1 = -0.15) compared to increasing the length of alkyl chain by 2 carbons (-0.475*2 = -0.95) indicating the former molecule is more hydrophilic which correlates with the larger increase in CCC95 [Zhang et al., 2012] and greater increase of gas holdup and water overflow rate.

Figure 6.7 shows that increasing the number of EO left the bubble size constant but did increase gas holdup and water overflow rate. Since gas holdup results represent bubble size conjointly with rising velocity [Rafiei et al., 2011], the apparent contradiction between bubble size and gas holdup results could be attributed to a decrease of bubble rise velocity by increasing the number of EO. The HLB group number for the EO is 0.33, i.e., the HLB increases with EO, the molecule becomes more hydrophilic and this correlates with the increased water overflow rate (and increased CCC).

The position of substituents is shown in Figure 6.8. Without changing HLB number and molecular weight, DETPPro with the linear hydrophobic-hydrophobic-hydrophilic-hydrophilic structure was found to be more effective than TPDEPro with the linear hydrophobic-hydrophilic-hydrophobic-hydrophilic structure in decreasing bubble size and increasing gas holdup and water overflow rate. Compared with the conventional strong frother DF250 (Table 6.4), DETPPro reveals a similar CCC95, but higher gas holdup and water overflow rate, respectively at the CCC95 concentration.

6.5 Conclusions

Five new potential frothers were synthesized combining three chemical groups of the Alcohol and Polyglycol families. Frother characterization was performed by measuring bubble size, gas holdup and water overflow rate.

The study has shown that increasing the number of PO decreases bubble size and increases gas holdup and water overflow rate. Compared with increasing the length of alkyl group, the trends in these three parameters are similar but less than caused by increasing the number of PO groups. Increasing the number of EO groups did not affect bubble size but increased gas holdup and water overflow rate.

Comparing a hydrophobic-hydrophobic-hydrophilic-hydrophilic structure to hydrophobic-hydrophilic-hydrophobic-hydrophilic by changing the location of the PO and EO groups, the former gave significantly higher gas holdup and water overflow rate and lower bubble size. The former also gave higher gas holdup and water overflow rate compared to the conventional strong frother DF250, but with a comparable CCC95.

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Chapter 7 - Conclusions

7.1 Conclusions

Frothers are heteropolar surface-active organic compounds containing various structural groups. The two prime functions of frother are to control bubble size and to stabilize the froth phase. This thesis aims to determine the relationship between frother molecular structure and function, through a flow of structure-function related topics starting from single frothers to blends necessitating new analytical methods to designing new frothers.

A structure-function approach to characterizing frothers was explored using Hydrophile-Lypophile Balance (HLB) to represent chemical structure and Critical Coalescence Concentration (CCC) to represent the bubble size reduction function. The tests were conducted in a 0.8 m^3 mechanical cell on 36 pure surfactants and commercial frothers of Aliphatic Alcohol, Polypropylene Glycol Alkyl Ether and Polypropylene Glycol (Polyglycol) families. The result was a series of self-similar CCC-HLB trends dependent on n (number of C-atoms in alkyl group) and m (number of Propylene Oxide groups). The Alcohol data also showed an isomer effect at $n < 5$. Empirical models were developed for the Polyglycols and 1-Alcohols showing that CCC could be predicted knowing n and m, i.e., knowing the structure. This finding is a significant step towards modeling the effect of frother on bubble size in flotation systems.

A dual frother system was established to examine if the independent control over the froth property water overflow rate (J_{wO}) and two pulp hydrodynamic properties, Sauter mean bubble size (D_{32}) and gas holdup (E_g), could be achieved. The blends studied were Alcohols with either Polypropylene Glycols (PPG) or Polyethylene

Glycols (PEG). The pre-mixed style, represented as Alcohol/Propylene Oxide and Alcohol/Ethylene Oxide blends, did not give independent control over the two functions. In alternative base/additive approach, 1-Hexanol/TetraEG, 1-Butanol/DPG and 1-Butanol/TPG were rejected because of negative effects, such as an increase in bubble size; however, using 1-Butanol/PEG, independent control was demonstrated provided the PEG had four or more Ethylene Oxide groups.

Two techniques were developed to analyze individual frother concentration in dual frother blends, one using HPLC and a second using a novel NMR/TOC combination. The methods were used to determine frother partitioning between underflow and overflow in continuous testing in a bubble column. Strong partitioning to the overflow of 1-Butanol and 1-Pentanol was shown in blends with Dipropylene Glycol and F150, respectively, but little partitioning for 1-Butanol blended with Tetraethylene Glycol. These findings offer an explanation of the increase in bubble size reported in the former two cases. Together HPLC and NMR/TOC offer a flexible way to analyze frother blends to help interpret their action in flotation systems.

Five new potential frothers were synthesized combining three chemical groups of the Alcohol and Polyglycol families. Frother characterization was performed by measuring bubble size, gas holdup and water overflow rate. The study has shown that increasing the number of PO decreases bubble size and increases gas holdup and water overflow rate. Compared with increasing the length of alkyl group, the trends in these three parameters are similar but less than caused by increasing the number of PO groups. Increasing the number of EO groups did not affect bubble size but increased gas holdup and water overflow rate.

Comparing a hydrophobic-hydrophobic-hydrophilic-hydrophilic structure to hydrophobic-hydrophilic-hydrophobic-hydrophilic by changing the location of the PO and EO groups, the former gave significantly higher gas holdup and water overflow rate and lower bubble size. The former also gave higher gas holdup and water overflow rate compared to the conventional strong frother DF250, but with a comparable CCC95.

7.2 Contributions to Knowledge

1. The first to demonstrate the CCC95-HLB relationship by studying a sufficiently large frother database. Built on previous work [Laskowski, 2004; Nesset et al., 2012], it is the first work to show that each frother family has a unique CCC95-HLB relationship. Commercial frothers of known family are shown to fit the relationships. This ability to estimate CCC95 from structure/HLB information is a step in modeling the role of frother in controlling bubble size in flotation machines.

2. The first to demonstrate that 1-Butanol/PEG base/additive blend can achieve independent control of bubble size and water overflow rate.

3. The first to measure frother partitioning in dual-frother blends which helped explain the increase in bubble size noted with some blends.

4. The first to devise the NMR/TOC technique to determine frother concentration.

5. The first to synthesize and investigate properties of a new frother series comprised of three chemical groups, linear Alkyl-Ethoxy-Propoxylates ($C_nEO_lPO_m$) and Alkyl-Propoxy-Ethoxylates ($C_nPO_mEO_l$).

7.3 Recommendations for Future Work

1. Explore an alternative method for predicting the CCC95 values of frothers based on NMR spectrometry. The H-ratio can be determined by integrating signal

intensities in the NMR spectra, to substitute for HLB. Such a method is potentially fast and accurate and may predict CCC95 for most of the commercial frothers (but not blends) for which structures are seldom disclosed (i.e. HLB cannot be calculated using Davies equation).

2. Extend the HLB-CCC relationship found from two-phase experiments to three-phase (i.e. presence of solids); adding solids will provide further insight into the complex nature of flotation machine hydrodynamics. Validate the laboratory findings in a plant environment; ideally, the same Metso 0.8 m^3 mechanical cell could be used.

3. Some collectors such as fatty acids (e.g. sodium oleate) exhibit froth stabilization and bubble size reduction abilities. As a follow on from the dual-frother study, these frother-acting collectors might be considered as candidates to examine if independent control can be achieved by frother-collector combinations.

Appendix I − Metso RCS^{TM} 0.8 m^3 Mechanical Cell Geometrical Details – CAD Drawing

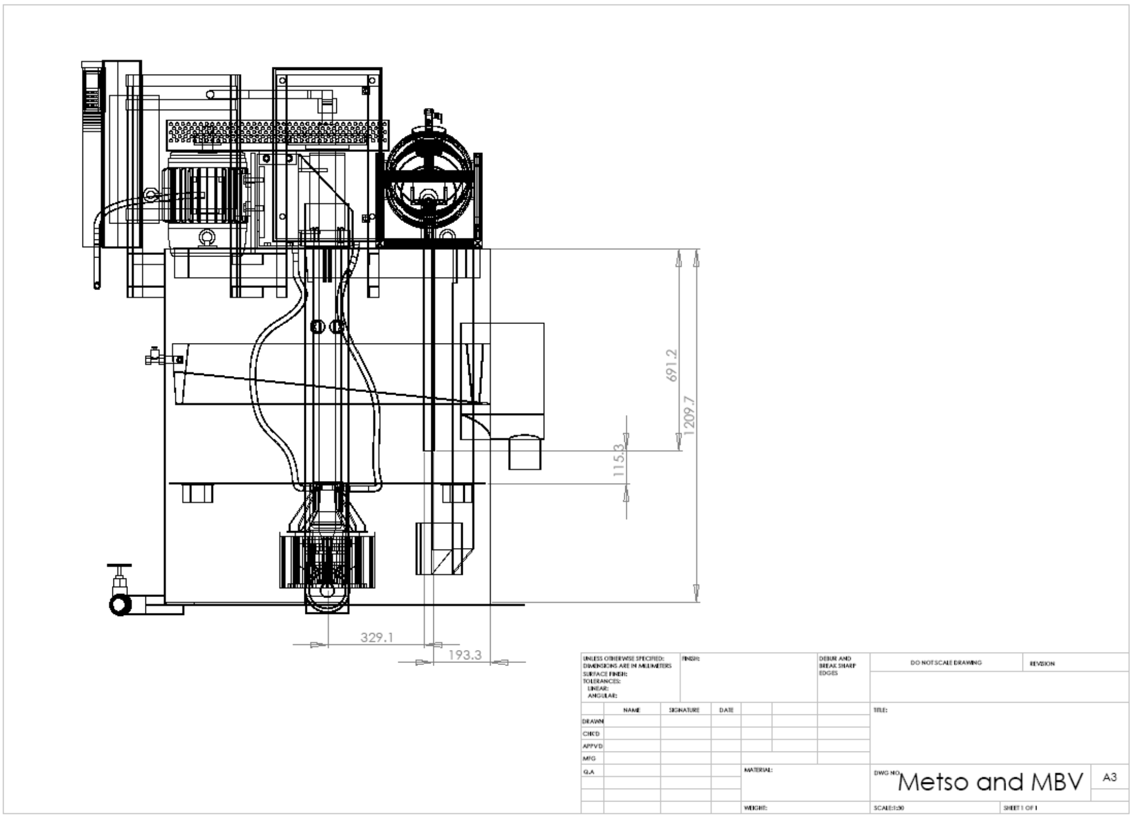
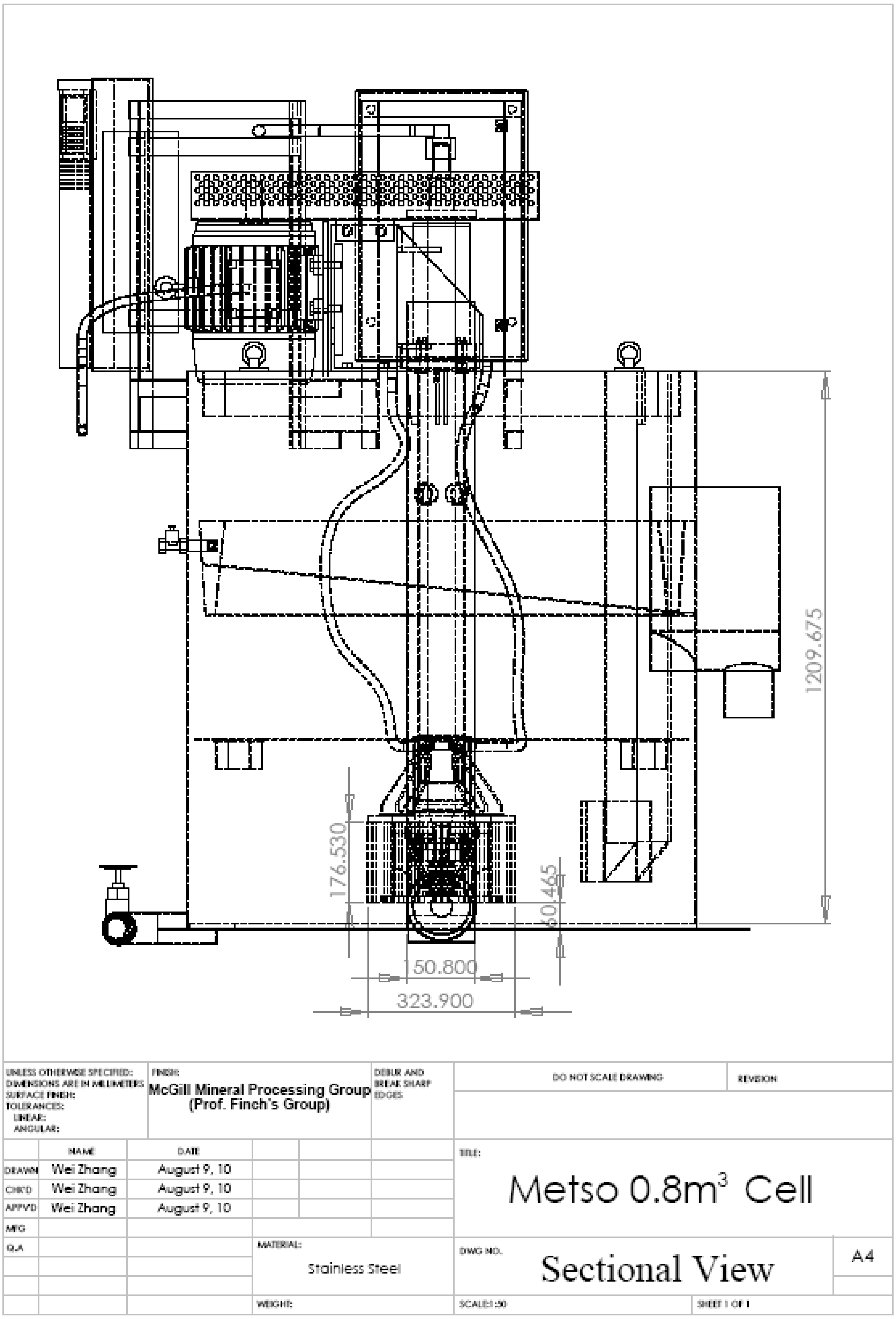


Figure AI-1: General arrangement drawing



UNLESS OTHERWISE SPECIFIED:
DIMENSIONS ARE IN MILLIMETERS
SURFACE FINISH:
TOLERANCES:
LINEAR:
ANGULAR:

FINISH:
McGill Mineral Processing Group
(Prof. Finch's Group)

DEBUR AND BREAK SHARP EDGES

DO NOT SCALE DRAWING

REVISION

	NAME	DATE
DRAWN	Wei Zhang	August 9, 10
CHK'D	Wei Zhang	August 9, 10
APPV'D	Wei Zhang	August 9, 10
MFG		
Q.A		

MATERIAL: Stainless Steel

WEIGHT:

TITLE: Metso 0.8m^3 Cell

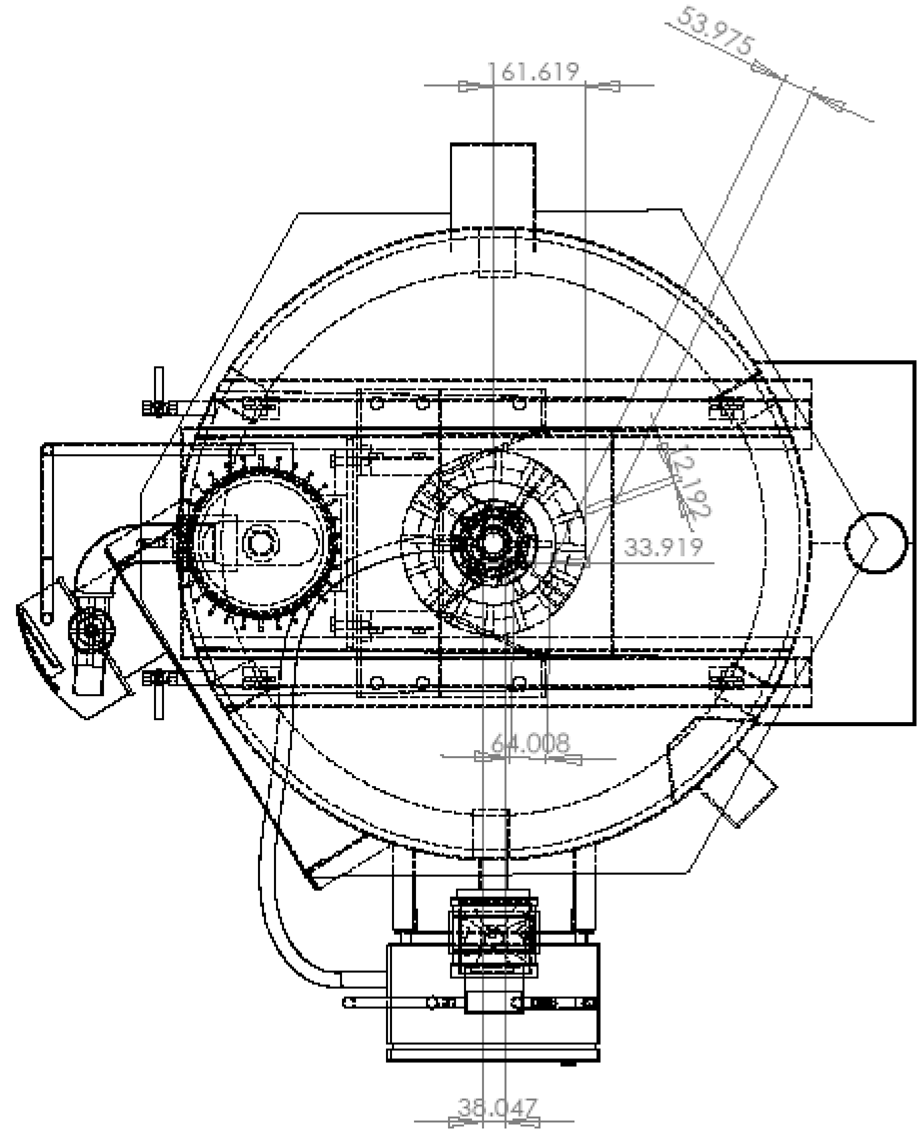
DWG NO. Sectional View

A4

SCALE:1:50

SHEET 1 OF 1

Figure AI-2: Cell sectional view



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DIMENSIONS ARE IN MILLIMETERS
SURFACE FINISH:
TOLERANCES:
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ANGULAR:

FINISH:
McGill Mineral Processing Group
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DEBUR AND BREAK SHARP EDGES

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REVISION

	NAME	DATE
DRAWN	Wei Zhang	August 9, 10
CHK'D	Wei Zhang	August 9, 10
APPV'D	Wei Zhang	August 9, 10
MFG		
Q.A		

TITLE:
Metso 0.8m³ Cell

MATERIAL:
Stainless Steel

DWG NO.
Vertical View

A4

WEIGHT:

SCALE:1:50

SHEET 1 OF 1

Figure AI-3: Cell vertical view

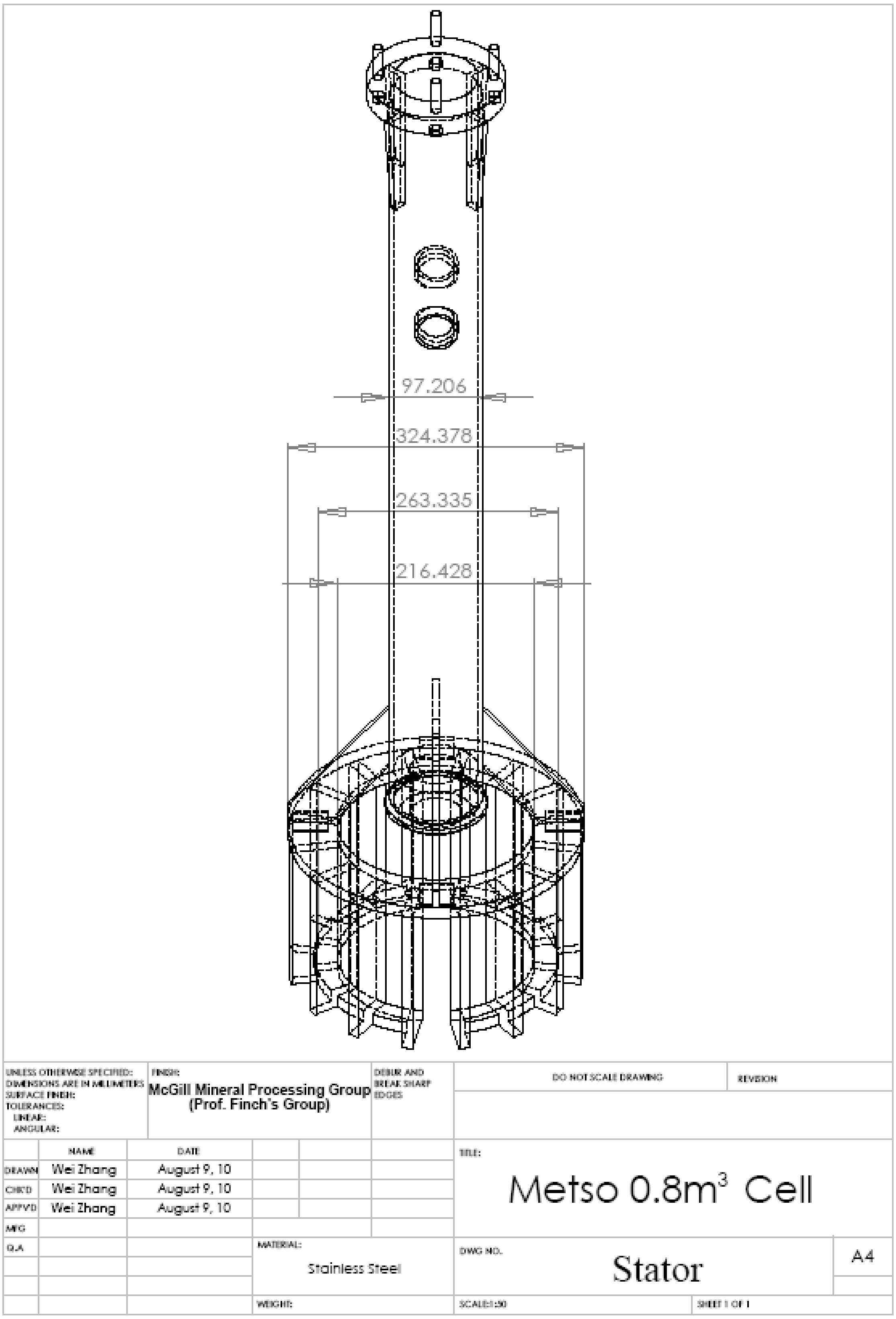


Figure AI-4: Cell impeller/stator mechanism – stator

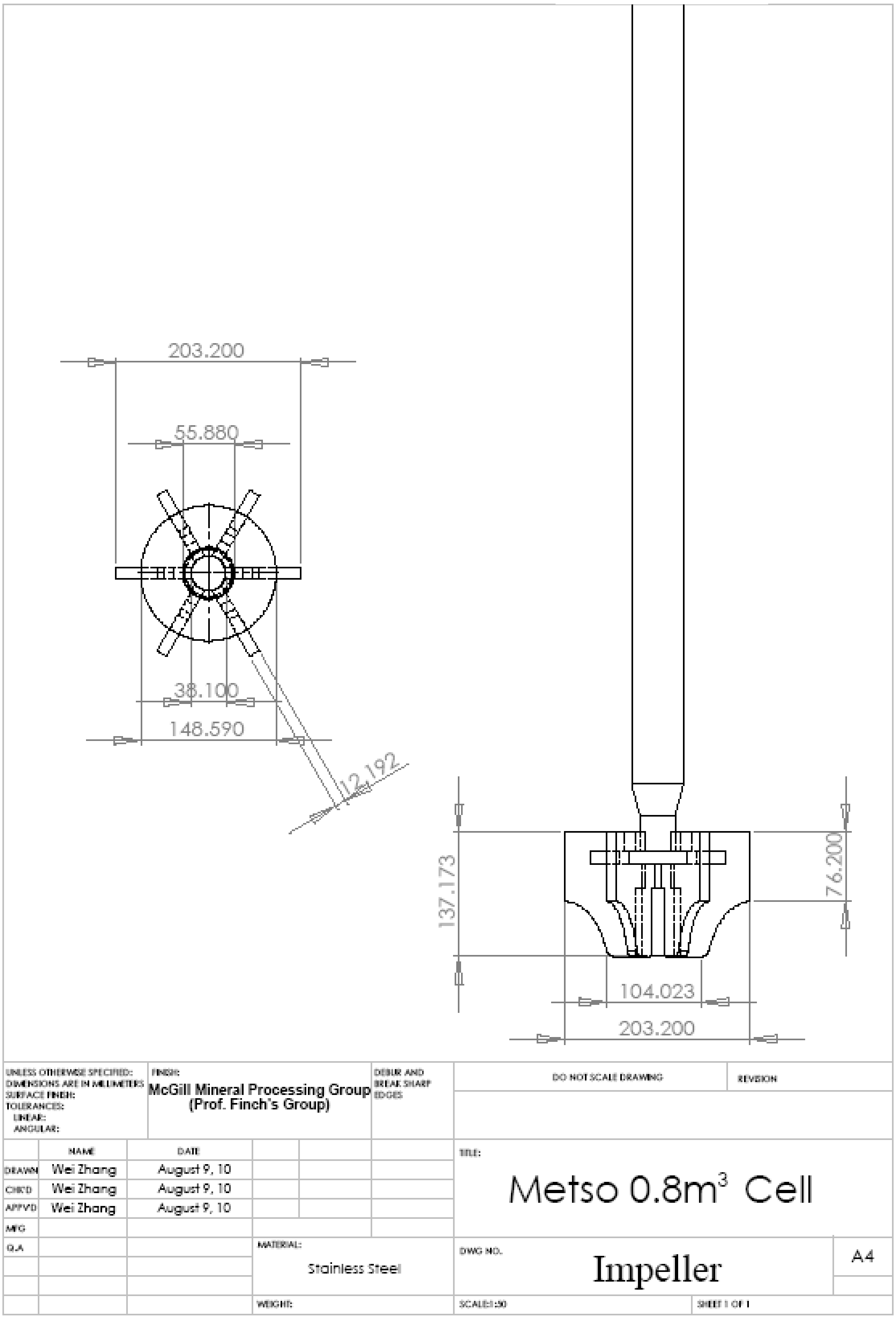


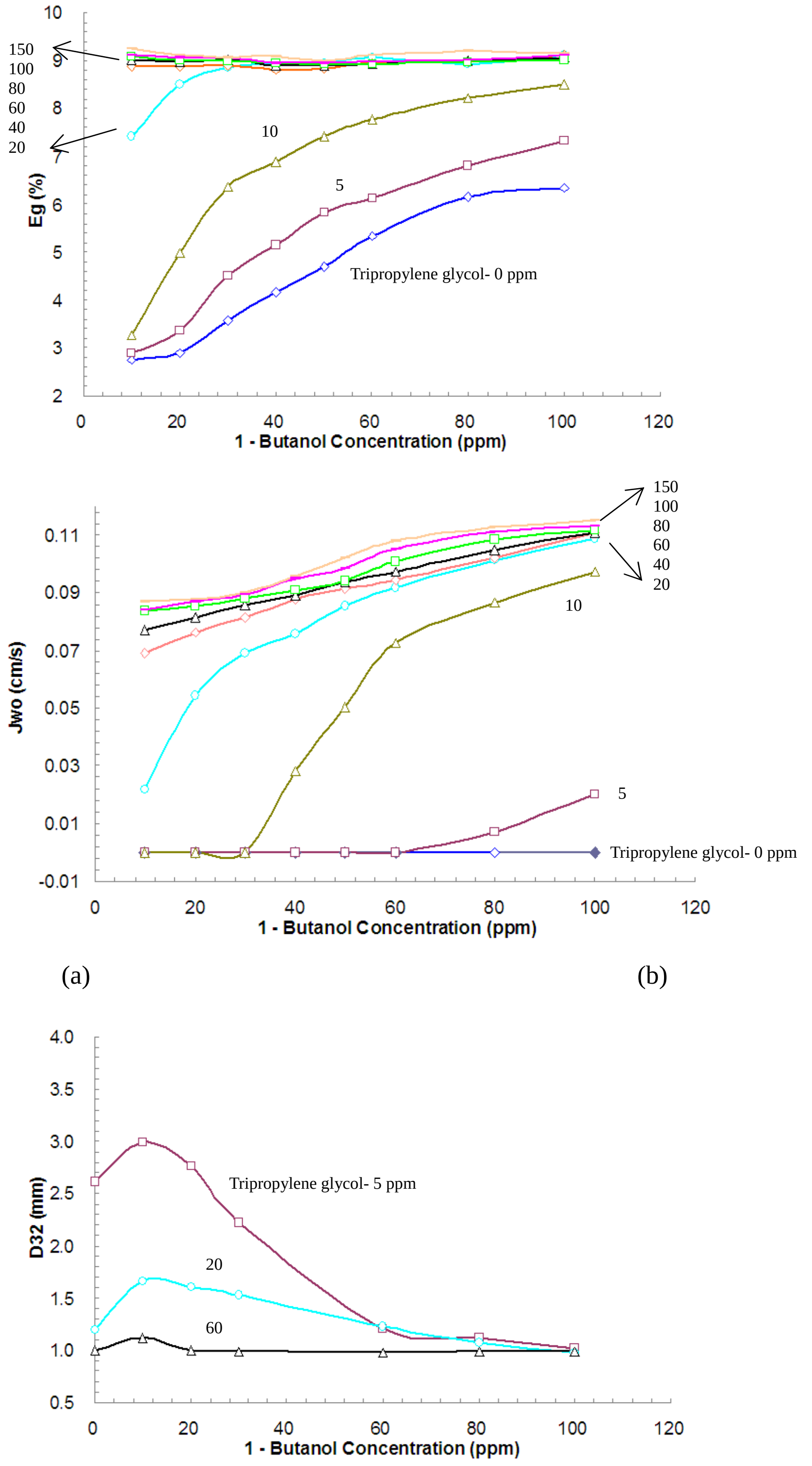
Figure AI-5: Cell impeller/stator mechanism - impeller

Appendix II ‒ Supplementary Experimental Data for Chapter 3

Table AII-1 ‒ Hydrophile-Lipophile Balance (HLB) group numbers – all functional groups (according to the Davies method)

Functional group	***Group contribution number***
Hydrophilic	
$-SO_4Na^+$	38.7
$-COO^-H^+$	21.1
$-COO^-Na^+$	19.1
N (tertiary amine)	9.4
Ester (sorbitan ring)	6.8
Ester (free)	2.4
-COOH	2.1
OH (sorbitan ring)	0.5
OH (free)	1.9
-O-	1.3
Lipophilic (or hydrophobic)	
-CH-	-0.475
-CH2-	-0.475
CH3-	-0.475
=CH-	-0.475

Appendix III – Supplementary Experimental Data for Chapter 4



(a) (b)

(c)

Figure AIII-1: Effect of 1-Butanol (additive) concentration on (a) gas holdup – E_g; (b) water overflow rate – J_{wO}; and (c) bubble size – D_{32}, in the presence of Tripropylene glycol (base)

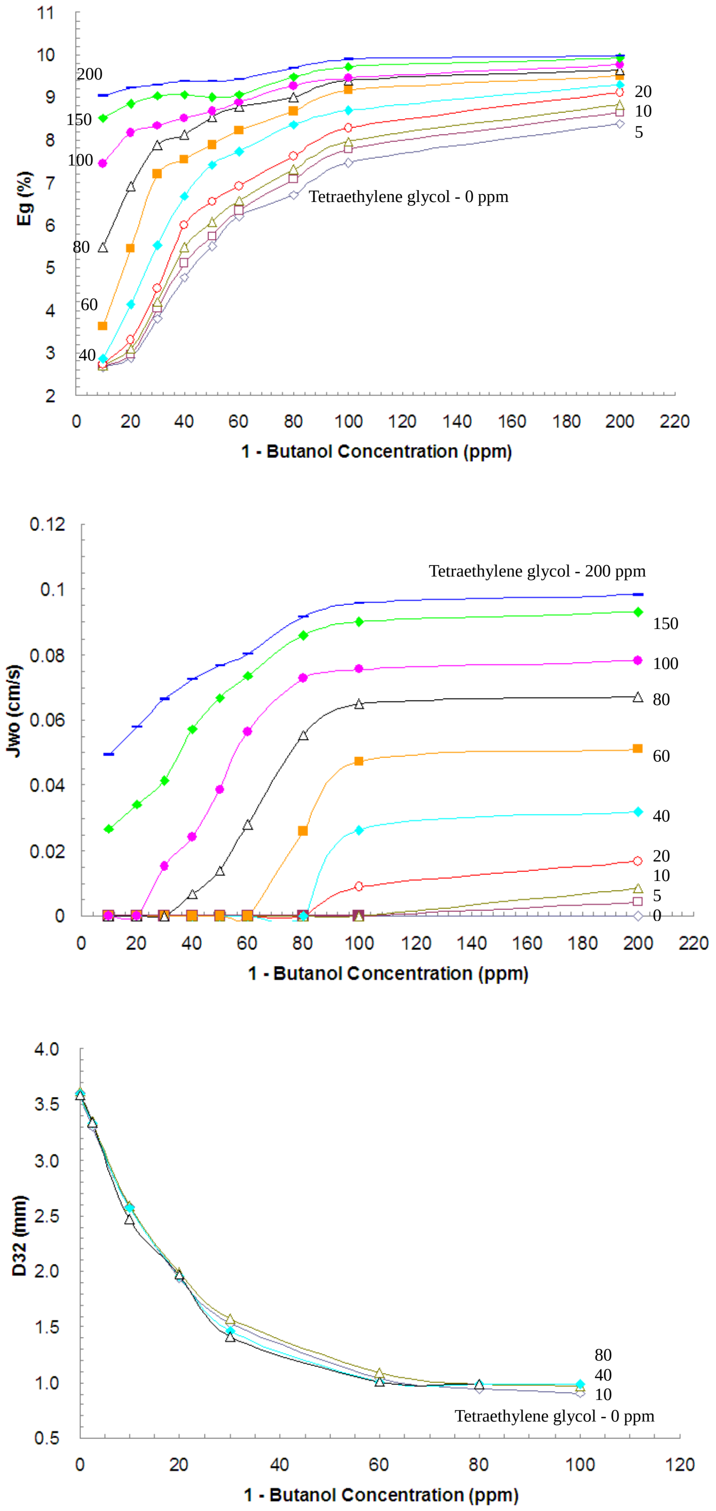


Figure AIII-2: Effect of 1-Butanol (additive) concentration on (a) gas holdup – E_g; (b) water overflow rate – J_{wO}; and (c) bubble size – D_{32}, in the presence of Tetraethylene glycol (base)

Appendix IV – Supplementary Experimental Data for Chapter 5

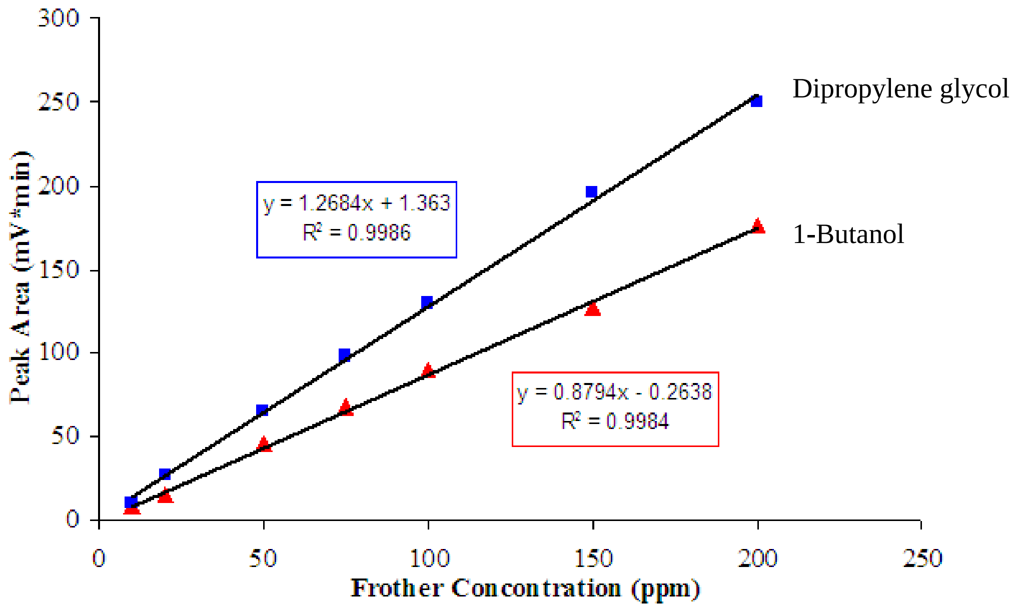


Figure AIV-1: HPLC Calibration plot of 1-Butanol and Dipropylene Glycol in the blend

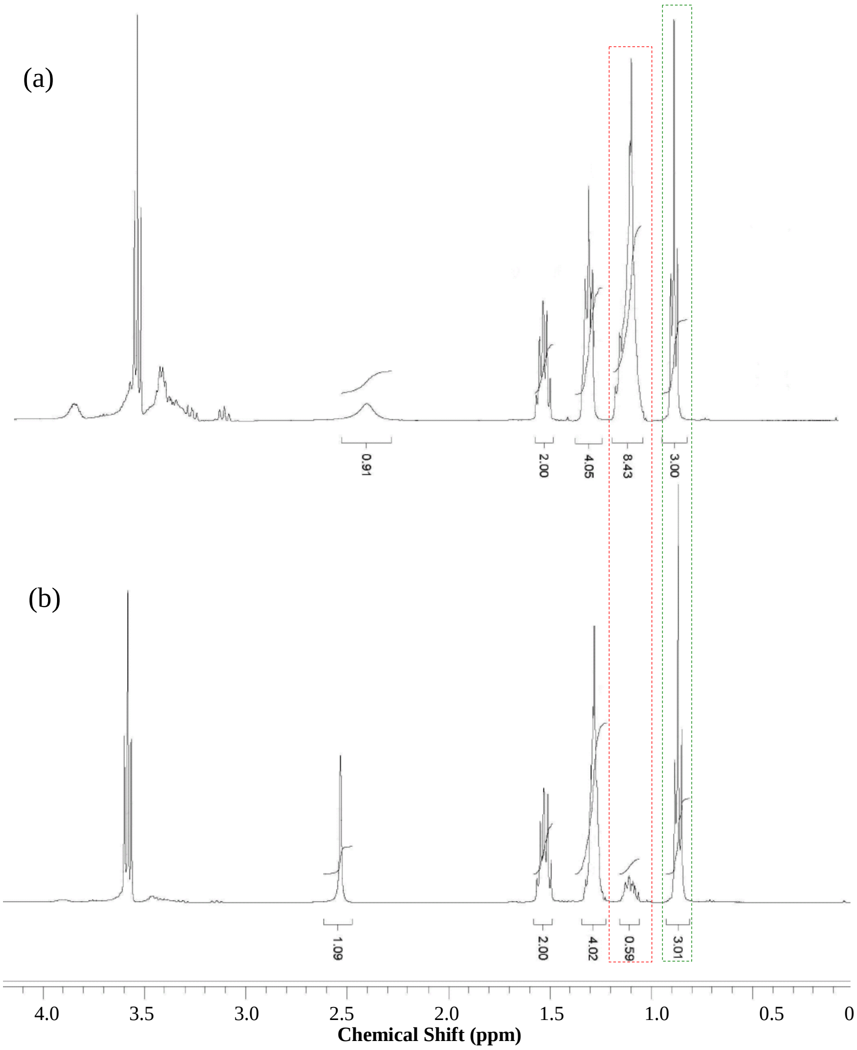


Figure AIV-2: An example NMR spectra and signal integrations of the mixed frothers in (a) overflow and (b) underflow, at the system concentration of 40 ppm 1-Pentanol (base) and 5 ppm F150 (additive)

Appendix V – Supplementary Experimental Data for Chapter 6

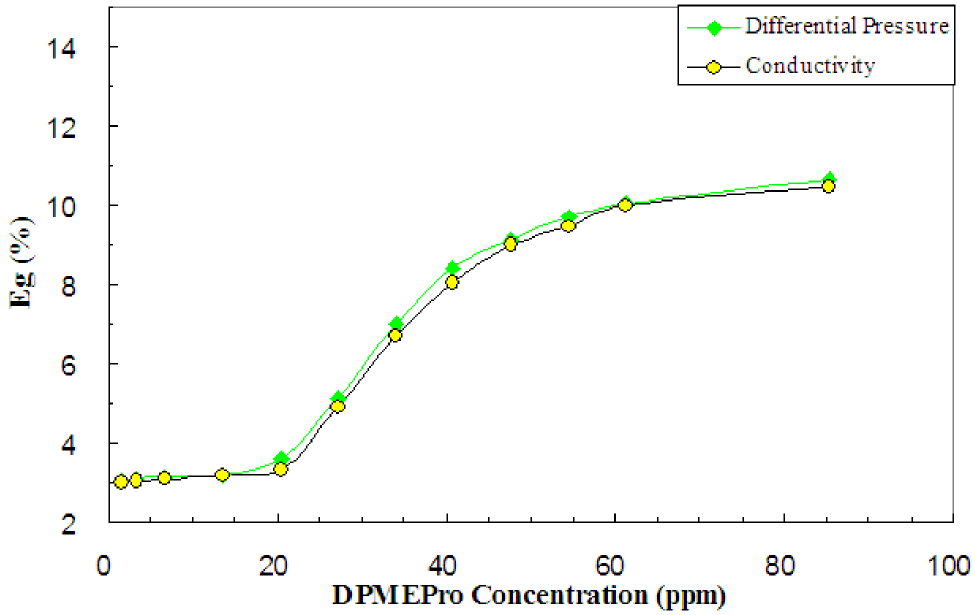


Figure AV-1: Validation Test: gas holdup (Eg) measured by differential pressure method compares well with conductivity method - use DPMEpro as an example

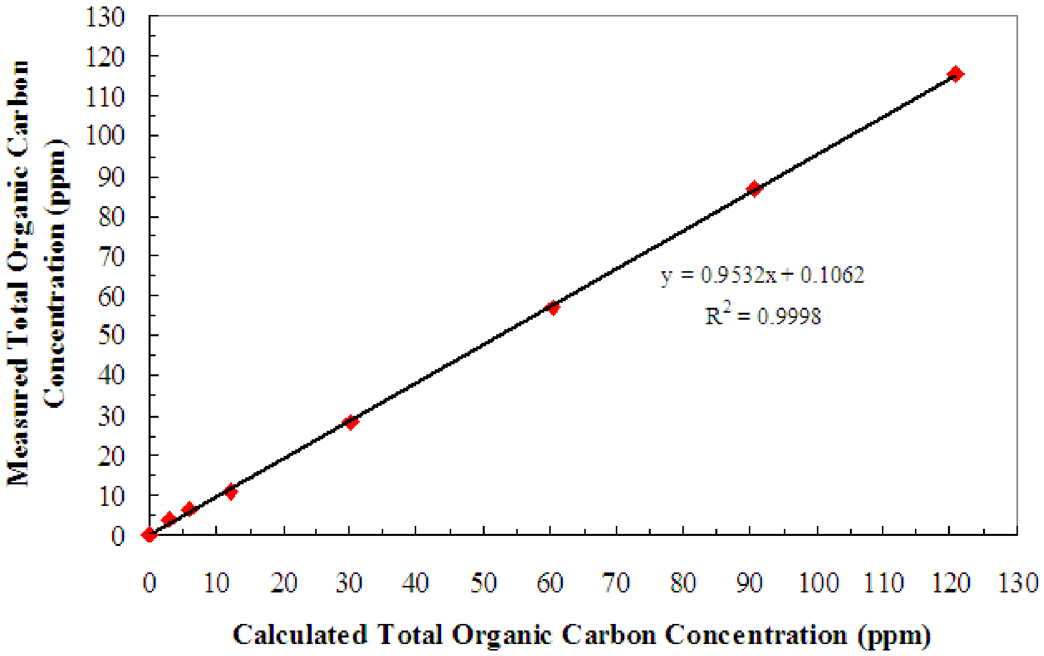


Figure AV-2: Calculated total organic carbon concentration of TPMEPro compares well with measured concentration by TOC analysis

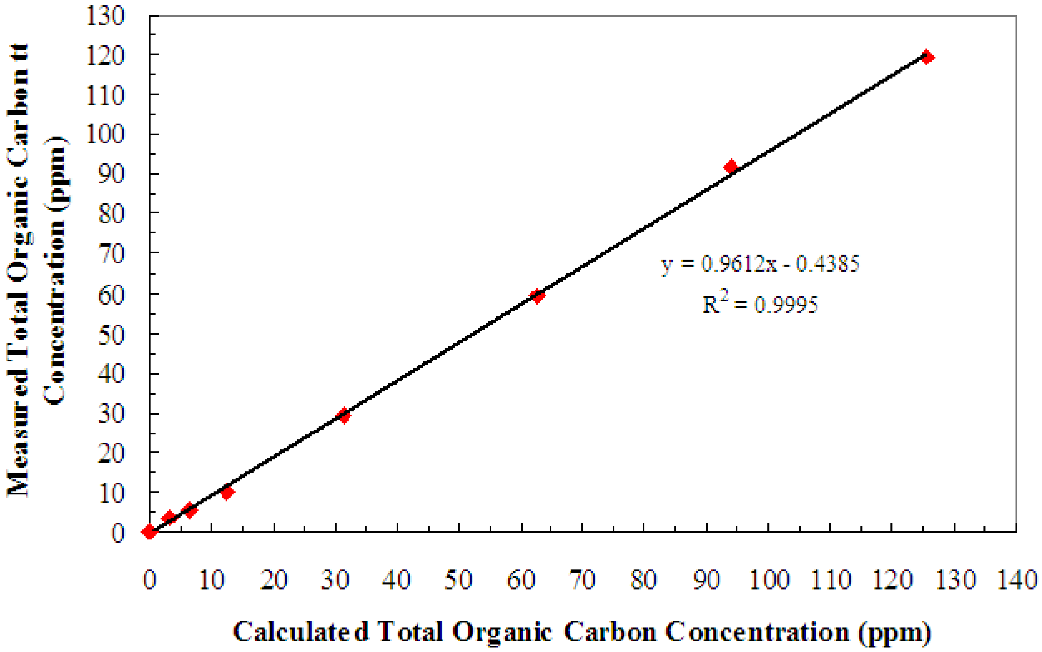


Figure AV-3: Calculated total organic carbon concentration of TPMEPen compares well with measured concentration by TOC analysis

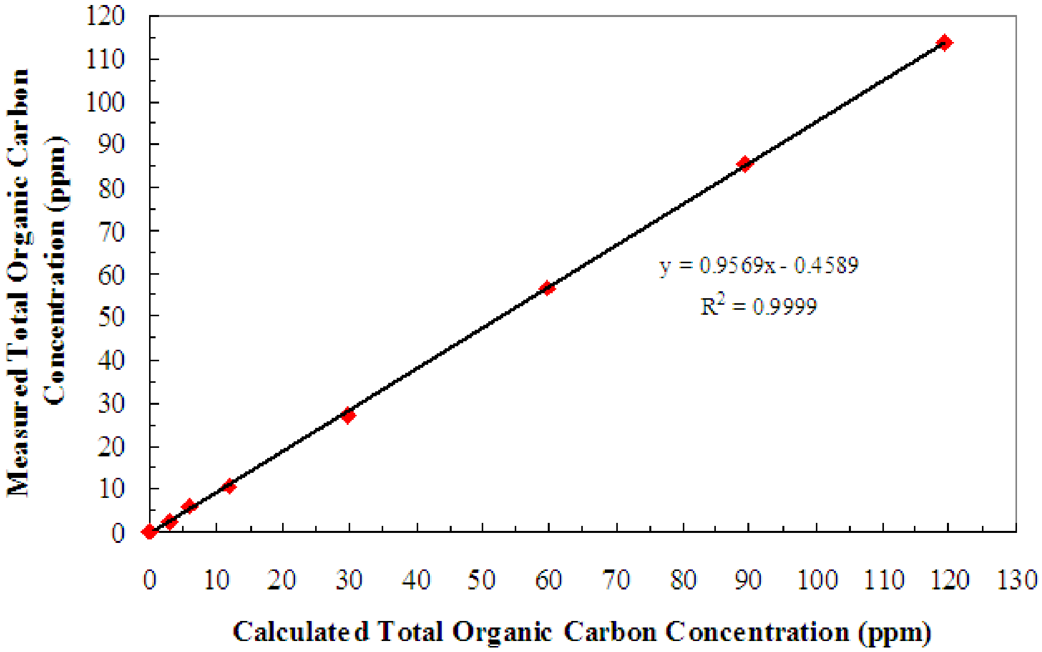


Figure AV-4: Calculated total organic carbon concentration of TPDEPro compares well with measured concentration by TOC analysis

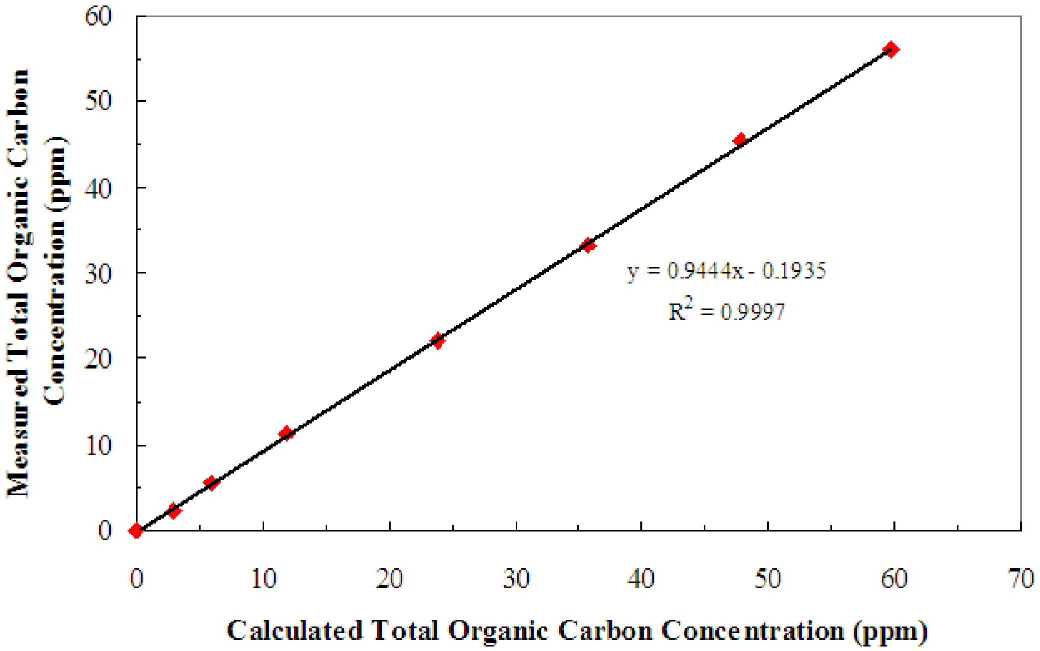


Figure AV-5: Calculated total organic carbon concentration of DETPPro compares well with measured concentration by TOC analysis

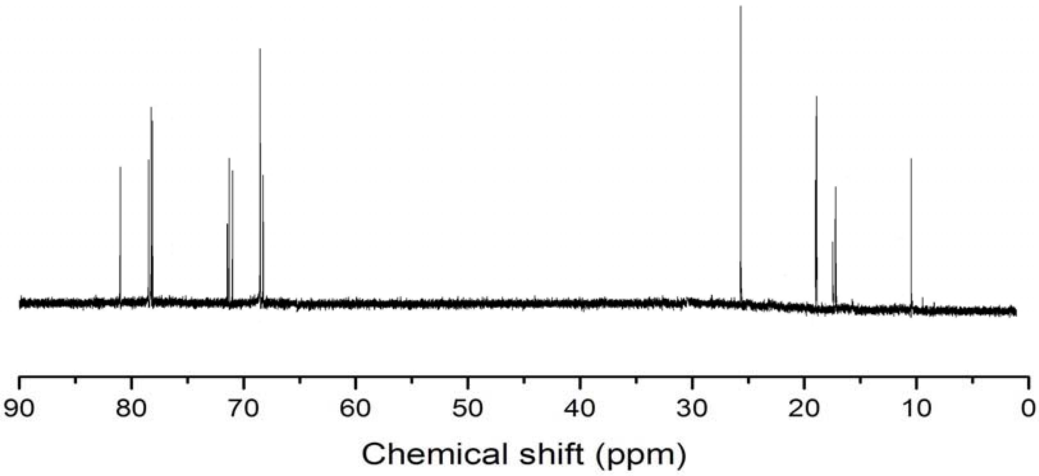


Figure AV-6: An example of ^{13}C NMR spectra of DPMEPro