

FROTHING PROPERTIES OF FATTY ACID COLLECTORS

by

Avishan Atrafi

M.Sc., University of Tehran, 2008

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES
(MINING ENGINEERING)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

February 2015

© Avishan Atrafi, 2015

Abstract

The gas dispersion and foaming properties of aqueous solutions of fatty acids of different hydrocarbon chain lengths were assessed through measurements of bubble size distributions, gas hold-up, foam volume and growth rate. The adsorption behavior of the tested fatty acids at the gas-solution interface was assessed and the results were supplemented by measurements of the partition of each surfactant between the bulk solution and foam phase as a result of continuous aeration.

Two mechanisms of gas dispersion were identified depending on the pH and speciation of the tested solutions. Solutions of long chain fatty acids containing colloidal precipitates at low pH exhibited low surface tensions, and only a small decrease in bubble sizes was observed for such solutions compared to bubble sizes measured in water. This relatively small change in bubble sizes could theoretically be predicted based only on the corresponding change in the surface tension of the solutions. In contrast, true solutions of long chain fatty acids affected bubble sizes to a much greater extent even though their surface tension values were higher and in some cases comparable to the surface tension of water. A combination of the surface tension and surface tension gradient effects was found to be operative in this case.

Experimental results strongly suggested that the associated acid species were more surface-active and more capable of reducing bubble sizes than the dissociated carboxylate anion.

The ability of the surfactants to quickly generate a large foam volume was found to be a strong function of the chain length. Although bubble size measurements in bulk solution pointed towards similar gas dispersing abilities of fatty acids of different chain lengths, their foamabilities under the same conditions were remarkably enhanced by increasing chain length. Creation of large volumes of persistent foam was correlated with strong tendency to partition into the foam phase.

Overall, the gas dispersing properties of fatty acids were comparable to those of a weak frother such as methyl isobutyl carbinol (MIBC), while only the foaming capabilities of hexanoate were similar to those of MIBC. Longer chain fatty acids were much stronger foaming agents than MIBC.

Preface

The author performed all the experiments described in this thesis. Chapters 1, 2 and 3 provide respectively an introduction to the research, literature review and experimental set up constructed or adopted for the purpose of this research.

Chapter 4 includes the initial surface tension characterization performed by the author to characterize the anionic reagents used in the research.

Chapter 5 contains the results of gas dispersion measurements of the tested anionic reagents. The preliminary measurements for sodium oleate were performed during a one-month visit by the author in the Department of Materials and Chemical Engineering at McGill University (included in appendix 4). Those results in combination with part of the data from Chapter 6 led to publication of the following paper: Atrafi, A., Gomez, C.O., Finch, J.A., Pawlik, M., 2012, Frothing behavior of aqueous solutions of oleic acid, *Minerals Engineering*, 36-38, 138-144.

Chapter 6 provides the results of foamability measurements on selected anionic reagents performed with the use of a foamability set-up built by the author.

The special column for bubble size and gas hold-up measurements was constructed and instrumented by the author based on a similar set up at McGill University in Montreal (Prof. James Finch's lab). Compared to the McGill column, the UBC column for bubble size measurement was modified as follows: A tubing connection was designed for the bubble viewer to be able to fill it up automatically and a valve was designed at the connection of bubble viewer to the sampling tube to eliminate the use of a cork stopper at the bottom of sampling tube. In this set up, a stable gas hold up value is read from the display screen of differential pressure transmitter instead of gathering the historical data through a control system.

Table of contents

Abstract.....	ii
Preface.....	iii
Table of contents	iv
List of tables.....	vii
List of figures.....	viii
Acknowledgements	xiv
Dedications.....	xv
1. Introduction.....	1
1.1 Fatty acids in flotation	1
1.2 Frothing action.....	2
1.3 Scope of the dissertation.....	3
1.4 Objectives	3
2. Literature review	5
2.1 General properties of fatty acids as flotation reagents	5
2.1.1 Species distribution.....	5
2.1.2 Domain diagram.....	8
2.1.3 Critical micelle concentration (CMC)	10
2.1.4 The pK_a value.....	11
2.1.5 Solubility	13
2.2 Flotation of semi soluble salt type minerals using fatty acids	16
2.2.1 Effect of pH.....	16
2.2.2 Effect of conditioning time	17
2.3 Gas dispersion characteristics of surfactants	19
2.3.1 Terminology.....	19
2.3.2 CCC and HLB.....	23
2.4 Foamability behaviour	26
2.4.1 Theories of foamability	26
2.4.2 Foamability measurement.....	29
2.4.3 Effect of surfactant structure on foamability	33
2.5 Adsorption behaviour at the gas-liquid interface	34
2.5.1 Gibbs adsorption theory	34
2.5.2 Dynamic surface tension (DST).....	36
2.6 Electrokinetic properties.....	38
2.6.1 Electrokinetic properties of bubbles in presence of weak electrolyte surfactants ..	38
2.6.2 Role of precipitates in electrokinetic behaviour	41
2.6.2.1 Effect of Ca^{2+} ions on electrokinetic behaviour of fatty acids	42

3.	Experimental set up	44
3.1	Procedures, methods and equipment	44
3.1.1	Surface tension measurements	44
3.1.1.1	Wilhelmy plate method	45
3.1.1.2	Pendant drop method	46
3.1.1.3	Maximum bubble pressure (MBP)	50
3.1.1.4	Comparison of surface tension methods.....	50
3.1.2	Turbidity measurements.....	51
3.1.3	Foamability measurement methods	52
3.1.3.1	Dynamic Foamability Index (DFI)	52
3.1.3.2	Froth Growth Rate	53
3.1.4	Frother partitioning between bulk solution and foam phase (TOC analysis)	54
3.1.5	Water recovery measurements.....	55
3.1.6	Gas dispersion measurements	56
3.1.6.1	Bubble size measurements.....	56
3.1.6.2	Gas hold-up measurements.....	60
3.2	Reagents sources and preparation procedure.....	62
3.2.1	Fatty acids (oleate, laurate, hexanoate and tall oil).....	62
3.2.2	Sulfates (sodium dodecyl and octadecyl sulfate).....	63
3.2.3	MIBC	63
4.	Interfacial properties of fatty acids.....	65
4.1	Equilibrium surface tension.....	65
4.1.1	Sodium oleate.....	65
4.1.2	Sodium laurate	69
4.1.3	Sodium hexanoate	72
4.1.4	Sodium dodecyl and octadecyl sulfate.....	73
4.1.5	Comparison of different reagents.....	74
4.2	Turbidity	76
5.	Gas dispersion properties of fatty acids.....	78
5.1	Bubble size measurements.....	78
5.1.1	Sodium oleate.....	78
5.1.2	Sodium laurate	88
5.1.3	Sodium hexanoate	95
5.1.4	MIBC and reagent comparison	96
5.1.5	Sodium dodecyl sulfate.....	99
6.	Foamability and partition of anionic surfactants	103
6.1	Sodium oleate	103
6.1.1	Effect of solution volume.....	106
6.1.2	Effect of pH.....	107
6.1.3	Partitioning between the foam phase and bulk solution	110

6.1.3.1	Concentration effect	110
6.1.3.2	pH effect	112
6.1.3.3	Mixture with MIBC	116
6.1.3.4	Effect of ionic strength	118
6.2	Sodium laurate	121
6.3	Sodium hexanoate	123
6.4	Sodium octadecyl sulfate	124
6.5	Sodium dodecyl sulfate	126
Summary and conclusions.....		131
Recommendations for future work		135
Bibliography		137
Appendices.....		146
	Appendix 1: Dynamic surface tension	146
	Appendix 2: Gas hold-up measurements	152
	Appendix 3: Mixture of sodium oleate and MIBC	156
	Appendix 4: Gas dispersion measurement (in McGill set up)	157
	Appendix 5: Foamability and gas dispersion set ups	160

List of tables

Table 2-1. Structure and solubility of undissociated molecules of fatty acids	14
Table 2-2. Solubility of fatty acids in mol/L water at different temperatures	14
Table 2-3. Dynamic foamability index (Czarnecki et al 1982)	33
Table 5-1. Precipitation boundary for different concentrations of sodium oleate	79
Table 5-2. Standard deviation of bubble size distributions at natural pH.....	81
Table 5-3. Precipitation boundary for different concentrations of lauric acid.....	89
Table 6-1. Water content and foam surfactant concentration for different reagents	129

List of figures

Figure 2-1. Species distribution diagram for an aqueous laurate solution for a total laurate concentration of 10^{-4} mol/L, pK_a and S were assumed 5 and 1.2×10^{-5} mol/L in the figure	6
Figure 2-2. Species distribution diagram for an aqueous oleate solution for a total oleate concentration of 3×10^{-4} mol/L (Pugh and Stenius 1985), pK_a and S were assumed 4.95 and 2.5×10^{-8} mol/L in the figure	7
Figure 2-3. Domain diagram of aqueous solutions of oleic acid-oleate system	9
Figure 2-4. Domain diagrams of sodium laurate and sodium oleate (Parekh and Miller 1999), CMC of 2.1×10^{-3} mol/L for sodium oleate is obtained from Zimmels and Lin, 1974	9
Figure 2-5. Equilibrium surface tension versus concentration in a pH range of 7-13 for sodium oleate at 25°C and in a buffered solution with an ionic strength of 0.1 kmol/m ³ (Theander and Pugh 2001)	11
Figure 2-6. Schematic diagram of a typical C18 fatty acid pH titration curve and the degree of aggregation versus pH expected in the aqueous solution (a) At $pH > pK_a$ the solution is clear and contains soluble potassium salts (b) At $pH < pK_a$ crystals begin to appear in solution. The crystals keep forming at lower pH values (c) until total conversion to insoluble fatty acid (d or e) (Kanicky and Shah 2002)	12
Figure 2-7. pK_a values versus degree and nature of unsaturation of C18 fatty acids, obtained by acid-base titration at 20°C (Kanicky and Shah 2002)	13
Figure 2-8. Phase diagram for aqueous sodium laurate solutions at varying pH. Arrows indicate Krafft points (Dai and Laskowski 1991b). Solid symbols indicate the CMC values while open symbols denote total solubility	15
Figure 2-9. The effect of conditioning time and pH on the flotation response of fluorite and hematite (Laskowski and Nyamekye 1994)	18
Figure 2-10. Surface tension gradient	20
Figure 2-11. Frame of video imaging of bubbles blown in (a) pentanol and (b) F150. The texture results from fluid flow due to gravity and the Marangoni effect drawing liquid from the pool below (Finch et al 2008)	20
Figure 2-12. The opposing forces from nearby frother molecules induce instabilities in the surface (Finch et al 2008, Miller and Neogi 1985)	22

Figure 2-13. Definitions and determination of the CCC (Cho and Laskowski 2002b) and CCC95 (Finch et al 2008), experimental points are taken from this thesis and show bubble sizes measured in oleic acid solutions at pH 10.4	25
Figure 2-14. Parameters characterizing each phase in foamability and gas dispersion measurements	30
Figure 2-15. Determination of rt values for different concentrations of n-heptanoic acid from 5×10^{-5} to 5×10^{-3} mol/L containing 0.005 M HCl (Malysa et al 1991)	31
Figure 2-16. Typical effect of surfactant chain length on the surface tension of aqueous surfactant solutions (Leja 1982)	35
Figure 2-17. Zeta potential of microbubbles generated using different concentrations of sodium dodecyl sulfate and sodium oleate as a function of pH (Yoon and Yordan 1986).....	39
Figure 2-18. Effect of pH on electrophoretic mobility of colloidal precipitates in aqueous solutions of fatty acids (Laskowski 1993).....	40
Figure 2-19. Effect of pH on the zeta potential of micro bubbles generated in sodium oleate aqueous solutions (Laskowski et al 1989).....	40
Figure 2-20. (a) The pH of the iep of hematite in solutions of sodium oleate, (b) Domain diagram for oleic acid with iep of hematite superimposed from Aktar and Lai.....	42
Figure 2-21. Zeta potential of palmitate precipitates versus pH at different calcium levels. The particles at low pH are palmitic acid and calcium palmitate at higher pH; Arrows show the palmitic acid and calcium palmitate domains (Fuerstenau and Bunge 2006)	43
Figure 3-1. Equilibrium surface tension measurement by Wilhelmy plate method (Chamberlain and Rulison 2011).....	46
Figure 3-2. Pendant drop method.....	46
Figure 3-3. A pendant droplet created for calculating the surface tension of water	47
Figure 3-4. Calculations on pendent droplet.....	48
Figure 3-5. A bubble created by a J-needle in a cuvette filled with water for surface tension measurement.....	49
Figure 3-6. Turbiscan lab expert on the left and principle of Turbiscan measurement on the right	51
Figure 3-7. A single column of the foamability set up	52

Figure 3-8. Sample images at different conditions	57
Figure 3-9. Material flow and control system on gas dispersion experimental set up.....	59
Figure 3-10. Schematic of McGill bubble viewer (Gomez and Finch 2007)	60
Figure 3-11. UBC gas dispersion set up	61
Figure 4-1. Surface tension as a function of pH at different concentrations of sodium oleate measured by Wilhelmy plate method (pH values of precipitation demonstrated by arrows are 7.5, 8.1, 8.7, 9.3 and 10.3 respectively).....	65
Figure 4-2. Surface tension as a function of concentration of sodium oleate at different pH values (precipitates form at pH 4 and 6 regardless of concentration and precipitation concentration is 5×10^{-5} at pH 8, 5×10^{-4} at pH 9 and 5×10^{-3} mol/L at pH 10).....	67
Figure 4-3. Surface tension as a function of pH at 10^{-5} to 10^{-2} mol/L sodium laurate measured by Wilhelmy plate method (there is no precipitate at 10^{-5} mol/L and pH of precipitation at the subsequent tested concentrations are 5.4, 6.0, 6.6, 7.3 and 7.6).....	69
Figure 4-4. Surface tension of sodium laurate as a function of concentration at different pH values (precipitates form at pH 4 regardless of concentration and precipitation concentration is 2.5×10^{-4} at pH 6, 2.5×10^{-3} at pH 7, 2.5×10^{-2} at pH 8 and 0.25 mol/L at pH 9)	71
Figure 4-5. Surface tension as a function of pH at 2.3×10^{-4} to 5×10^{-2} mol/L of sodium hexanoate measured by Wilhelmy plate method	72
Figure 4-6. Surface tension of sodium hexanoate as a function of concentration at different pH values (MIBC data was obtained from Sweet et al 1997)	73
Figure 4-7. Surface tension as a function of pH at different concentrations of sodium dodecyl and octadecyl sulfate measured by Wilhelmy plate method	74
Figure 4-8. Surface tension as a function of pH at a concentration of 2.3×10^{-4} mol/L of different anionic reagents measured by Wilhelmy plate method	75
Figure 4-9. Transmission of oleic acid solutions of various concentrations as a function of pH (pH values of precipitation are 8.3, 9.3, 10.3 and 11.3 respectively, shown by arrows).....	77
Figure 5-1. Sauter mean bubble diameter in sodium oleate solutions at natural pH and pH 10.4	78
Figure 5-2. Bubble size distribution of different concentrations of sodium oleate solutions at natural pH	80
Figure 5-3. Bubble size distribution of sodium oleate at pH 10.4	81

Figure 5-4. Bubble size as a function of concentration of sodium oleate at different pH	82
Figure 5-5. Comparison of bubble size distribution in sodium oleate solution at pH 6.5 with water alone.....	86
Figure 5-6. Sauter mean diameter for sodium laurate at pH 4.5 and 10.4 (precipitate appears over a concentration of 2×10^{-5} mol/L at pH 4.5)	89
Figure 5-7. Bubble size distribution of 1.2×10^{-5} mol/L (2.67 mg/L) sodium laurate at pH 4.5 and pH 10.4	92
Figure 5-8. Bubble size distribution of 1.6×10^{-4} mol/L (36.51 mg/L) sodium laurate at pH 4.5 and pH 10.4.....	93
Figure 5-9. Comparison of bubble size distribution at different concentrations of sodium laurate solution at pH 4.5 with water only case.....	94
Figure 5-10. Bubble size of sodium hexanoate at pH 3.7 and 10.4	96
Figure 5-11. Sauter mean diameter of fatty acids of different chain lengths and MIBC as a function of concentration.....	97
Figure 5-12. Bubble size distribution at different concentrations of MIBC	98
Figure 5-13. Bubble size versus surface tension of MIBC, sodium laurate and oleate at pH 10.4 and sodium hexanoate at pH 3.7 (filled symbols represent bubble size data and empty symbols represent surface tension data)	99
Figure 5-14. Sauter mean bubble diameter of sodium dodecyl sulfate at natural pH (4.1-4.7) and pH 10	100
Figure 5-15. Sauter mean bubble diameter of sodium oleate, sodium dodecyl sulfate and sodium laurate at pH 10.4.....	101
Figure 6-1. Total gas volume as a function of time at $J_g = 0.5$ cm/s and natural pH for different concentrations of sodium oleate solution, initial solution volume is 100 mL.....	104
Figure 6-2. Foam growth rate and total gas volume at different concentrations of sodium oleate solutions.....	106
Figure 6-3. Total gas volume as a function of time at $J_g = 0.5$ cm/s and natural pH for different concentrations of sodium oleate solution, initial solution volume is 200 mL.....	107
Figure 6-4. Total gas volume versus time at $J_g = 0.5$ cm/s at different pH values for 6.5×10^{-5} mol/L (20 mg/l) sodium oleate solution (pH of precipitation is 8.1)	108

Figure 6-5. Total gas volume versus time at $J_g = 0.5\text{cm/s}$ at different pH values for 2.3×10^{-4} mol/L (70 mg/l) sodium oleate solution (pH of precipitation is 8.7)	109
Figure 6-6. Total gas volume as a function of time at $J_g = 0.5\text{cm/s}$ and pH 10 for different concentrations of sodium oleate aqueous solution, initial volume is 200 ml	111
Figure 6-7. Changes in the total organic carbon content in bulk solution at $J_g = 0.5\text{cm/s}$ and pH 10 for different concentrations of sodium oleate aqueous solution	111
Figure 6-8. Total gas volume versus time at $J_g = 0.5\text{ cm/s}$ and different pH values for 6.5×10^{-5} mol/L sodium oleate solution (this concentration is below CCC at natural pH).....	113
Figure 6-9. Changes in TOC in bulk solution at $J_g = 0.5\text{ cm/s}$ at different pH values for 6.5×10^{-5} mol/L sodium oleate solution (pH of precipitation is 8.1)	113
Figure 6-10. Total gas volume versus time in bulk solution at $J_g = 0.5\text{cm/s}$ at different pH values for 2.3×10^{-4} mol/L sodium oleate solution (pH of precipitation is 8.7)	114
Figure 6-11. Changes of TOC in bulk solution at $J_g = 0.5\text{cm/s}$ at different pH values for 2.3×10^{-4} mol/L sodium oleate solution, and for 9.7×10^{-4} mol/L of MIBC	114
Figure 6-12. The effect of MIBC addition on the foamability of 2.3×10^{-4} mol/L sodium oleate at pH 4.5	117
Figure 6-13. The effect of MIBC addition on surfactant transfer to the foam at 2.3×10^{-4} mol/L sodium oleate	117
Figure 6-14. Comparison of foamability of 6.5×10^{-5} mol/L sodium oleate solution in distilled water and 0.01 mol/L NaCl at $J_g = 0.5\text{ cm/s}$	119
Figure 6-15. Comparison of changes in TOC of bulk solution of 6.5×10^{-5} mol/L sodium oleate in distilled water and 0.01 mol/L NaCl at $J_g = 0.5\text{ cm/s}$	119
Figure 6-16. Comparison of changes in TOC in bulk solution of 2.3×10^{-4} mol/L sodium oleate in distilled water and 0.01 mol/L NaCl at $J_g = 0.5\text{ cm/s}$	120
Figure 6-17. Total gas volume as a function of time at $J_g=0.5\text{ cm/s}$ for different pH of 6.5×10^{-5} mol/L and 2.3×10^{-4} mol/L (15-51 mg/L) lauric acid aqueous solution.....	122
Figure 6-18. Changes of TOC in bulk solution as a function of time at $J_g=0.5\text{ cm/s}$ for different pH of 6.5×10^{-5} mol/L and 2.3×10^{-4} mol/L (15-51 mg/L) lauric acid aqueous solution.....	122
Figure 6-19. Foamability of 2.3×10^{-4} mol/L sodium hexanoate at pH 3.7 and 10	123
Figure 6-20. Total gas volume as a function of time at $J_g=0.5\text{ cm/s}$ for different pH of 6.5×10^{-5} and 2.3×10^{-4} mol/L octadecyl sulfate aqueous solution at 50°C	125

Figure 6-21. TOC changes in bulk solution as a function of time at $J_g=0.5$ cm/s for different pH of 6.5×10^{-5} and 2.3×10^{-4} mol/L octadecyl sulfate aqueous solution at 50°C	125
Figure 6-22. Total gas volume in bulk solution as a function of time at $J_g=0.5$ cm/s for different pH of 6.5×10^{-5} mol/L and 2.3×10^{-4} mol/L (20-67 mg/L) dodecyl sulfate solution	127
Figure 6-23. Changes of TOC in bulk solution as a function of time at $J_g=0.5$ cm/s for different pH of 6.5×10^{-5} mol/L and 2.3×10^{-4} mol/L (20-67 mg/L) dodecyl sulfate solution	127
Figure A1-1. Dynamic surface tension of 6.5×10^{-5} and 2.3×10^{-4} mol/L sodium oleate at pH 10 in addition to 3×10^{-3} mol/L oleic acid in a background electrolyte of 0.1 mol/L NaCl as a function of bubble surface age measured by maximum bubble pressure method at 23°C ..	147
Figure A1-2. Dynamic surface tension of sodium oleate as a function of concentration at natural pH measured by pendant drop method	148
Figure A1-3. Dynamic surface tension of 10^{-3} mol/L oleic acid at different pH values measured by pendant drop method, pH of precipitation is 9.3	149
Figure A1-4. Dynamic surface tension of 2.3×10^{-4} mol/L sodium oleate at different pH values measured by pendant drop method150Figure A1- 5. Dynamic surface tension of 6.5×10^{-5} and 2.3×10^{-4} mol/L sodium laurate at pH 4 and 9 measured by pendant drop method, pH values of precipitation at the tested concentrations are 5.3 and 5.9	151
Figure A2-1. Gas hold up of sodium oleate solutions at natural pH (6.7-10.5) and pH 10.....	152
Figure A2-2. Gas hold up of sodium oleate at pH 6.5, natural pH, pH 8.5 and pH 10 (natural pH values are labeled on the corresponding data points)	153
Figure A2-3. Gas hold-up of sodium Laurate at pH 4.5 and 10.4	154
Figure A2-4. Gas hold-up of sodium dodecyl sulfate at natural pH (4.1-4.7) and pH 10	154
Figure A2-5. Gas hold up of sodium oleate, dodecyl sulfate and laurate at pH 10.4	155
Figure A3-1. Average bubble size for MIBC and combinations of two concentrations of sodium oleate and MIBC at pH 10 (based on MIBC concentration)	156
Figure A4-1. Effect of sodium oleate and tall oil concentration on bubble mean diameter at $J_g=0.5$ cm/s, the MIBC data were taken from Azgomi et al 2007	157
Figure A4-2. Changes in the bubble size distribution as a function of oleate concentration at pH 10 (This type of data presentation was obtained from Finch et al, 2008)	158
Figure A4-3. Effect of collector concentration on gas hold-up	159
Figure A5-1. UBC foamability set up.....	160
Figure A5-2. UBC gas dispersion set up	161

Acknowledgements

I want to express my sincere thanks to Dr. Marek Pawlik for giving me the opportunity to go through the PhD journey. I truly appreciate all his supports, which greatly contributed to the completion of this work. I would like to thank my supervisory committee members, Professors Janusz Laskowski and Elode Gyenge for their valuable comments and expert feedback that have been very helpful in completing this thesis. I'm thankful to Professor James A. Finch for his inspirations and invaluable discussions, which directed my PhD work. I would also like to thank Dr. Cesar Gomez and Dr. Mitra Mirnezami for all their supports during my visits at McGill University.

I'm especially thankful to the assistance provided by Mrs. Sally Finora due to her generous support and the very nice environment she provided at the surface chemistry lab. I'd like to thank Mr. Aaron Hope and Mr. Howard Vornbrock who helped a lot in constructing my research set ups at UBC and Mr. Pius Lo for his support at the CMP lab. I'd like to express my appreciation to my friends in the surface chemistry group, Jophat Engwayu, Esau Arinaitwe, Leopoldo Gutierrez, Bhajan Lal, Sarthak Kaushik, Claudio Garcia, Frank Yan, Leonardo Barro and Wenying Liu. They made my everyday stay at UBC more enjoyable.

Financial support from Natural Sciences and Engineering Research Council (NSERC) and the Canadian Centre for Clean Coal/Carbon and Mineral Processing Technologies (C5MPT) at the University of Alberta (Edmonton, AB) is gratefully acknowledged.

The years I spent as a PhD student took a lot of my time away from my husband Sadegh and all he gave back was unlimited love, understanding and support, always encouraging and motivating me to excel. His inspiration in completing this thesis is immeasurable.

I cannot find words to express my thanks to my mother, father and sister, who gave me the foundation to be who I'm today and for all their precious guidance. Mom, thank you for all your sacrifices and supports. Dad, thanks for your encouragement and unwavering belief in me. To my father, mother, sister and brother-in-law: I greatly appreciate your support and friendship and for tolerating all the years Sadegh and I were far from you.

I'm grateful to God for helping me in all I have accomplished in my life.

Dedications

To my dear mother, father and sister: These are the fruits of your sacrifices and inspirations through the years. Thank you so much.

To my dear husband: What you contributed is immense and the least I can do is to dedicate this dissertation to you.

1. Introduction

This thesis focuses on characterizing and quantifying the gas dispersion and foaming capabilities of anionic surfactant solutions specifically fatty acids. Frothing capabilities of anionic reagents in flotation have never been adequately quantified in literature. Assessing the role of different fatty acid species including colloidal species on the interfacial properties of fatty acids is of particular interest to this research.

The interfacial behavior of fatty acids in the froth flotation process strongly depends on their chemical state in solution, which is a function of concentration, pH, and ionic strength. These are the parameters of interest in this study.

1.1 Fatty acids in flotation

Fatty acids and their alkali metal salts are primarily used as flotation collectors in the processing of non-sulfide minerals. The froth flotation of salt-type water-insoluble minerals, such as phosphates or carbonates, is routinely carried out using a range of anionic surfactant-type collectors with carboxylic fatty acids (e.g., oleic acid and tall oil) being the main reagents

While in most flotation processes two different surfactants are selected to perform the collecting and frothing tasks, there are cases in which an industrial grade fatty acid is used as both a collector and frother. In these processes excess collector acts as a frothing agent, but it is not very clear whether such a strategy is more beneficial to the process than the simultaneous use of a dedicated frother. Better understanding of the frothing action of fatty acids by investigating the physiochemical phenomena taking place in flotation systems relying on fatty acids, should result in improved selection of reagent types and their dosages. The characteristics of fatty acids as collectors are discussed in literature extensively, with the emphasis on surfactant-mineral interactions, but there are no systematic data on their frothing characteristics. The vast majority, if not all, of the work on the subject of frothing in flotation is dedicated to applications of nonionic alcohol-type and polyglycol-type surfactants.

The effect of fatty acids on gas bubble sizes, gas hold-up, foamability, and froth stability is basically unknown even though the ability of fatty acid surfactants to generate foam is well known. The same experimental techniques that are used for characterizing the frothing properties of alcohol- and polyglycol-type surfactants may therefore prove very useful for assessing the

frothing action of fatty acid solutions, particularly in comparison to the action of standard frothers.

Long chain fatty acids (e.g., oleic and linoleic acids) are the main components of technical grade industrial reagents. Fatty acids are weak electrolytes and their behavior is a strong function of pH, so pH should always be kept as a variable in this type of research.

Sparingly soluble salt-type minerals are mainly salts of calcium and magnesium. As a result, calcium and magnesium ions, upon release into process water, affect the behavior of fatty acids. Therefore, contributions of those ions should also be taken into account when analyzing the interfacial phenomena involving anionic surfactants.

1.2 Frothing action

Frothers have two main functions: controlling the bubble size and providing froth building capacity (Finch et al 2008). Small bubbles during the flotation process increase the bubble surface area flux, which increases the rate of flotation. Small bubble sizes (typically 0.1–4 mm) produced in flotation systems result from interactions of the air delivery system (e.g., through the impeller in a mechanical flotation machine) with the frother (Kracht and Finch 2009).

The frothing action of surfactants originates from the preferential orientation of their hydrophilic and hydrophobic groups upon adsorption at the gas-liquid interface. The hydrophilic group pointing away from the bubble surface stabilizes the water layer around the bubble and keeps the bubble at its original size, i.e., the size delivered by the aeration system. Break-up of the air mass due to opposing forces on the bubble surface as a consequence of surfactant adsorption-driven surface tension gradients is viewed as another mechanism leading to the formation of small bubbles (Finch et al 2008).

The frothing "power" of frothers is typically characterized by measuring gas dispersion properties (bubble size distribution, critical coalescence concentration (CCC), gas hold-up) and foam or froth properties (water overflow rate, foam stability, foam volume and growth rate, dynamic foamability index – DFI) (Czarnecki et al 1982, Malysa 1992, Sweet et al 1997, Cho and Laskowski 2002, Moyo et al 2007, Finch et al 2008).

The tests produce a number of additional parameters, such as the retention time of gas in the froth phase, all of which can be used to analyze the frothing action of a surfactant.

Difference in the generated bubble size and also in the volume, growth rate and stability of the generated foam for the various surfactants may originate from different adsorption mechanisms.

1.3 Scope of the dissertation

This research focuses on fatty acids, primarily sodium oleate as the most important representative of long-chain fatty acids used in froth flotation. Experiments are carried out on shorter chain fatty acids, such as lauric acid as a 12-carbon carboxylic acid and sodium hexanoate as a 6-carbon carboxylic acid.

Experiments performed on alkyl sulfates such as sodium dodecyl sulfate and sodium octadecyl sulfate as 12 and 18-carbon sulfates provide further insight into understanding the effect of different species on the interfacial properties of fatty acids. The tested alkyl sulfates are water-soluble strong anionic surfactants, fully dissociated in aqueous solutions. As such, their effect on gas dispersion and foaming properties provides a baseline measure of the behavior of true solutions of surfactants of the same chain length, i.e., in the absence of colloidal species.

Additional experiments were also performed with the use of MIBC as a reference standard frother, as well as using mixtures of MIBC with sodium oleate to detect any synergistic effects.

Turbidity, equilibrium and dynamic surface tension measurements were initially performed to characterise the reagents. Gas dispersion measurements (including bubble size distribution, critical coalescence concentration and gas hold-up measurements), foamability measurements, and total organic carbon analysis (TOC), were the main research tools of this thesis.

1.4 Objectives

In summary, this thesis had the following research objectives:

- 1) To understand the effect of various species of long chain fatty acids on the gas dispersion properties of fatty acid solutions (concentration and pH are the controlling factors). This part includes measurements of bubble size distributions and gas hold-up.

- 2) To determine the foamability characteristics of fatty acid solutions under the same conditions as those of the gas dispersion studies.
- 3) To identify the mechanisms of gas dispersion and foamability phenomena in fatty acid solutions.

The first two macro-phenomena (gas dispersion and foamability properties) result from adsorption of surfactant molecules at the gas liquid interface, or on the surfaces of gas bubbles. Therefore, another key fundamental objective was:

- 4) To characterize the adsorption behaviour of fatty acids at the gas-liquid interface (on air bubbles) through surface tension measurements, and to assess the partition of the tested surfactants between the foam and bulk solution phases using total organic carbon content (TOC) analysis.

2. Literature review

2.1 General properties of fatty acids as flotation reagents

2.1.1 Species distribution

In aqueous solutions, carboxylic acids reversibly dissociate:



And the dissociation constant, K_a , is given by:

$$K_a = \frac{[RCOO^-][H^+]}{[RCOOH]} \quad \text{OR} \quad pK_a = p[RCOO^-] - p[RCOOH] + pH \quad (2-2)$$

When the concentrations of $RCOOH$ and $RCOO^-$ species are equal, then $pK_a = pH$. The pK_a values for fatty acids are at 4.7 ± 0.5 (Morrison and Boyd 1994). For any total acid concentration, C_T , the pH of precipitation can be calculated using the following formula:

$$[H^+] = \frac{S \cdot K_a}{C_T - S} \Rightarrow pH_{precip} = p(S \cdot K_a) - p(C_T - S) \quad (2-3)$$

In which S is the concentration of neutral form above which precipitates start forming and C_T is the total concentration.

The concentrations of individual species (ionized, associated, and/or precipitate) in aqueous solutions may be represented in the form of a species distribution diagram.

$$C_T = [RCOO^-] + [RCOOH] + [RCOOH]_{precip}. \quad (2-4)$$

A species distribution diagram for lauric acid ($C_T = 10^{-4}$ mol/L) can be constructed as follows:

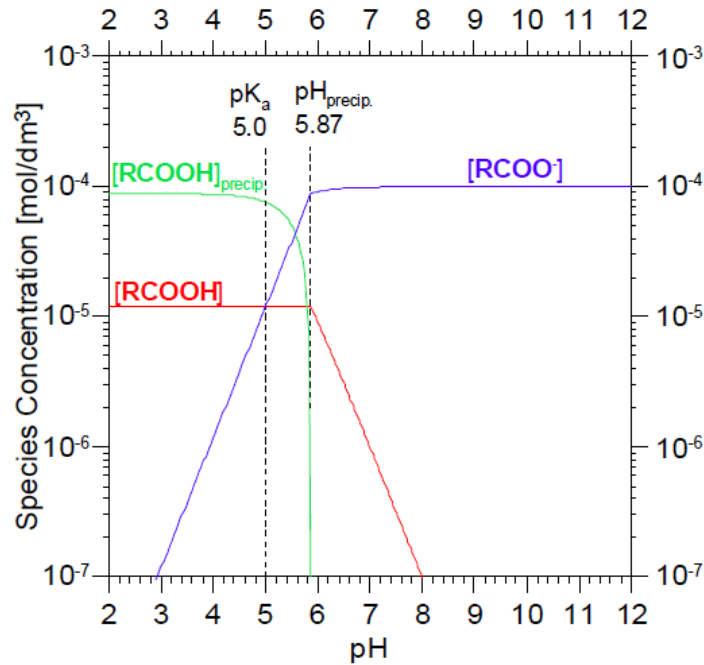
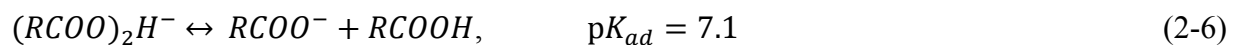
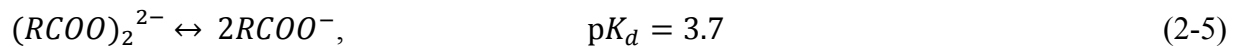


Figure 2-1. Species distribution diagram for an aqueous laurate solution for a total laurate concentration of 10^{-4} mol/L, pK_a and S were assumed 5 and 1.2×10^{-5} mol/L in the figure

So lauric acid species could be either RCOOH itself or the carboxylate anion (RCOO⁻) and if the concentration of RCOOH exceeds the solubility limit, S , the [RCOOH]_{precip.} forms.

Oleic acid as a longer chain surfactant is a more complex system and forms various additional species in aqueous solutions. Those are the fatty acid (RCOOH) itself, the carboxylate ion (RCOO⁻), the neutral acid-salt (RCOOH.RCOONa), the ionic acid-oleate complex (RCOOH.RCOO⁻, or (RCOO)₂H⁻) and the oleate dimer [(RCOO)₂]²⁻. The latter 3 are referred to as premicellar aggregates (Ananthapadmanabhan and Somasundaran 1982). The formation of such mixed and dimeric complexes can considerably affect the surface activity of surfactants. The magnitude of this effect can be estimated only if the relative amounts of these species in solution can be determined. This requires the knowledge of the formation constants for acid salts and dimers, which are defined as follows for the oleic acid system (Ananthapadmanabhan and Somasundaran 1982).



Using the above thermodynamic constants, for any given total oleate concentration and pH, one can calculate the activities of various oleate species in solution. The chemical equilibria and dissociation constants for oleic acid and oleate species can be given as (Ananthapadmanabhan and Somasundaran 1982):



In which the subscript (*l*) refers to the precipitate form, and (*aq*) refers to the soluble molecular form. A speciation diagram illustrating the concentrations of the various oleate species in solution as a function of pH at 25°C is shown in Figure 2-2 (Pugh and Stenius 1985).

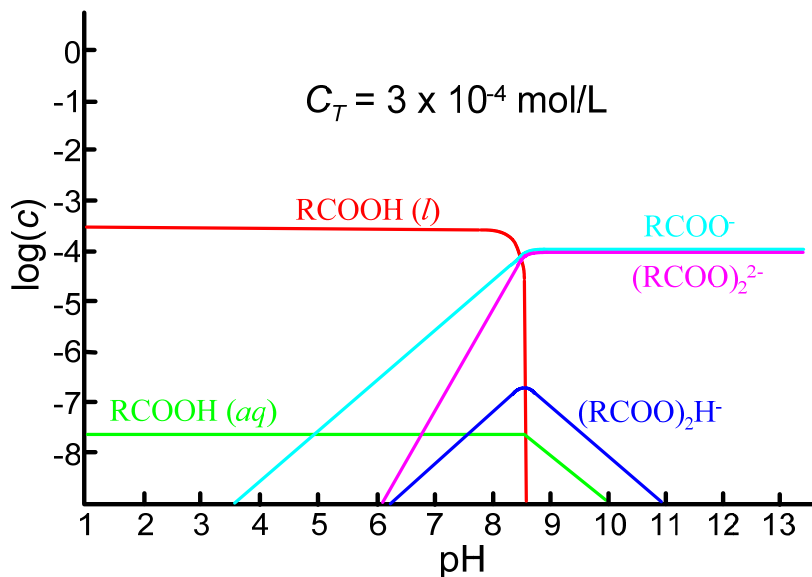


Figure 2-2. Species distribution diagram for an aqueous oleate solution for a total oleate concentration of 3×10^{-4} mol/L (Pugh and Stenius 1985), pK_a and S were assumed 4.95 and 2.5×10^{-8} mol/L in the figure

It is noteworthy that the pK_a value for oleic acid used in the equilibrium calculations is 4.95 rather than 4.7. It can be seen in this figure that:

- 1- The maximum activity of ionomolecular species $(RCOO)_2H^-$ occurs at pH 8.8 for a total oleate concentration of 3×10^{-4} mol/L.

- 2- The activities of the ionic oleate (RCOO^-) and the dimer $(\text{RCOO})_2^{2-}$ increase as the pH is increased up to pH 8.8, and then remain equal and constant at higher pH values.
- 3- Neutral associated oleic acid (RCOOH) starts to precipitate from this aqueous solution at pH values lower than 8.8, and the concentration of the soluble nonionic species is constant and in equilibrium with precipitates at this pH.

Leja (1982) suggested that for an ionizable surfactant the regions of pH where the two main species (ionized and associated) occur in appreciable quantities coincide with the region of their dual action as a collector and a frother. Outside such a region the surfactant can act either as a collector only or as a frother only. At a concentration of 3×10^{-4} mol/L of sodium oleate, the region of dual action occurs around pH 8.8.

2.1.2 Domain diagram

The precipitation-dissolution equilibrium can be controlled by adjusting pH since the concentration of RCOOH decreases as pH increases. This could be demonstrated in a domain diagram which shows the pH-concentration domains of a true solution and that of colloidal precipitates. Figure 2-3 illustrates the domain diagram of oleic acid. At the pH of precipitation (pH_s), the concentration of neutral species (RCOOH) exceeds the solubility limit, S . For any total acid concentration, $C_T > S$, the pH of precipitation could be calculated using equation (2-9), which is used to construct the domain diagram in Figure 2-3 (Laskowski 1994). In this diagram $\text{pK}_a = 4.7$ and solubility (S) equals 2.5×10^{-8} mol/L (Ananthpadmanabhan et al 1979, Fuerstenau et al 1985).

$$\text{pH}_s = \text{pK}_a - \log S + \log (C_T - S) \quad \text{OR} \quad [H^+] = \frac{S \cdot K_a}{C_T - S} \quad (2-9)$$

Domain diagrams of oleic acid and lauric acid are compared in Figure 2-4. It is noteworthy that the difference in the location of the domain diagrams for these two fatty acids primarily results from the difference in their corresponding solubility limit values, S , and to a much smaller degree in the assumed pK_a values.

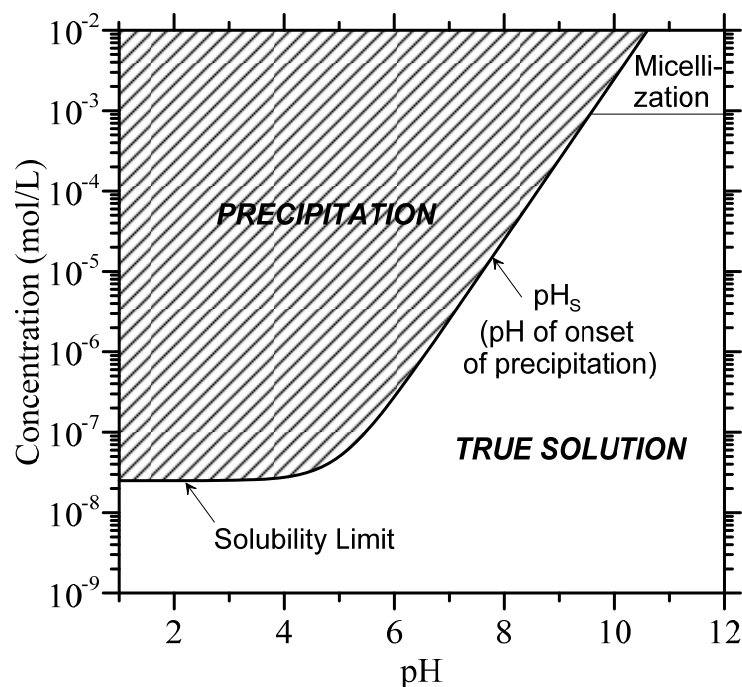


Figure 2-3. Domain diagram of aqueous solutions of oleic acid-oleate system
(Laskowski 1994)

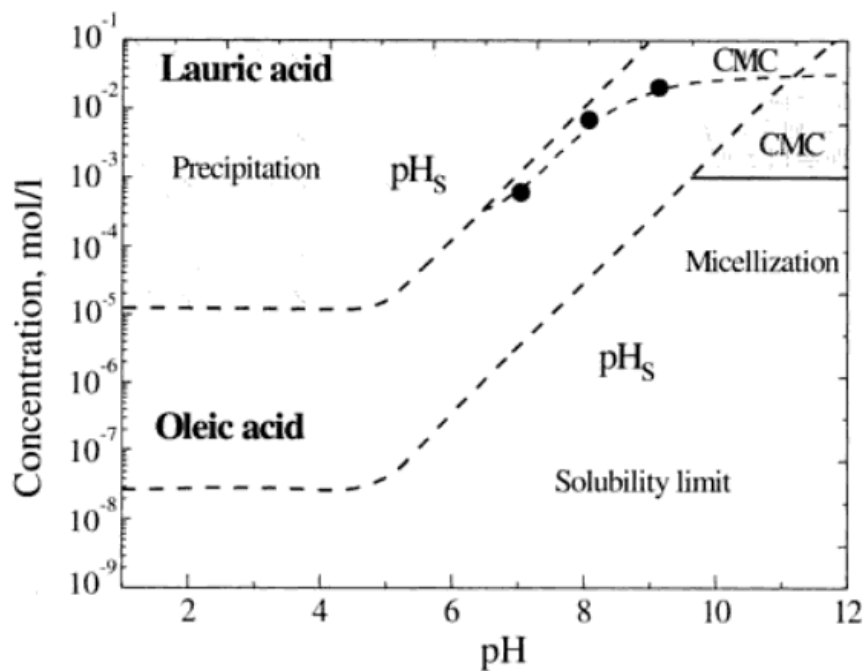


Figure 2-4. Domain diagrams of sodium laurate and sodium oleate (Parekh and Miller 1999), CMC of 2.1×10^{-3} mol/L for sodium oleate is obtained from Zimmels and Lin, 1974

2.1.3 Critical micelle concentration (CMC)

There is a surfactant concentration above which the surface tension of surfactant solutions does not change significantly, and this transition concentration is defined as the critical micelle concentration (CMC). Below the CMC, the surface-active molecules tend to accumulate at the air-solution interface but above the CMC, the interface is saturated with the surfactant, and additional surfactant molecules form micelles in bulk solution instead of adsorbing at the interface.

In Figure 2-4, the critical micelle concentration for sodium oleate is shown at 2.1×10^{-3} mol/L (Zimmels and Lin 1974). The critical micelle concentration (CMC) is an important characteristic of a surfactant since the CMC provides a measure of the surface activity of a reagent. Before reaching the CMC, the surface tension changes strongly with the concentration of the surfactant. After reaching the CMC, the surface tension remains relatively constant or changes with a lower slope. The value of the CMC for a given surfactant depends on temperature, pressure, and (sometimes strongly) on the presence and concentration of other surface-active substances and electrolytes.

There are different critical micelle concentration (CMC) values reported for oleic acid in literature. Mukerjee and Mysels (1971) reported a CMC value of 2.3×10^{-3} mol/L. Theander and Pugh (2001) measured the equilibrium surface tension of sodium oleate at different pH values in high ionic strength buffered solutions and concluded that at most pH values it was only possible to obtain a CMC region, and that the CMC of the system increased with pH within the pH range of 8-12. The CMC increased from 4.7×10^{-5} mol/L at pH 7 to 5.7×10^{-5} mol/L at pH 10 (Figure 2-5).

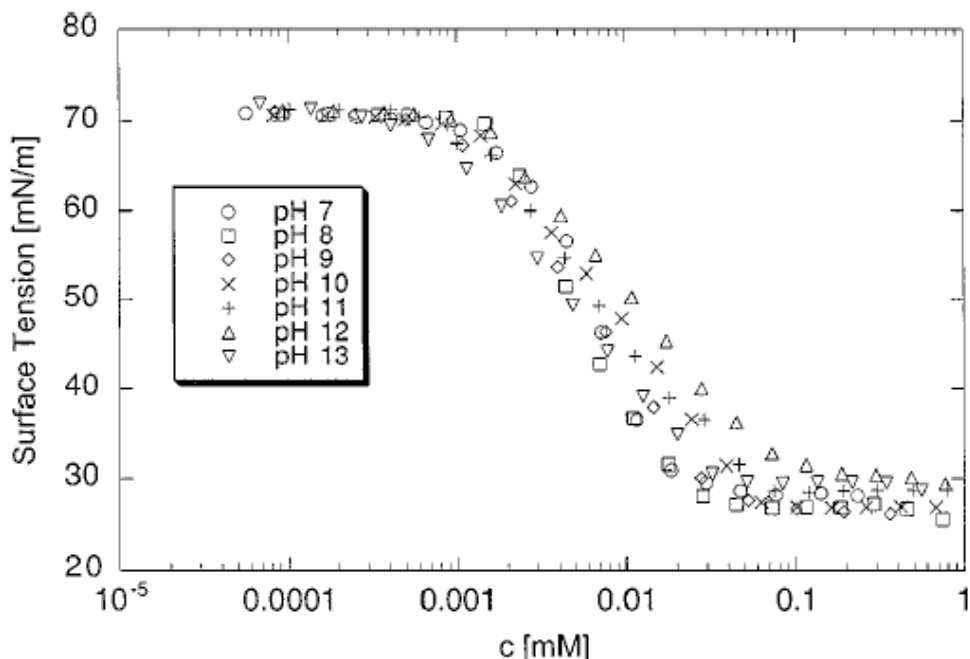


Figure 2-5. Equilibrium surface tension versus concentration in a pH range of 7-13 for sodium oleate at 25°C and in a buffered solution with an ionic strength of 0.1 kmol/m³ (Theander and Pugh 2001)

As can be seen from the speciation diagram for oleic acid (Figure 2-2), it should be noted that on approaching neutral pH from the alkaline range toward the precipitation edge of oleic acid, the activities of oleate monomers and oleate dimers do not change appreciably, but there is a significant increase in the activities of the neutral acid and neutral acid-salt in the bulk. This highlights the role of complex species forming in the mid pH range.

The CMC of sodium laurate was reported as a function of pH by Dai and Laskowski (1991b), which was 2×10^{-2} mol/L at pH 9 and 7×10^{-4} mol/L at pH 7. This is also detectable in Figure 2-8.

2.1.4 The pK_a value

Different pK_a values were reported for carboxylic acids. pK_a of 4.7 is usually used for fatty acids (Fuerstenau 1982) but there are recent studies, which reported pK_a values of oleic acid as high as 9.85 (Figure 2-6). In this case, the pK_a value was determined by titration at 20°C with 0.1 M hydrochloric acid using a Metrohm 726 titroprocessor. The neutralization endpoint was first determined as the first point of inflection on the S-shaped titration curve. The pK_a was subsequently calculated as the pH of the solution at half the neutralization volume (i.e., half the

volume of hydrochloric acid needed to reach the neutralization endpoint) (Kanicky et al 2000, Kanicky and Shah 2002).

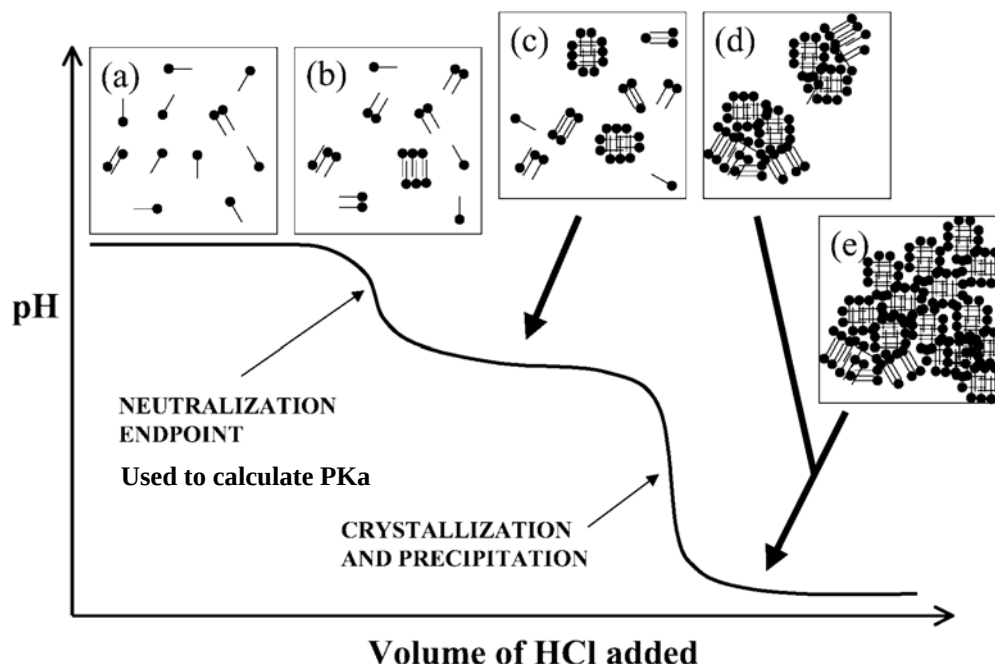


Figure 2-6. Schematic diagram of a typical C18 fatty acid pH titration curve and the degree of aggregation versus pH expected in the aqueous solution (a) At $\text{pH} > \text{p}K_a$ the solution is clear and contains soluble potassium salts (b) At $\text{pH} < \text{p}K_a$ crystals begin to appear in solution. The crystals keep forming at lower pH values (c) until total conversion to insoluble fatty acid (d or e) (Kanicky and Shah 2002)

The $\text{p}K_a$ values of stearic, elaidic, oleic, linoleic, and linolenic acids, which are all 18-carbon fatty acids, determined by the titration method are compared in Figure 2-7. A $\text{p}K_a$ value of 4.7, reported previously, indicates that the surfactant is a weak acid, but a value of 9.8 indicates that the surfactant is a base. A value of 4.7 was used for speciation calculations in this thesis, as the $\text{p}K_a$ value as high as 9.8 for oleic acid translates to a very high pH of precipitation, which is not consistent with observations made during the experimental work.

As the area per molecule increases, the intermolecular distance increases, and the $\text{p}K_a$ decreases due to reduced interaction between adjacent carboxyl groups (Kanicky and Shah 2002).

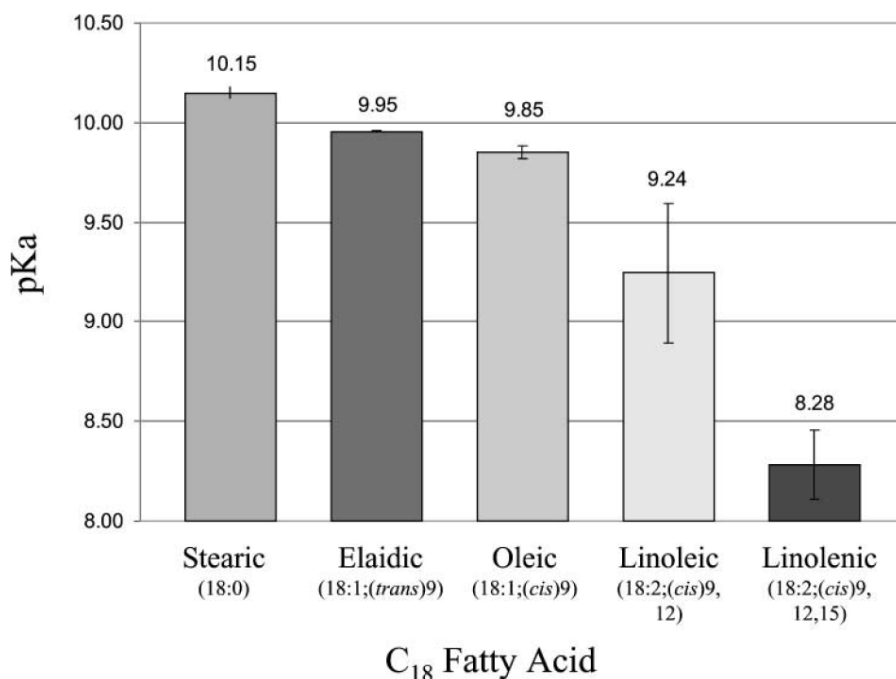


Figure 2-7. pK_a values versus degree and nature of unsaturation of C18 fatty acids, obtained by acid-base titration at 20°C (Kanicky and Shah 2002)

2.1.5 Solubility

The solubility, S , of the undissociated acid (RCOOH) is low and decreases quickly with the length of the hydrocarbon chain, as shown in Table 2-1. At concentrations higher than the solubility limit, fatty acids form precipitates. Precipitation/dissolution equilibrium can be controlled by adjusting pH since the concentration of RCOOH decreases as pH increases.

The solubility of those species containing double bonds in their hydrocarbon chains, such as oleic acid, is greater than that of the saturated homologues, such as stearic acid. The double bonds have a polar character and polar water molecules are attracted to them (Fuerstenau et al 1985). These fatty acids may form liquid emulsions rather than solid precipitates. One way to dissolve fatty acids is to convert them to their sodium or potassium salt.

**Table 2-1. Structure and solubility of undissociated molecules of fatty acids
(Fuerstenau et al 1985)**

Common name	Systematic name	Chemical formula	Solubility (mol/L)
Caproic (C ₆)	Hexanoic acid	CH ₃ (CH ₂) ₄ COOH	8.4×10^{-2}
Capric (C ₁₀)	Decanoic acid	CH ₃ (CH ₂) ₈ COOH	3.0×10^{-4}
Lauric (C ₁₂)	Dodecanoic acid	CH ₃ (CH ₂) ₁₀ COOH	1.2×10^{-5}
Myristic (C ₁₄)	Tetradecanoic acid	CH ₃ (CH ₂) ₁₂ COOH	1.0×10^{-6}
Palmitic (C ₁₆)	Hexadecanoic acid	CH ₃ (CH ₂) ₁₄ COOH	6.0×10^{-7}
Stearic (C ₁₈)	Octadecanoic acid	CH ₃ (CH ₂) ₁₆ COOH	3.0×10^{-7}

Solubility of n-alkyl saturated fatty acids in water according to Ralston and Hoerr (1942) is presented in Table 2-2. For clarity, however, it should be mentioned that Ralston and Hoerr understood the term solubility as total solubility, which is as the total concentration of soluble species (anionic plus undissociated acid).

**Table 2-2. Solubility of fatty acids in mol/L water at different temperatures
(Ralston and Hoerr 1942)**

Number of atoms in the alkyl chain	0° C	20° C	30° C	45° C	60° C
6	7.4×10^{-2}	8.3×10^{-2}	8.8×10^{-2}	9.4×10^{-2}	1.0×10^{-1}
8	3.1×10^{-3}	4.7×10^{-3}	5.5×10^{-3}	6.6×10^{-3}	7.8×10^{-3}
10	5.5×10^{-4}	8.7×10^{-4}	1.0×10^{-3}	1.3×10^{-3}	1.6×10^{-3}
12	1.9×10^{-4}	2.8×10^{-4}	3.1×10^{-4}	3.7×10^{-4}	4.3×10^{-4}
14	5.7×10^{-5}	8.8×10^{-5}	1.1×10^{-4}	1.3×10^{-4}	1.5×10^{-4}
16	1.8×10^{-5}	2.8×10^{-5}	3.2×10^{-5}	3.9×10^{-5}	4.7×10^{-5}
18	6.4×10^{-6}	1.0×10^{-5}	1.2×10^{-5}	1.5×10^{-5}	1.8×10^{-5}

The concentration-temperature diagram of sodium laurate is shown in Figure 2-8, which shows how the solubility of the surfactant changes with temperature (Dai and Laskowski 1991b). Such diagrams are a common way of presenting solubility data for various ionic surfactants. The diagram shows that solubility generally increases with temperature, and that micelles form only above a critical temperature above which the total solubility of the surfactant becomes high enough for micellization. This critical temperature, or basically the intersection point of the CMC curve with the total solubility curve, is known as the Krafft point (Shinoda and Becher 1978, Moroi et al 1984). In contrast to ionic surfactants, the solubility of non-ionic surfactants is known to decrease by increasing temperature. This transition point is known as the cloud point. It is also noteworthy that generally the CMC does not markedly change with temperature at a given pH value, but at the same time the CMC is a strong function of pH at a given temperature. For lauric acid at a given temperature, the CMC increases as pH increases.

It is characteristic that the total solubility of ionic surfactants increases dramatically above the Krafft point. According to Figure 2-8 sodium laurate behaves like a typical ionic surfactant at pH 9, but at pH 7 and 8 the total solubility curve flattens soon after the Krafft point, which indicates that the ionic character of laurate diminishes at lower pH when the concentration of the nonionic undissociated form gradually becomes significant (Dai and Laskowski 1991b).

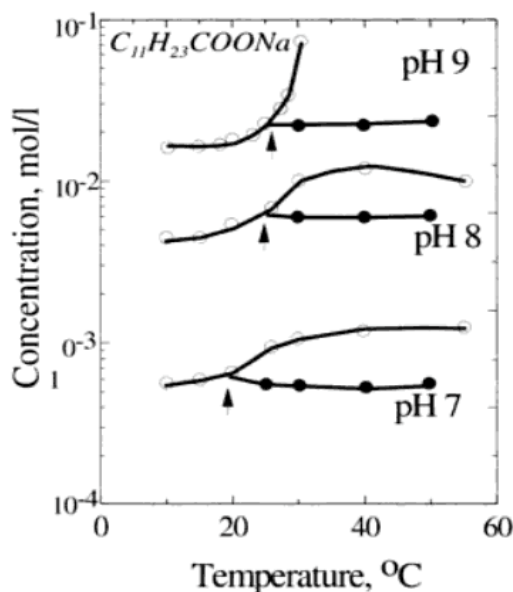


Figure 2-8. Phase diagram for aqueous sodium laurate solutions at varying pH. Arrows indicate Krafft points (Dai and Laskowski 1991b). Solid symbols indicate the CMC values while open symbols denote total solubility

Generally the Krafft point of fatty acids changes as a function of pH. At lower pH values, solubility may even decrease with temperature and a cloud point may appear instead of a Krafft point.

2.2 Flotation of semi soluble salt type minerals using fatty acids

The selectivity of carboxylic fatty acids towards the salt-type minerals results from the strong chemical affinity of fatty acids towards the surfaces of these minerals (Peck and Wadsworth 1964). Fuerstenau and Bunge 2006 also indicated that flotation of semi soluble salt type minerals such as apatite, calcite and fluorite is controlled by a chemical reaction of the lattice ions with carboxylate collectors, which could be confirmed by IR spectroscopy. At lower pH, physical adsorption was observed, however in such a system collector uptake goes beyond a monolayer and a new salt phase may form at the surface which implies that the collection process is a surface reaction rather than physical adsorption (Fuerstenau and Bunge 2006).

Several researchers emphasized the role of colloidal or bulk calcium precipitate on flotation behaviour (Fa et al 2003; Fuerstenau and Elgilanni 1966). Laskowski et al (1999) performed a detailed study on weak electrolyte collectors with an emphasis on the role of precipitates in the flotation of sparingly soluble salt type mineral.

2.2.1 Effect of pH

Several research works attempted to elucidate the effect of various species of fatty acids on the wettability and flotation behaviour of semi soluble salt type minerals. Optimum flotation conditions were correlated with maximum surface activity as determined by surface tension measurements. In some works, high mineral recovery was correlated with minimum surface tension of the aqueous phase in the flotation of oxide minerals (Pugh and Stenius 1985). For example, for fluorite and apatite the minimum surface tension of the aqueous phase occurred in the neutral pH range, apparently due to the formation of premicellar complex species (Pugh and Stenius 1985). According to Finch and Smith (1972), the interfacial tension between freshly formed bubbles and the aqueous phase is more relevant to flotation than the equilibrium interfacial tension value. According to the Harkin's wetting theory (Harkins 1952), a high interfacial tension between liquid and vapour exerted by fresh bubbles facilitates particle-bubble adhesion.

Zones of pH values corresponding to maximum flotation of semi soluble salt type minerals (pH 8-10) correlated with the presence of a highly hydrophobic interfacial film on the solution surface. According to Pugh and Stenius, this film was produced in those pH zones by a synergistic co-operative adsorption mechanism involving a mixture of several premicellar ionic and molecular species in solution (Pugh and Stenius 1985). A similar maximum flotation response with oleate was observed in the neutral pH range (7-8) for different silicate and oxide minerals such as zircon, rutile, ilmenite, garnet, and tourmaline (Polkin and Najfonow 1964).

Recently, a fundamental study was performed on the impact of colloidal bulk precipitate of calcium carboxylate $[(RCOO)_2Ca]$ on flotation of fluorite. After adding a fatty acid, such metal carboxylate precipitates form easily during flotation of sparingly soluble salt type minerals since the amount of metal ions leached from the mineral surface is usually sufficient to exceed the solubility product of the corresponding metal carboxylate. It was revealed that the boundary region between palmitic acid, as a model carboxylic acid, and calcium carboxylate formation coincided with maximum flotation recovery of fluorite (Fuerstenau and Bunge 2006).

2.2.2 Effect of conditioning time

In literature flotation-pH curves for various minerals and different collectors, including fatty acids, exhibit a maximum in the neutral pH region (Laskowski and Nyamekye 1994). Assuming neutral pH as the pH of maximum recovery can be misleading in some cases; conditioning time of the mineral suspension with the collector could be a determining factor. Regarding oleic acid adsorption, the adsorption equilibrium is achieved quickly in the oleate zone but it takes significantly more time in the colloidal zone. Laskowski and Nyamekye described the flotation response of fluorite and hematite as a function of pH in the presence of 10^{-5} mol/L sodium oleate after a constant flotation time but after varying conditioning times with the surfactant. The results (Figure 2-9) reveal that while the recovery of the minerals is independent of conditioning time at pH higher than 8-9, it is strongly dependent on the conditioning time at lower pH (Laskowski and Nyamekye 1994). Transport of collector species towards mineral particles is a flotation-controlling step at pH values corresponding to the presence of colloidal precipitates (Laskowski 1999).

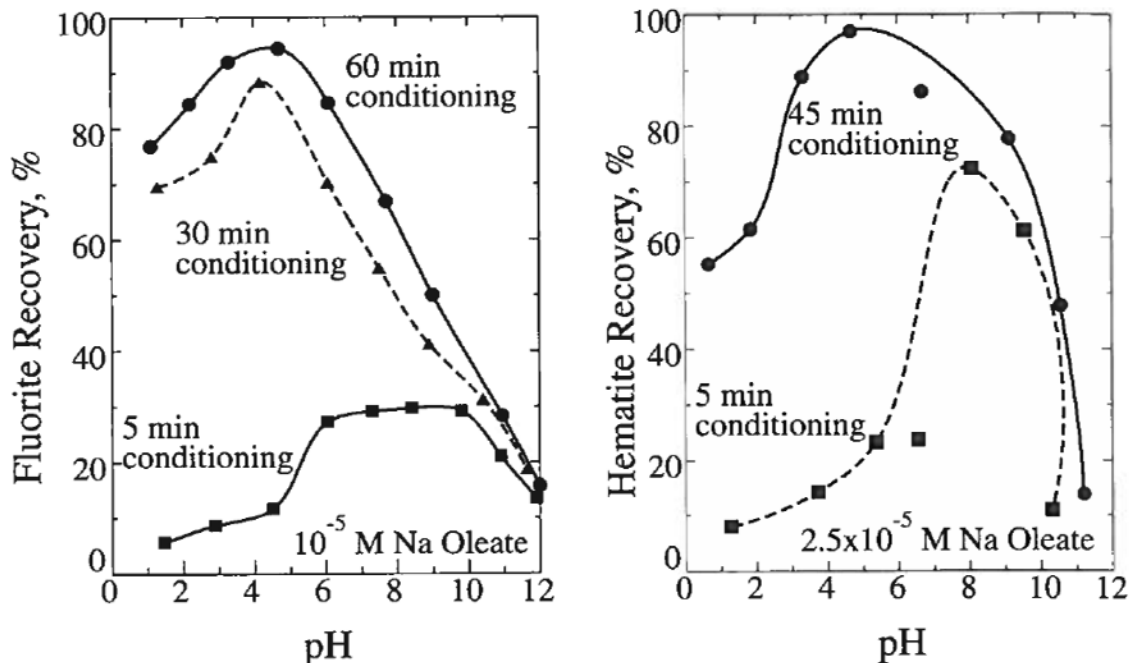


Figure 2-9. The effect of conditioning time and pH on the flotation response of fluorite and hematite (Laskowski and Nyamekye 1994)

Colloidal precipitates of cationic alkyl amines are also known to slow down the adsorption process and longer times are needed to reach steady-state conditions. It was also reported in literature that the effect of precipitates with a low diffusion rate in high pH range of amine causes delay in adsorption equilibrium as determined from surface tension measurements (Finch and Smith 1972).

In some cases, such as the flotation of phosphates, long conditioning with the collector at high solids content is often required to initiate the flotation process. The main purpose of long conditioning at high solids content is to give the collector plenty of time to adsorb on the phosphate particles, and the high solids content promotes faster transport of the collector molecules through the solution phase to the mineral surfaces.

The adsorption kinetics of a surfactant is often characterized through dynamic surface tension measurements in the case of adsorption at the air-solution interface, but this approach has its own limitations depending on the surface tension technique, and how closely the technique can reproduce the timescale of real flotation conditions.

2.3 Gas dispersion characteristics of surfactants

2.3.1 Terminology

Different parameters were proposed to quantify the effectiveness of surfactants as frothers in flotation systems. An argument can be made that the bubble size is the flotation-driving factor as it provides a measure of the surface area of air bubbles available for mineral attachment at the liquid/gas interface which is also related to flotation kinetics (Flotation Rate $\propto \frac{1}{D_b}$) (Gorain et al 1997, Hernandez et al 2005).

The surface area flux (S_b) is the total surface area of bubbles generated during flotation, which is also defined as a ratio of the superficial gas velocity (J_g) and average bubble size (D_b) (equation 2-10) (Nesset et al 2007, Nesset et al 2006). The superficial gas velocity is the volumetric flow rate of air divided by the cross-sectional area of the flotation column or cell.

$$S_b = \frac{6J_g}{D_b} \quad (2-10)$$

The gas hold-up (ϵ_g) is the volume fraction of the pulp occupied by gas, which is determined by the volumetric gas flow rate and velocity. The bubble velocity itself is a function of bubble shape, which in turn is a function of surfactant concentration. The more spherical the bubble the lower the terminal velocity (Kracht and Finch 2010), so the presence of a surface-active substance in solution reduces the bubble terminal velocity. This phenomenon was also explained in terms of an enhanced viscosity of interface due to surfactant adsorption, by Boussinesq (Malysa 1992).

The most popular theory explaining the effect of surfactants on the shape and velocity of air bubbles in surfactant solutions is the “surface tension gradient” theory. According to Levich (1962), the viscous drag of the medium acting on the surface of a rising bubble leads to redistribution of frother molecules on the surface of the bubble, with a higher concentration of surfactant at the bottom than at the top of the bubble (Figure 2-10).

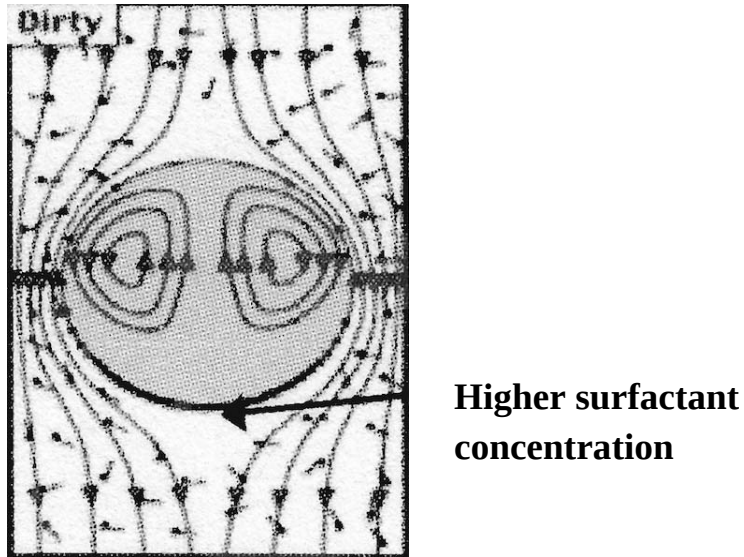


Figure 2-10. Surface tension gradient

This difference in surfactant concentration induces a surface tension gradient around the bubble surface, which generates a net force directed to the top of the bubble and produces a flow of water in the adjoining water film, a phenomenon known as the *Marangoni effect*. The textural fluctuations on the bubble surface caused by the Marangoni effect are demonstrated in Figure 2-11 for two surfactants, a short chain alcohol (pentanol) and a high molecular weight polyglycol (F150).

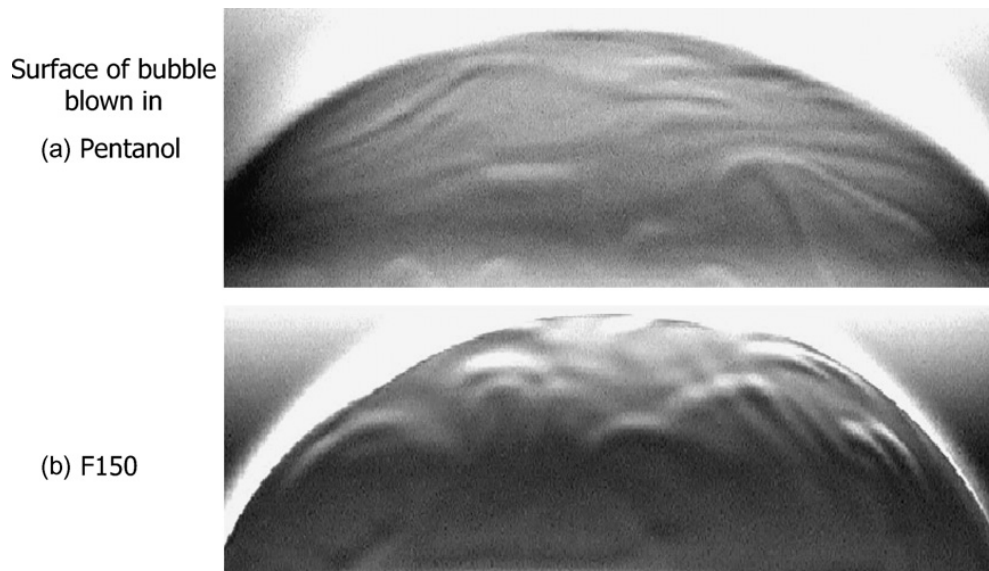


Figure 2-11. Frame of video imaging of bubbles blown in (a) pentanol and (b) F150. The texture results from fluid flow due to gravity and the Marangoni effect drawing liquid from the pool below (Finch et al 2008)

These nearly simultaneous processes increase the rigidity of small bubbles, which prevents bubble deformation by external forces in the presence of a surfactant and preserves the spherical shape of the bubble. The energy of resistance to external deformation is taken from the kinetic energy of the moving bubble, which affects (decreases) the bubble velocity as well. So the higher the concentration of frother on the bubble surface, the higher the surface tension gradient, which leads to a more spherical shape of the bubble and to a lower bubble rise velocity. Finally, lower bubble velocities allow the bubbles to stay for a longer period of time in the solution phase, which manifests itself by an increased gas hold-up.

Regarding the changes in gas bubble sizes in the presence of surfactants, two main theories, that is the “coalescence prevention” theory (Cho and Laskowski 2002) and the “bubble break-up” theory supported by a surface tension gradient (Finch et al 2008), are most frequently cited. The main assumption behind the “coalescence prevention” theory is that a bubble is initially generated at a characteristic size (as defined by the size of openings of the sparger system, flotation cell dimensions, configuration, and operating conditions) but its equilibrium size is controlled by coalescence with other bubbles. The role of the frother is simply that of dispersant preventing bubble coalescence. This idea was primarily developed by Cho and Laskowski (2002).

The Sauter mean (d_{32}) diameter is of primary interest in bubble size measurements since froth flotation is driven by the surface area of gas bubbles available for particle-bubble attachment at a given volumetric flow rate of air. It is calculated from the bubble size distribution using the following formula:

$$d_{32} = \frac{\sum_{i=1}^{i=n} d_i^3}{\sum_{i=1}^{i=n} d_i^2} \quad (2-11)$$

Which characterizes the relative change in bubble volume (d^3) to the corresponding change in the bubble surface area (d^2) as a result of surfactant additions.

Gibbs elasticity and Marangoni effects are the two characteristics mentioned in literature as the parameters preventing bubble coalescence (Harris 1982, Pugh 1996). Dukhin et al (1998) also explained the bubble shape stabilization in terms of surface tension gradient driven phenomena, Gibbs elasticity and Marangoni effect. *Gibbs elasticity* is defined as the ratio of the increase in the dynamic surface tension resulting from a small increase in the surface area; this

could be the surface area of a droplet or bubble. The concept of Gibbs elasticity is explained in more detail in section 2.3.2.

Arguments against the bubble coalescence theory, as the only mechanism defining bubble sizes, were also presented. Among those is the fact that not all frothers are anti-coalescence agents (Finch et al 2008). Also, for example, since sixty four 1-mm spherical bubbles are needed to coalesce to form a single 4-mm bubble (typical bubble sizes in flotation), the probability of such a multi-bubble collision and therefore the rate of the coalescence process do not seem to be quite realistic (Finch et al 2008).

The “bubble break-up” theory indicates that the frother is also involved in affecting the initial bubble size through processes other than preventing coalescence. According to this theory, the opposing forces on the surface of a larger bubble generated by the surface tension gradient also create a bulge in the bubble surface that promotes break-away of smaller bubbles as shown in the following Figure 2-12 (Finch et al 2008). The mechanism by which a frother enhances instability on the bubble surface is that when a frother molecule resides in a surface, a force directed away from this point is generated. The opposing force promotes a bulge in the surface that promotes breakaway resulting from low surface tension at the neck where the frother molecules are residing. An increase in frother concentration leads to a closer packing of molecules forming a smaller bulge, and thus the breakaway bubbles are smaller.

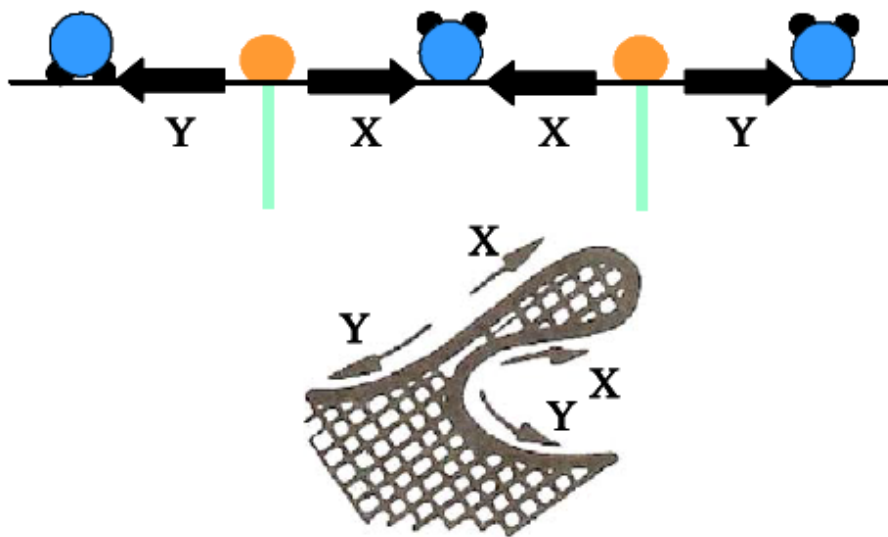


Figure 2-12. The opposing forces from nearby frother molecules induce instabilities in the surface (Finch et al 2008, Miller and Neogi 1985)

One way of characterising the frothing behaviour of different surfactants is to investigate the effects of their chemical composition and structure on the bubble size, gas hold-up and water recovery. Recently there were some efforts to correlate these behaviours to parameters such as Hydrophile-Lipophile Balance, HLB (Zhang et al 2012).

The amount of water recovered in the froth could also be an indication of the amount of frother transferred to the froth with the help of bubbles, which correlates with the mechanical entrainment of mineral particles during froth flotation. In literature, the water-carrying rate is correlated with the gas hold-up and bubble surface area flux (Moyo et al 2007 and Zhang et al 2010). Based on the bubble surface area flux and gas hold-up measurements, it seems that frothers recognized as strong give higher water recovery at a certain gas hold-up and bubble surface area flux.

2.3.2 CCC and HLB

The concept of the critical coalescence concentration (CCC) was introduced by Cho and Laskowski (2002 a, b) who defined the CCC as a concentration of surfactant in solution above which the coalescence of bubbles is completely prevented. Cho and Laskowski (2002b) proposed that in order to graphically determine the CCC value, two asymptotes need to be drawn through the experimental bubble size data: one approximating the experimental curve at low surfactant concentrations and a horizontal asymptote approximating the experimental data at higher surfactant concentrations. This approach requires a sufficiently large number of data points in the lower concentration range, which is hardly ever the case as far as published data permit to conclude. Also, the experimental results at higher surfactant concentrations very often do not reach a clearly defined plateau so the location of the horizontal asymptote is not always easy to determine. Because of these ambiguities in the graphical procedure of Cho and Laskowski (2002b), Finch et al (2008) proposed a curve fitting procedure to estimate a value of the critical coalescence concentration. Finch et al (2008) used an empirical equation that can be written as:

$$D_{32} = D_L + (D_0 - D_L) \cdot \exp(-b \cdot c) \quad (2-12)$$

Where D_{32} is the Sauter mean bubble size, D_L is the lowest (limiting) Sauter mean bubble size at high surfactant concentrations, D_0 is the initial Sauter mean bubble size at $c = 0$, b is the decay constant, and c is the surfactant concentration. Rearranging equation 2-12, the following expression is obtained:

$$\frac{D_{32}-D_L}{D_0-D_L} = \exp (-b \cdot c) \quad (2-13)$$

From this equation, Finch et al (2008) defined the critical coalesce concentration as such a surfactant concentration at which the difference between the mean bubble size D_{32} and the lowest bubble size D_L is within 5% of the difference between the initial (D_0) and lowest (D_L) bubble sizes. In other words, the following condition must be met:

$$0.05 = \exp (-b \cdot c) \quad (2-14)$$

And the required concentration to meet the above condition is $c = \ln (0.05)/b$. The whole procedure then comes down to finding b using equation 2-12 to fit the experimental data and then calculating the corresponding value of c from the above expression. The critical coalescence concentration obtained through this model fitting procedure is most commonly designated as CCC95 (Finch et al 2008).

Figure 2-13 explains the terminology and procedures for obtaining the CCC, as defined by Cho and Laskowski (2002b), and for calculating the CCC95, as proposed by Finch et al (2008).

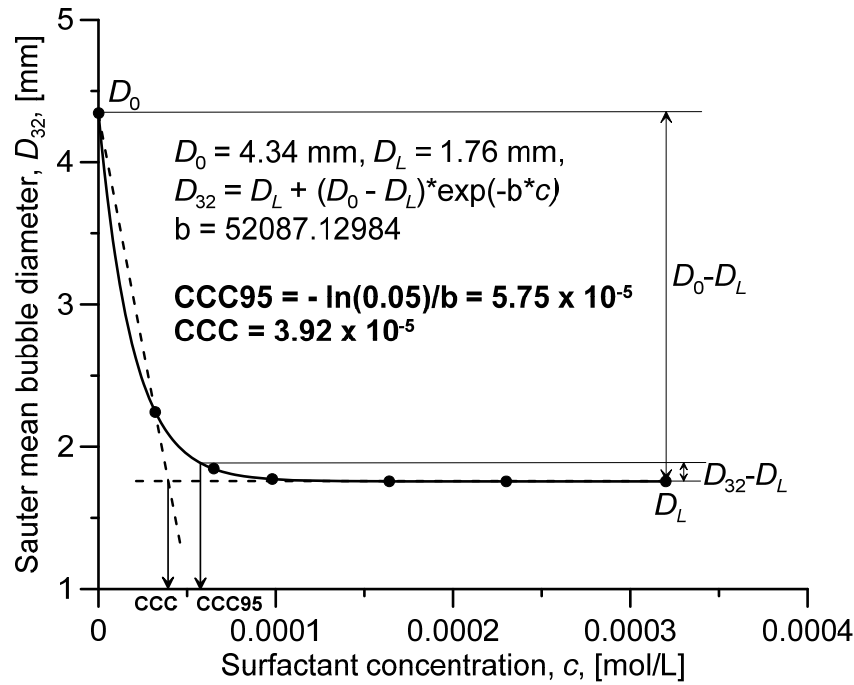


Figure 2-13. Definitions and determination of the CCC (Cho and Laskowski 2002b) and CCC95 (Finch et al 2008), experimental points are taken from this thesis and show bubble sizes measured in oleic acid solutions at pH 10.4

It should be noted that the CCC and CCC95 values would hardly ever be the same for a given set of experimental data so caution should be taken when comparing the CCC and CCC95 values obtained using different graphical procedures.

HLB (Hydrophile-Lipophile Balance) is a property indicative of surfactant structure and according to the Davis method (Davies and Rideal 1961) the HLB of a surfactant is calculated as follows:

$$\text{HLB} = \Sigma (\text{hydrophilic group numbers}) + \Sigma (\text{hydrophobic group numbers}) + 7 \quad (2-15)$$

HLB values for different reagents are calculated based on the group number of the components in their structure. HLB for ionic surfactants also depends on their state in solution and their electrical charge. For example, for the $-\text{COOH}$ group the HLB value is 2.1 but for the $-\text{COO}^-\text{K}^+$ group the HLB is 21.1 while for $-\text{COO}^-\text{Na}^+$ it is 19.1 (Davies and Rideal 1961).

The HLB values of the anionic reagents used in this study are calculated as follows. The group number of $-\text{CH}_3$, $-\text{CH}_2-$ and $-\text{CH=}$ is 0.475 and that of $-\text{COO}^-\text{Na}^+$ and $-\text{SO}_4^-\text{Na}^+$ are 19.1 and 38.7, respectively.

Sodium Oleate [$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COONa}$]	$\text{HLB} = 19.1 + 17 * (-0.475) + 7 = 18.0$
Sodium Laurate [$\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$]	$\text{HLB} = 19.1 + 11 * (-0.475) + 7 = 20.9$
Sodium Hexanoate [$\text{CH}_3(\text{CH}_2)_4\text{COONa}$]	$\text{HLB} = 19.1 + 5 * (-0.475) + 7 = 23.7$
Sodium Dodecyl Sulfate [$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$]	$\text{HLB} = 38.7 + 12 * (-0.475) + 7 = 40.0$
Sodium Octadecyl Sulfate [$\text{CH}_3(\text{CH}_2)_{17}\text{OSO}_3\text{Na}$]	$\text{HLB} = 38.7 + 18 * (-0.475) + 7 = 37.1$

Zhang et al (2012) proposed a methodology to characterize frothers by relating the CCC to frother structure, as represented by HLB. Frothers from three families including aliphatic alcohols, polypropylene glycol alkyl ethers (PPGAE) and polypropylene glycols (PPG) were tested. A unique CCC-HLB relationship dependent on n and m (n is the total number of carbon atoms in the molecule and m is the number propylene oxide groups) was demonstrated for each family. The CCC-HLB relationship for the aliphatic alcohols showed that there was an initial decrease in the CCC95 as HLB decreased, but the CCC95 tended to level off above 6 carbons in the molecule, or basically for higher molecular weight homologues (Zhang et al 2012).

Neset et al (2007) suggested that the minimum bubble diameter decreased as the CCC95 increased, or as the HLB increased, and it was shown by Zhang et al (2012) that the relationship between the minimum bubble size and the CCC was linear.

2.4 Foamability behaviour

2.4.1 Theories of foamability

In foam the gas bubbles are separated from each other by thin liquid films. These films (or lamellae) consist of thin layers of bulk liquid sandwiched between two liquid-gas interfaces. The degree of stability of lamellae depends on the bulk liquid viscosity and on effects due to the adsorption of surfactants at the liquid-gas interface (or interfacial phase). The main theories of foams are related to the effect of a surface-active solute on the surface tension and surface viscosity (Prud'homme and Khan 1995). Malysa (1992) listed three physical processes that contribute to foam instability: drainage of liquid out of the foam, coalescence and rupture of bubbles, and Ostwald ripening or gas diffusion from one bubble to another.

Deryaguin (1989) suggested that the properties of liquid in the thin film are different from those of the bulk phase and introduced the concept of *disjoining pressure* as a measure of the corresponding change in thermodynamic properties. According to the following equation, an increase in the chemical potential, $\Delta\mu$, of the thin liquid film equals the disjoining pressure (π) multiplied by the volume per molecule of surfactant (v).

$$\Delta\mu = -\pi v \quad (2-16)$$

By convention, a positive disjoining pressure ($\pi > 0$) means action towards disjoining of the thin liquid film surfaces or towards thickening of the film.

The surface tension of a liquid tends to flatten any curvature at the liquid surface. The surface tension is generally opposed by a pressure difference between the inside and outside lamellar surfaces of a bubble. The gas pressure inside a bubble may be expressed by (Prud'homme and Khan 1995):

$$\Delta p = \frac{4\gamma_{lg}}{r} \quad (2-17)$$

As equation 2-17 indicates, smaller bubbles have a greater inside pressure than larger bubbles; smaller bubbles are therefore more thermodynamically unstable. Thus, smaller bubbles spontaneously disappear since gas diffuses from small bubbles to larger bubbles (Prud'homme and Khan 1995).

The pressure gradient exerted on the liquid film by the adjacent bubbles thins the film by pushing out the liquid sandwiched between the interfaces. As the film becomes thinner, the foam becomes more susceptible to rupture.

Solutes may have a greater affinity for either the liquid-gas interface or for the bulk solution phase. The former is the case for flotation surfactants. This accumulation of the surfactant at the gas-liquid interface is quantified in terms of the surface excess concentration, which is related to the surface tension and surfactant concentration through the Gibbs equation:

$$\Gamma = -\frac{a}{RT} \frac{d\gamma}{da} \quad (2-18)$$

Where Γ is the surface excess, R is the gas constant, T is the temperature (K), γ is the surface tension of the surfactant solution, and a is the concentration of the surfactant in solution.

A solute with a positive Γ can produce an effect known as the *Gibbs elasticity*, E . The Gibbs elasticity is a measure of the resistance against the creation of a surface tension gradient, and can be given as follows:

$$E = \frac{2d\gamma_{lg}}{d\ln A} \quad \text{or} \quad E = -\frac{2d\gamma_{lg}}{d\ln \Gamma} \quad (2-19)$$

In which A is the area of the surface (which could be the surface of a bubble or droplet), γ_{lg} is the dynamic surface tension, and Γ is surface excess concentration. Since in this case non-equilibrium surface tension is measured as a function of a change in surface area, it is considered dynamic surface tension.

If E is positive, a surface expansion causes a decrease in the excess surface concentration and consequently an increase in the dynamic surface tension. As a consequence, the loss of liquid between the interfaces is balanced by a counter flow of liquid, and further thinning is prevented. This foam stabilization phenomenon is referred to as the *Gibbs-Marangoni effect* (Marangoni 1897). As mentioned earlier, the Gibbs elasticity results from an infinitesimal increase in surface area while the *Marangoni elasticity* is a dynamic non-equilibrium property; in theory, film stabilization also depends on the initial high, non-equilibrium surface tension lasting long enough for a surface flow to occur, as this surface flow of liquid is the cause of film stability. The critical time required is dependent upon diffusion of the solute molecules along the bubble surface from the more concentrated to the less concentrated area. The Gibbs-Marangoni effect predicts that a pure liquid will not foam since a surface tension gradient cannot be formed (Prud'homme and Khan 1995).

The least soluble molecules are often the most readily adsorbed at the gas-liquid interface. Thus the molecular interactions between solvent and solute must be just sufficient to dissolve the solute. The addition of long-chain alcohols to anionic surfactants increases the stability of foams (Sharma et al 1984). The increased stability is attributed to the shielding of the negatively-charged groups of anionic surfactants by the hydroxyl groups of the alcohol

molecules, which allows both types of surfactant molecules to much more densely adsorb at the gas-liquid interface (Prud'homme and Khan 1995).

Although there is a continuous spectrum of properties between weakly foaming and strongly foaming solutions, terms such as transient, wet, or unstable foams on one hand, and dry or metastable foams on the other are often used to describe the two opposite limits. Wet or transient foams are an assembly of spherical bubbles separated by thick liquid walls/films (lamellae). They can exist only during an action of a foam forming force, and when the foam formation is stopped (e.g., aeration stops) a wet foam collapses in a few seconds. In contrast, in dry or metastable foams, bubbles gradually acquire a polyhedral shape and the bubbles are separated by planar or slightly curved liquid films of very small thickness. Such foams can be stable for hours after foam formation ceases. Metastable (dry) foams must pass during their formation through a stage at which they consist of spherical bubbles separated by thick liquid films (Malysa 1992). The total volume fraction of liquid in wet foam is high, around 30%, but in the top layer of the foam it is only about 5%. This observation implies that foam rupture takes place practically only in the top layer and the durability of these top foam layers affects the stability and volume of the whole foam column (Malysa 1992).

It was shown that the stability of wet foams could be explained in terms of the effective elasticity forces and/or in terms of the viscosity of the liquid film, which primarily affects the kinetics of film drainage - *effective elasticity forces* are elasticity forces induced under actual non-equilibrium conditions. For dry foams with a film thickness of 1000 Angstrom or less, the disjoining pressure starts to be of a meaningful magnitude. It was shown by Malysa et al (1991) that effective elasticity forces are the major factor determining the formation and stability of foams formed from fatty acid solutions at very low pH. Surface elasticity forces as a function of frequency are measured using the oscillating bubble method (Lunkenheimer and Kretzschmar 1975, Wantke and Miller 1980).

2.4.2 Foamability measurement

Gas dispersion measurements focus on the effect of surfactants on the behavior of air bubbles in the solution phase as the bubbles form and rise through the flotation pulp. Another way of investigating the frothing capabilities of surfactants is through foamability studies, or studies on the behavior and properties of air bubbles as they reach the solution surface and start

forming foam. The main parameters of interest in foamability are the foam volume, foam growth rate, and foam stability over time. Figure 2-14 schematically shows the distinction between the foam and solution phases, along with the relevant characterization parameters and experimental techniques.

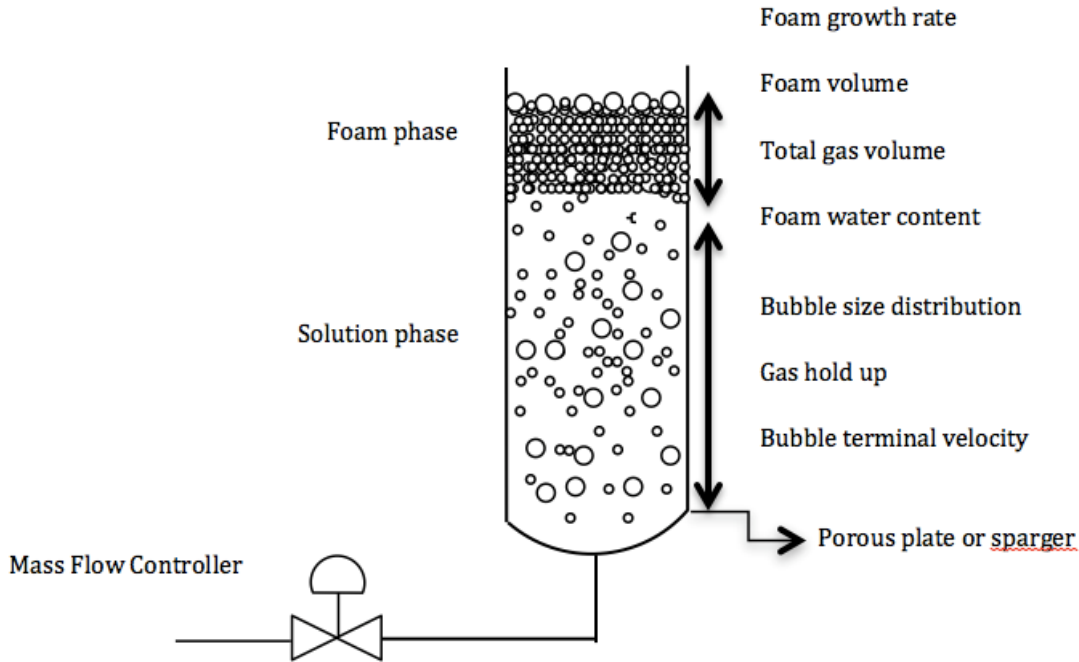


Figure 2-14. Parameters characterizing each phase in foamability and gas dispersion measurements

In principle, two types of foamability measurements can be distinguished: dynamic and static. In the dynamic measurement, the foam is allowed to form under continuous aeration until a steady state is reached between the rates of foam formation and foam collapse/decay. In the static measurement, aeration ceases and the rate of foam formation is zero and the foam once formed is allowed to collapse. Dynamic measurements are typically used for transient foams and static ones are for stable foams. The following sections describe the most important methods for characterizing these types of foam behavior.

Bikerman defined the average bubble life time (Σ) as the slope of the linear relationship between foam volume and gas flow rate (equation 2-20), which was found to be independent of the shape and size of the measuring column and of the average pore size of the sintered glass sparger (Bikerman 1953). In the following equation V_f is the steady state foam volume read at

the gas flow rate U . Coalescence of the bubbles and the volume of the liquid in the foam are neglected.

$$\Sigma = \frac{V_f}{U} \quad (2-20)$$

Czarnecki and co-workers re-examined the dependence of foam volume on the gas flow rate. The term rt was defined as the slope of the linear part of the gas volume-flow rate diagram (equation 2-21), in which ΔV_f is the change in foam volume (units of volume) and ΔU is the change in the gas flow rate (units of volume per time). The parameter rt corrects for the error in Bikerman's approach caused by neglecting the volume of liquid contained within the foam (Czarnecki et al 1982).

$$rt = \frac{\Delta V_f}{\Delta U} \quad (2-21)$$

Figure 2-15 demonstrates typical results of the rt measurements for a range of n-heptanoic acid concentrations.

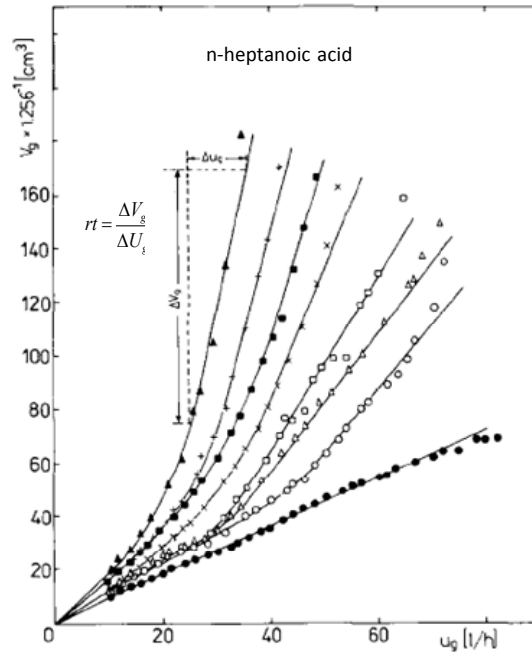


Figure 2-15. Determination of rt values for different concentrations of n-heptanoic acid from 5×10^{-5} to 5×10^{-3} mol/L containing 0.005 M HCl (Malysa et al 1991)

It should be noted that the rt parameter has units of time and is thus often referred to as the retention time. Physically, the rt could be interpreted as the average time that a bubble spends in the system from the moment of formation in solution to the moment of rupture in the foam (Czarnecki et al 1982). Therefore, higher retention time values indicate higher stability of the produced foam. Since the rt changes with frother concentration, another parameter called the dynamic foamability index (DFI) was defined as (Czarnecki et al 1982):

$$DFI = \left(\frac{\partial(rt)}{\partial c} \right)_{c=0} \quad (2-22)$$

According to this definition, in order to graphically obtain the DFI of a surfactant, the rt values are plotted as a function of frother concentration, c , and the slope of a line tangent to the resulting curve at c approaching zero is taken as the DFI . To minimize errors in the graphical determination of DFI , an expression was provided by Czarnecki et al (1982) for fitting experimental values of rt for various concentrations, c :

$$rt - 2.4 = rt_{\infty}[1 - e^{-kc}] \quad (2-23)$$

Where k is a constant and 2.4 is the rt value of distilled water. Analysis of least squares leads to the calculation of rt_{∞} and k values of the best fitting equation. It should also be noted in Figure 2-15 that the rt values (slopes of the linear sections of the curves) initially increase with surfactant concentration but at higher surfactant concentrations the slopes do not significantly change and the rt results for a given surfactant approach a plateau at higher concentrations. Therefore, the rt_{∞} value can also be graphically defined from the data as the limiting rt value for c approaching infinity. The DFI values of selected surfactants are presented in Table 2-3:

Table 2-3. Dynamic foamability index (Czarnecki et al 1982)

Substance	DFI ($\text{sec.mol}^{-1} \text{ dm}^3$)	DFI ($\text{sec.g}^{-1} \text{ dm}^3$)
Ethyl alcohol	5.6×10	1.2
n-Propyl alcohol	2.8×10^2	4.7
n-Butyl alcohol	1.6×10^3	21.6
n-Amyl alcohol	4.6×10^3	52.3
n-Hexyl alcohol	1.7×10^4	166.7
Diacetone alcohol	2.9×10^3	25.0
Mesityl oxide	4.5×10^3	45.9
α - Terpineol	1.1×10^5	713.3

The DFI can physically be viewed as a measure of the ability of a given surfactant concentration to generate a foam volume over a period of time. Overall, the DFI and rt_{∞} parameters are used as *dynamic* measures of foam volume and foam stability, respectively.

2.4.3 Effect of surfactant structure on foamability

Beneventi et al (2001) looked at the role of surfactant structure on the foaming properties of surfactants by measuring the surface tension, adsorption kinetics, and foam stability. Beneventi et al also used the retention time, rt , at a flow rate specific for each concentration (to avoid overflow), as a measure of foam stability. Comparing a number of cationic surfactants (with a trimethylammonium bromide hydrophilic group), with different hydrocarbon chain lengths, it was shown that the longer the hydrophobic chain, the more stable foam was produced, which was explained in terms of the high surface activity and high surface dilational modulus of the surfactants with longer hydrocarbon chains.

On the other hand, adsorption kinetics was shown to be lower for the long chain amines, which was interpreted as an indication that the impact of structural properties of a surfactant on foam stability was more significant than the kinetics of their adsorption. However, sodium oleate created more stable foam compared to sodium stearate even though both acids had the same

hydrocarbon chain length (C18) (Beneventi et al 2001). The difference in the results for these two acids was explained by the higher surface activity induced by the double bond in the oleate molecule. Since oleate diffused more slowly than stearate, this effect was treated as another indication for the dominant role of structural properties over the diffusion rate (Beneventi et al 2001). Adsorption kinetics and the diffusion rate were quantified by the kinetic rate constant and the surface modulus of these surfactants.

On the other hand, Malysa et al (1991) studied the stability of wet foams of fatty acid solutions (n-pentanoic to n-decanoic) in a dilute hydrochloric acid as the background electrolyte using retention time (*rt*) values as measures of foam stability. The results indicated that the foamability of the carboxylic acids increased with increasing chain length (up to C₈) but then decreased for C₉ and C₁₀ acids. Malysa et al showed that there was an agreement between the dependence of foamability parameter (retention time, *rt*) and the effective elasticity forces on the number of carbon atoms in fatty acid molecules. The lowest foam stability observed for n-nonanoic acid, despite its highest surface activity (ability to reduce the surface tension of water) was explained by the elasticity forces, which were the decisive parameter in the formation and stability of such wet foams. As a result, foam stability could not directly be correlated to surface activity since the surface activity of a surfactant is a parameter characterising the solution/gas interface under steady state conditions (Malysa et al 1991).

2.5 Adsorption behaviour at the gas-liquid interface

2.5.1 Gibbs adsorption theory

The Gibbs adsorption isotherm can be used to calculate the amount of surfactant adsorbed at the interface (surface excess). The surface excess concentration is affected by dynamics of diffusion, adsorption and desorption.

$$\Gamma_{ads} = -\frac{1}{mRT} \cdot \frac{d\gamma}{d\ln c} = -\frac{c}{mRT} \frac{d\gamma}{dc} \quad (d\ln c = \frac{dc}{c}) \quad (2-24)$$

Where Γ_{ads} is the surface excess or the adsorption density of the surfactant, R is the gas constant, T is the temperature (K), γ is the surface tension of the surfactant solution, and *c* is the

concentration of the surfactant in solution. The factor m is called the salt parameter and is given by (Matijevic and Pethica 1958):

$$m = 1 + \frac{C_s}{C_s + C_{salt}} \quad (2-25)$$

Where C_s is the surfactant concentration and C_{salt} is the background electrolyte (salt) concentration. When $C_{salt} = 0$, i.e., only the surfactant is present in solution, m assumes a value of 2. On the other hand, when the electrolyte concentration is much higher than the surfactant concentration, m approaches a value of 1. As a result, as illustrated in Figure 2-16, an addition of a neutral salt causes an overall shift of the γ -concentration curve towards lower surface tension values. The figure shows the effect of chain length on the surface tension as well. According to the Gibbs equation, the more rapid the change in the surface tension vs. concentration curve, the higher the adsorption density at the air-solution interface. The Gibbs equation can be used only for surfactant solutions with surfactant concentrations lower than the CMC. As demonstrated in Figure 2-16 the presence of another surfactant in small quantities (as an impurity) may cause the appearance of a minimum around the CMC (Leja 1982).

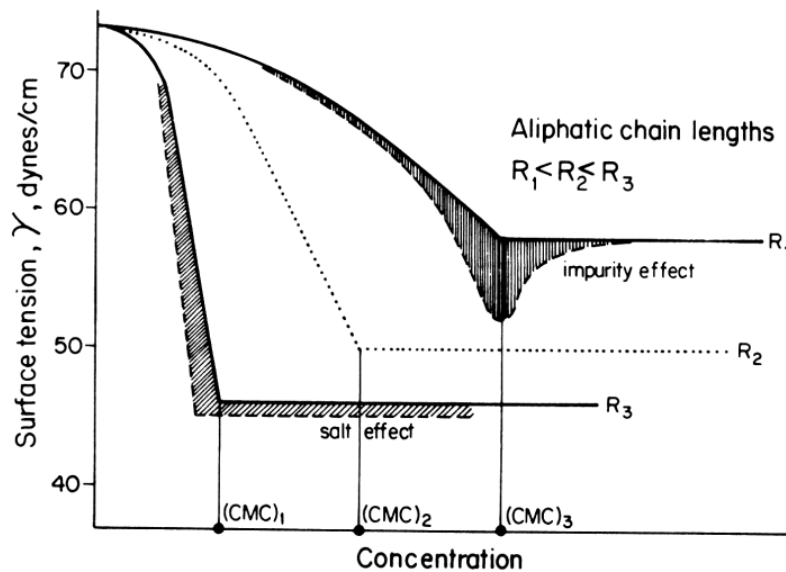


Figure 2-16. Typical effect of surfactant chain length on the surface tension of aqueous surfactant solutions (Leja 1982)

2.5.2 Dynamic surface tension (DST)

According to the Ward and Tordai model, a decrease in the dynamic surface tension can be described as a process of diffusion-controlled adsorption to a clean surface (Ward and Tordai 1946). If back diffusion is considered, the adsorption equation becomes:

$$\Gamma(t) = 2C_0 \left(\frac{Dt}{\pi}\right)^{1/2} + 2\left(\frac{D}{\pi}\right)^{1/2} \int_0^t C_s(t-\tau) d\tau^{1/2} \quad (2-26)$$

Where $\Gamma(t)$ is the adsorption density or concentration at the surface at time t , C_0 is the bulk concentration, D is the diffusion coefficient, C_s is the sub-surface concentration (the concentration in the solution layer adjacent to the interface) and τ is the dummy variable of integration. In the above equation the first term represents the mass transport from the bulk phase to the interface and the second term is the mass transport from the surface to the sub surface.

At the very beginning of the diffusion process, at which desorption from subsurface to the bulk is negligible; the surface concentration could be measured by neglecting the integral term in equation 2-26. At this stage the surface is sufficiently free to take up solute molecules as fast as they arrive and the subsurface concentration is zero. Under these conditions, the adsorption density can be given by:

$$\Gamma(t) = 2C_0 \left(\frac{Dt}{\pi}\right)^{1/2} \quad (2-27)$$

Theander and Pugh (2001) developed two equations describing the surface tension at short and long time scales by substituting equation 2-27 for the adsorption density, Γ , in the expression ($\gamma_{eq} = \gamma_0 - nRT\Gamma$):

$$\gamma_{t \rightarrow 0} = \gamma_0 - 2nRTC_0 \sqrt{\frac{Dt}{\pi}} \quad (2-28)$$

$$\gamma_{t \rightarrow \infty} = \gamma_{eq} - \frac{\Gamma^2 RT}{C_0} \sqrt{\frac{\pi}{Dt}} \quad (2-29)$$

The diffusion coefficient could be calculated from the surface tension versus $t^{-1/2}$ plots.

Enhanced flotation at higher temperatures was also reported by several researchers. Theander and Pugh (2001) claimed that an increase in temperature could increase the diffusion rate of the oleate species. Their dynamic surface tension measurements revealed that the surface tension decreased more rapidly with an increase in temperature and showed that the diffusion coefficient of oleate also increased with temperature. The diffusion coefficient D was related to the temperature by Stokes-Einstein equation (Theander and Pugh 2001):

$$D = \frac{kT}{6\pi\eta a} \quad (2-30)$$

Where k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of water and a is the hydrodynamic radius of the particle.

An aspect of dynamic surface tension application was presented by Comley et al (2002).

They looked at the surface tension data and the bubble sizes for a number of n-alcohols. In the short time during which bubble coalescence occurred, the surface excess concentration of the longer chain frothers was significantly lower than the equilibrium value, so the coalescence rate that defined the observed bubble sizes could only be affected by the fractional surface coverage of the bubble by the frother within such a short time frame. The surface coverage of a bubble within a specific time, and not the bulk concentration of the surfactant, was the determining factor for the bubble size. Therefore the dynamic surface tension rather than equilibrium one appeared to be a more appropriate criterion for interpretation of bubble size data in a flotation system (Comley et al 2002).

Although the very low concentration of frother used in flotation may cause a very small change in the surface tension, it can be estimated that the concentration of the frother in the froth phase should be directly related to the transfer rate of water (water carrying rate) to the froth which could be helpful in modeling froth phase performance (Comley et al 2002).

2.6 Electrokinetic properties

Adsorption of ionic surfactants and polymers leads to the generation of surface charges on particles/bubbles. The surface itself does not have to be charged but the adsorbing ionic species will impart a charge to such a surface. When a charged particle is placed in a solution of an electrolyte, an ion concentration profile develops around the particle, which is referred to as the electrical double layer (EDL). The surface potential of charged surface is defined as the work required to bring a unit charge from infinity to the charged surface. However, because of the presence of the double layer of ions, one can only measure some effective potential at a distance away from the surface, and this potential is commonly called the zeta potential (ζ).

The zeta potential is more important than the surface potential because when colloidal particles randomly move in an electrolyte solution, the diffuse layer of EDL consisting of weakly attached ions is sheared off, and the compact (Stern) layer of strongly adsorbed ions becomes exposed to other approaching or colliding particles. Due to this shearing effect, the Stern layer is said to end at the shear plane. Therefore, the Stern potential (or the zeta potential) is the effective energy barrier that a charged particle senses as it approaches another charged particle. There are a number of methods that can be used to obtain the zeta potential. They are collectively referred to as electrokinetic effects to stress the fact that they all involve some form of particle motion with respect to the surrounding medium (electrolyte solution).

2.6.1 Electrokinetic properties of bubbles in presence of weak electrolyte surfactants

Air bubbles are negatively charged in the absence of surfactants, which is most often explained by differences in the hydration energies of H^+ and OH^- ions. Cations have significantly higher hydration energies than anions, and as a result the OH^- ion will preferentially adsorb on inert gas surfaces compared to hydrated and more slowly diffusing hydrogen cations.

Healy and Fuerstenau (2007) also argued that the double layer charge on air bubbles is due to increased concentration of OH^- ions at the gas-liquid interface. However, they noted that the iso-electric point (iep) of air bubbles is in the pH range of 1-3, which is characteristic of acidic surfaces. Considering that the air bubble surfaces do not possess any functional acidic groups, they attributed such a low iep value to a large shift by 6 orders of magnitude in the ionization constant of water in the interfacial region compared to the ionization constant of bulk water. As a result, a much higher concentration of OH^- ions could be expected at the interface.

The type of ionic surfactant (anionic or cationic) determines the sign of the zeta potential of a gas bubble in solution of strong electrolyte type of surfactants (Yoon and Yordan 1986), but for weak electrolyte surfactants the bubbles are either negatively or positively charged depending on pH (Laskowski et al 1989). The zeta potential of air bubbles in the presence of sodium dodecyl sulfate and sodium oleate were measured as a function of pH by Yoon and Yordan (1986) and demonstrated in Figure 2-17.

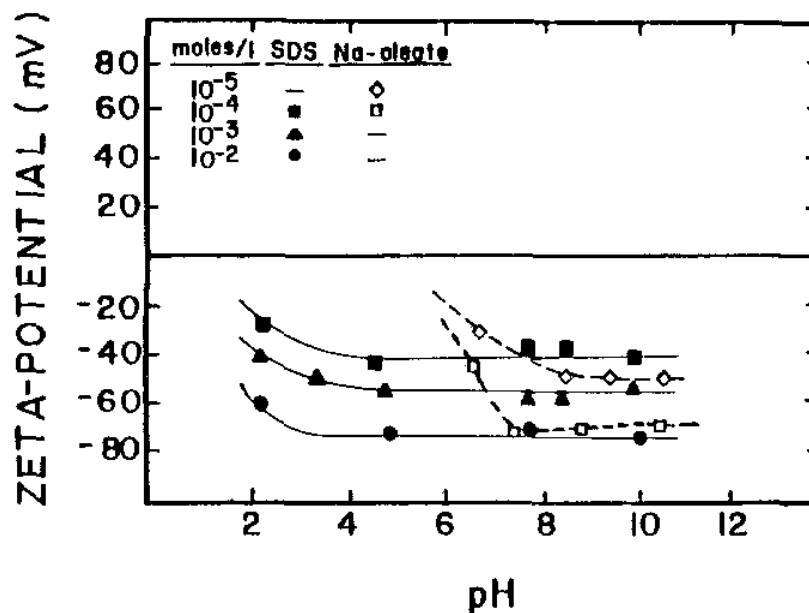


Figure 2-17. Zeta potential of microbubbles generated using different concentrations of sodium dodecyl sulfate and sodium oleate as a function of pH (Yoon and Yordan 1986)

The iep values of colloidal fatty acid precipitates, as well as of gas bubbles were all found to be very similar around pH 2.5-3, as shown in Figures 2-18 and 2-19, respectively. Laskowski et al (1989) suggested that colloidal fatty acid precipitates are partially hydrophobic, they coat the bubbles and make the iep of the bubbles close to that of the precipitate alone. However, the iep of air bubbles in the absence of surfactants is about pH 2-3. The iep of fatty acid precipitates is also near pH 2-3. As a result, there is a possibility that there is no interaction at all (no coating) between bubbles and precipitates since electrostatic repulsion should prevent coating.

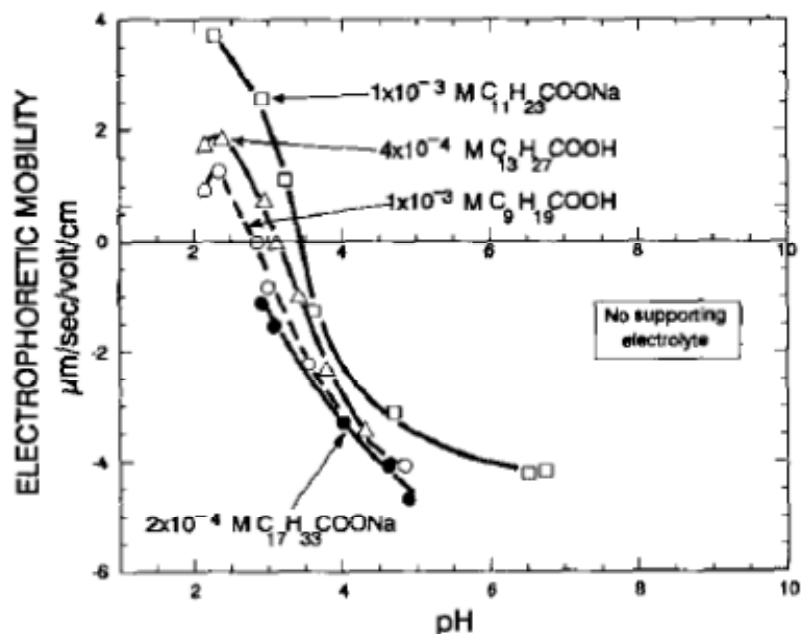


Figure 2-18. Effect of pH on electrophoretic mobility of colloidal precipitates in aqueous solutions of fatty acids (Laskowski 1993)

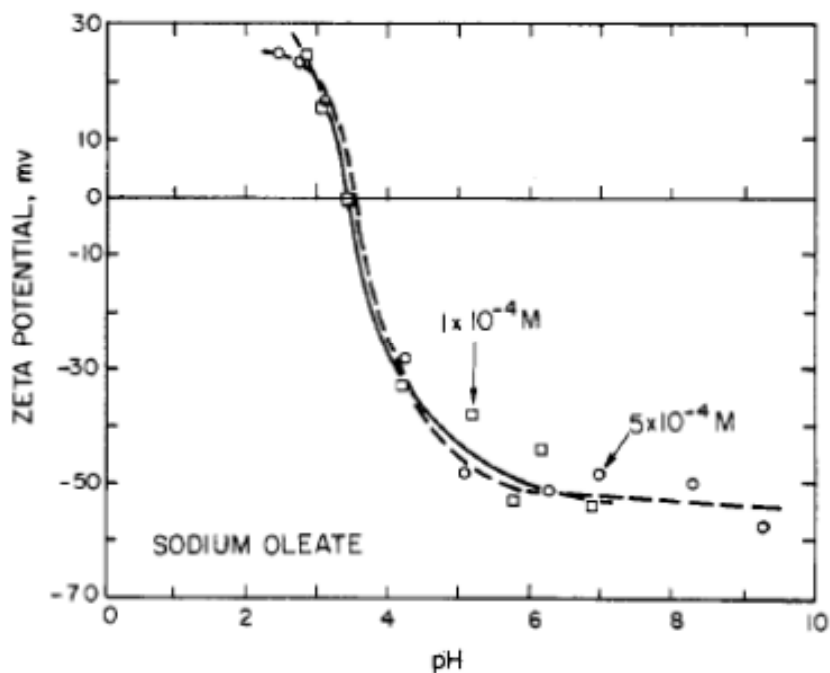


Figure 2-19. Effect of pH on the zeta potential of micro bubbles generated in sodium oleate aqueous solutions (Laskowski et al 1989)

2.6.2 Role of precipitates in electrokinetic behaviour

The zeta potential of gas bubbles in the presence of weak electrolyte surfactants is also affected by the adsorption/adhesion of colloidal surfactant precipitates to the surfaces of bubbles. So changes in the zeta potential of bubbles could be an indication of the onset of precipitation at the gas/solution interface. This precipitation point (pH or ion concentration) at the interface can be different from the precipitation conditions in the bulk solution. Such differences were documented for the solid-liquid interface in the theory of hemimicellization (Somasundaran and Krishnakumar 1997). Peters and Heller (1970) indicated that in solid colloidal systems the rate of coagulation could increase in the presence of liquid/gas interface. Laskowski et al (1989) demonstrated through measurement of the bubble zeta potential in solutions of dodecylamine that precipitation at the liquid-gas interface begins at lower pH than precipitation in the bulk solution. Therefore, zeta potential measurements may provide information not only about surfactant adsorption but also about precipitation phenomena occurring at the gas-liquid interface.

The determination of the adsorption density of surfactant precipitates is very difficult, but a lot of information on the adsorption of these surfactants may be obtained from electrokinetic measurements (Laskowski et al 1989). Figure 2-20 (a) shows the i.e.p of hematite particles in the presence of oleic acid; the higher the concentration of oleic acid, the lower the i.e.p of hematite which shifted closer to the i.e.p of oleic acid precipitate. According to Laskowski et al (1989), this result indicated the presence of colloidal oleate on the surface of the mineral particles. The role of precipitate could be more clearly presented when the same data were superimposed on the domain diagram of oleic acid in Figure 2-20 (b). It can be concluded that the i.e.p of hematite is strongly affected in the concentration and pH range in which the precipitate appears in oleic acid solution (Laskowski 1993).

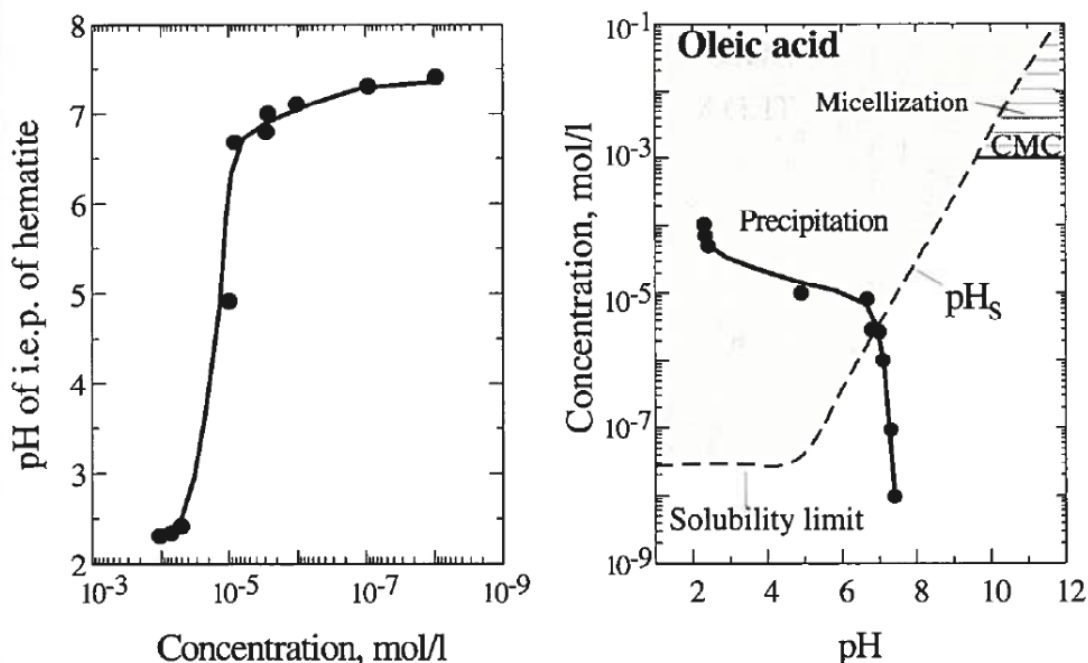


Figure 2-20. (a) The pH of the iep of hematite in solutions of sodium oleate, (b) Domain diagram for oleic acid with iep of hematite superimposed from Aktar and Lai

(Laskowski 1993)

However, this figure could be interpreted from another point of view. The iep of hematite is about pH 7, so at pH values higher than 7 the hematite surface is negatively charged and electrostatic repulsion should prevent adsorption of anionic oleate. Under such conditions the iep of hematite could be expected to be independent of oleate concentration, which is what Figure 2-20 (b) is showing. In the acidic range, since iep of oleic acid precipitate is at pH 3, at pH values lower than 3, both hematite and oleic acid precipitate are positively charged and electrostatic repulsion should prevent any adsorption, and again the iep of hematite should not change with pH, which is also seen from the figure. Only when the precipitate and hematite particles are oppositely charged (in the pH range from 3 to 7), does the iep of hematite significantly change with pH – interaction is driven by electrostatic attractive forces.

2.6.2.1 Effect of Ca^{2+} ions on electrokinetic behaviour of fatty acids

Electrophoretic measurements show that calcium oleate particles are strongly negatively charged even in moderate excess of calcium. Bung and Fuerstenau (2006) investigated the role of calcium palmitate precipitates on the zeta potential of fluorite. The zeta potential of palmitate species versus pH at different calcium levels is demonstrated in Figure 2-21. At low pH values

the curves coincide with the palmitic acid curve, but then level off at higher pH depending on calcium concentration. This could be due to the fact that after precipitation, the concentration of palmitate ions in equilibrium with calcium salt is fixed by the solubility product.

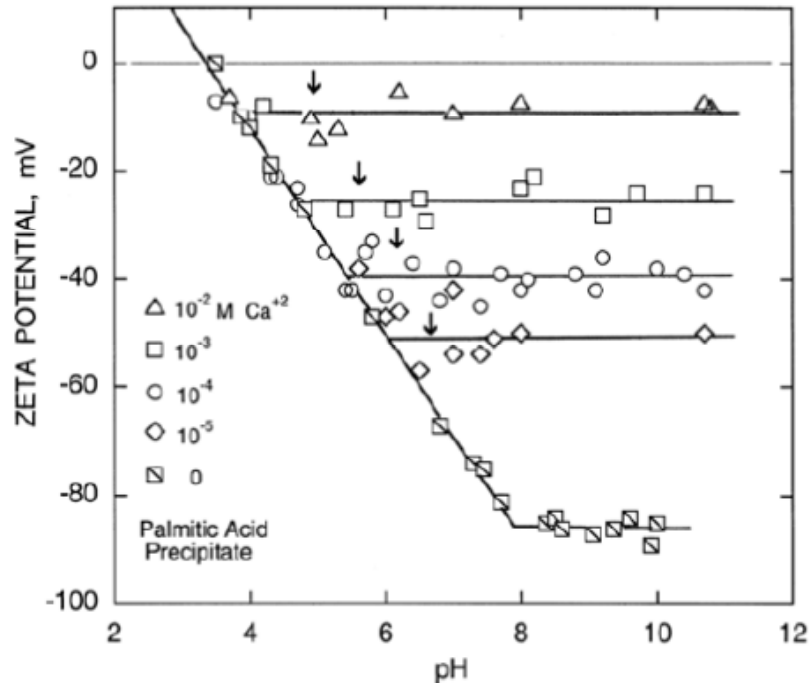


Figure 2-21. Zeta potential of palmitate precipitates versus pH at different calcium levels. The particles at low pH are palmitic acid and calcium palmitate at higher pH; Arrows show the palmitic acid and calcium palmitate domains (Fuerstenau and Bunge 2006)

3. Experimental set up

3.1 Procedures, methods and equipment

Surface tension and turbidity measurements were initially performed for characterizing the solution properties of reagents, introduced in section 3.2, while gas dispersion and foamability measurements were carried out to assess the frothing properties of these reagents.

3.1.1 Surface tension measurements

Surface tension measurements provide information on the surface activity and adsorption of surfactants at the gas-liquid interface under different experimental conditions. Moreover, the critical micelle concentration (CMC) of the reagent can also be determined through these measurements. Since pH changes the species distribution of most of fatty acids, the effect of pH on the surface activity of the surfactants was of primary interest to this investigation.

Various methods are available for the surface tension measurement. Some methods are more suitable for equilibrium surface tension measurements and others for non-equilibrium measurements. In the ideal case, the initial surface tension of the freshly prepared surfactant solution is the same as that of the solvent. In reality, the equilibrium value is not achieved until after a certain time, which can range from milliseconds to hours depending on the rate of surfactant adsorption at the gas-liquid interface. In dynamic measurements, the decisive factor is the surface tension value that is achieved during the time from the formation of the surface to the instant of the use of that surface in an interfacial process. A good example is the case of air bubble formation at the tip of a capillary immersed in an aqueous solution. As soon as a bubble is formed the dynamic surface tension measurement will start. The bubble continues to change its shape and creates a new surface available to surfactant adsorption and to rearrangement of surface-active species. This leads to a decrease in the measured surface tension, and the bubble will eventually detach, rise to the liquid surface, and rupture at the surface. A surface tension value at a specific time interval could then be defined. The bubble volume and the rate of formation of the bubble are usually adjusted to be the same for different test conditions, so that the surface of the bubbles is equally exposed to the aqueous phase before the test started. So the assessment of the surface activity of surfactants is highly dependent on the surface age. Typical time scales for interfacial phenomena (e.g., film thinning and rupture, particle bubble-

attachment, etc.) during mineral flotation are assumed to be 10-1000 milliseconds (Bike-Krause and Thomsen 2011).

Among surface tension measurement methods, “Du Nouy ring” and “Wilhelmy plate” methods are mostly used for equilibrium surface tension measurements or for very long surface ages, while the “maximum bubble pressure” and “pendant drop” methods are more suitable for non-equilibrium dynamic surface tension measurements. Measurements of the dynamic surface tension provide an indication of how fast a surfactant transfers to the gas/solution interface.

3.1.1.1 Wilhelmy plate method

The tensiometer K11 Mk4 with a display panel KB0803 from Kruss GmbH was used for the measurements.

In the plate method the liquid is raised until the contact between the surface or interface and the plate is registered. On contact with the surface or interface, the surface or interfacial tension acts on the plate. This vertical force is detected by a force sensor; the surface or interfacial tension is calculated from the measured force and wetted length of the plate. The tension is calculated using the following equation:

$$\gamma = \frac{F}{L \cdot \cos\theta} \quad (3-1)$$

Where γ is the surface or interfacial tension, F is the force acting on the force sensor, L is the wetted length and θ is the contact angle.

The plate is made of roughened platinum and is optimally wetted so that the contact angle is virtually 0. So the value of $\cos\theta$ is 1 and only the measured force and length of the plate need to be taken into consideration. Correction calculations are not necessary with the plate method.

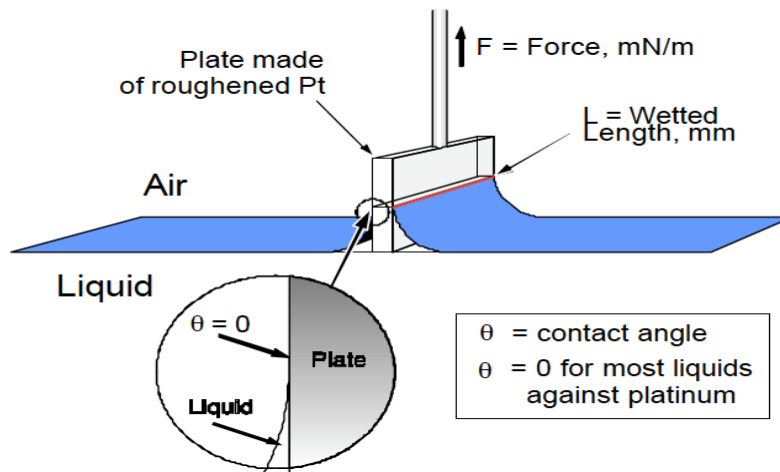


Figure 3-1. Equilibrium surface tension measurement by Wilhelmy plate method (Chamberlain and Rulison 2011)

3.1.1.2 Pendant drop method

A picture of the FTA 1000 B-class instrument used for surface tension measurement by the pendant drop method is demonstrated in Figure 3-2.

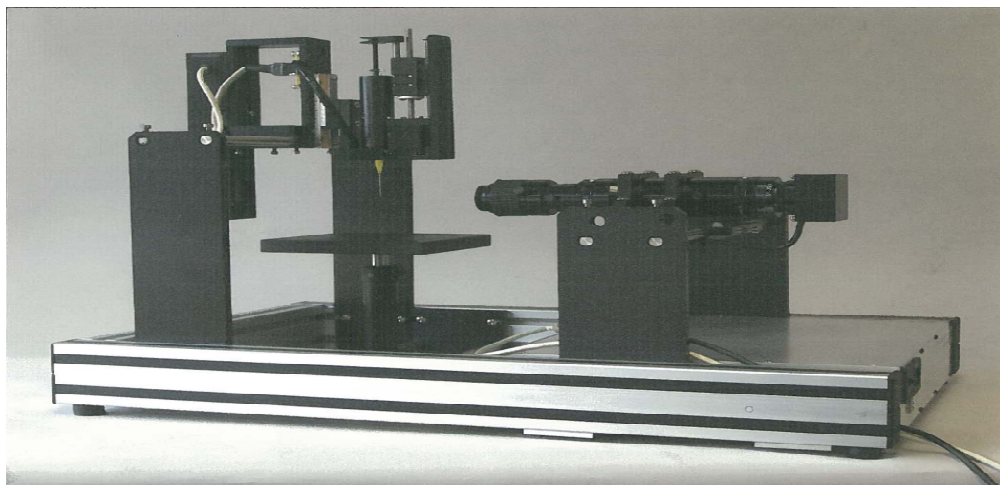


Figure 3-2. Pendant drop method

A droplet of a liquid is generated within either air (surface tension measurements) or another liquid (interfacial tension measurements), and an image of the hanging droplet is taken. In pendant drop method, gravity acts to elongate the drop while interfacial tension opposes

elongation because of the associated increase in interfacial area (Miller and Neogi 1985). The typical shape of a droplet used for calculating the surface tension in the DSA 1 software is demonstrated in Figure 3-3.

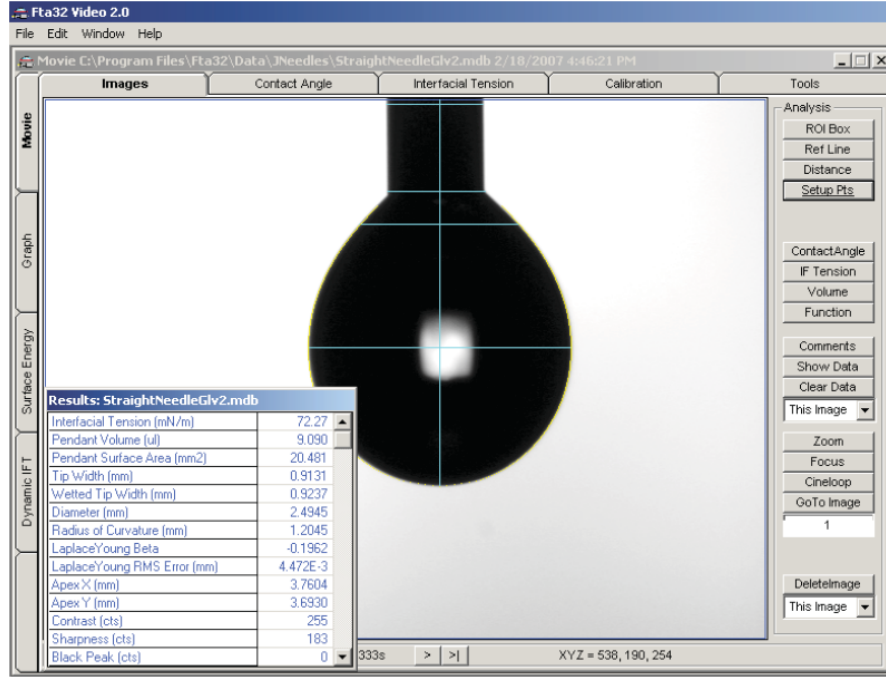


Figure 3-3. A pendant droplet created for calculating the surface tension of water

The droplet shape is analyzed via the Laplace equation. The pressure difference between any two points on the curved droplet surface equals:

$$\Delta p = \gamma \cdot \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (3-2)$$

Δp is the Laplace pressure, γ is the interfacial tension, and r_1 , r_2 are principal radii of curvature at the two points.

Generally, the surface tension forces the liquid to form spherical droplets with smallest surface area at a given volume. In the case of the pendant droplet method, gravity deforms the droplets; the droplet weight generates a hydrostatic pressure within the droplet and influences the radii of curvature r_1 and r_2 , which results in the characteristic “pear shape” of the pendant drop. The pressure difference within the drop between any two vertical positions equals:

$$\Delta p_{Hyd} = \Delta \rho \cdot g \cdot l \quad (3-3)$$

Where Δp_{Hyd} is the hydrostatic pressure; $\Delta\rho$ is the density difference between the liquid and the gas; g is the gravitational acceleration; and l is the vertical distance between the measuring point and needle opening. Those points could be used in pairs (Figure 3-4) with the equations given above to solve for surface tension.

$$\left(\left(\frac{1}{r_1} + \frac{1}{r_2}\right)_{at\ A} - \left(\frac{1}{r_1} + \frac{1}{r_2}\right)_{at\ B}\right)2\sigma = \Delta\rho g Z_{between\ A\ and\ B} \quad (3-4)$$

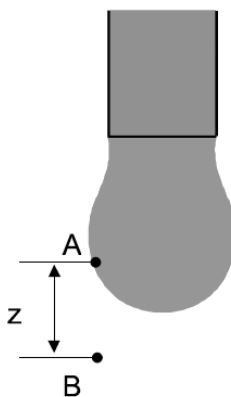


Figure 3-4. Calculations on pendent droplet

The above equation is solved by DSA 1 software for a few hundred pairs of points in less than one second. During a measurement the magnification of the image is taken into account for calculating the actual droplet dimensions. The droplet shape is determined from the image using gray level analysis. A numerical method is used to vary a shape parameter until the calculated drop shape coincides with the actual droplet shape.

For the dynamic surface tension measurement, a fresh droplet of the tested solution is expelled from the needle tip and the surface tension change (non-equilibrium surface tension) is followed as a function of time through the images taken from the droplet until a steady state value is attained. The pendant droplet method can cover a wide range of surface ages, depending on the growth phase of interest, to give surfactant adsorption rates as a function of parameters such as concentration and pH.

The relative surface activities of the tested surfactants can be established through dynamic surface tension measurements and correlated with other dynamic tests, such as foamability and

gas dispersion. Also by comparing the adsorption rates of oleic acid at different pH, an explanation can be proposed for a longer conditioning time required for flotation at acidic pH compared to alkaline pH as reported by Laskowski and Nyamekye (1994).

- FTA bubble method (Wet Cuvette)

This method is as an alternative to the pendant droplet method for measuring the dynamic surface tension with the FTA 1000 instrument in order to determine the adsorption behavior of oleic acid at the gas-solution interface. In this method, a cuvette is filled with a surfactant solution and a J-shaped needle is used to generate gas bubbles at the tip. A known volume of air is pumped from a micro syringe into the solution to form a stable bubble at the tip of the needle (Figure 3-5).

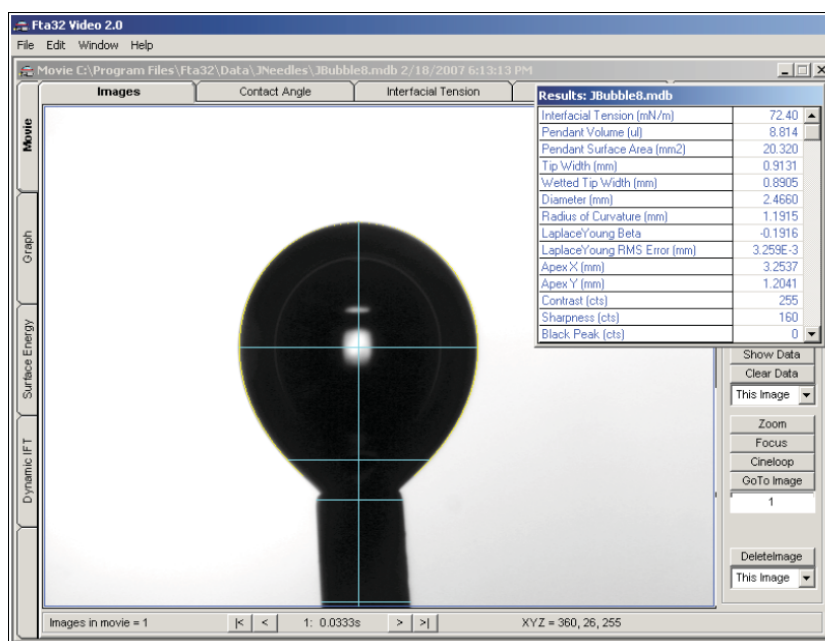


Figure 3-5. A bubble created by a J-needle in a cuvette filled with water for surface tension measurement

The tendency of the air to expand works against the surface tension of the air-water interface. The shape of the bubble is monitored as a function of time (dynamic surface tension) with a digital camera and then analyzed using the Laplace equation until a steady-state shape is attained (equilibrium surface tension). The equilibrium between the Laplace pressure and the buoyancy force applied on the bubble for a pair of points on the bubble circumference with

different radii of curvature could then be solved for surface tension. At steady state, the buoyancy force equals the hydrostatic pressure within the bubble due to its weight.

$$\left(\left(\frac{1}{r_1} + \frac{1}{r_2}\right)_{at A} - \left(\frac{1}{r_1} + \frac{1}{r_2}\right)_{at B}\right)2\sigma = \Delta\rho gl \quad (3-5)$$

The long optical path in water may cause some distortion of the image. By adjusting the backlight intensity, microscope aperture, or camera brightness and contrast, a perfect sharpness, focus quality and contrast can be achieved.

3.1.1.3 *Maximum bubble pressure (MBP)*

A capillary tube is held under the surface of the solution and an inert gas is slowly blown in to the solution while the pressure of the gas stream is carefully monitored. During each bubble formation at the capillary tip, the pressure rises as the curvature of the bubble surface gradually increases until it reaches a maximum, when the bubble has the same radius as the capillary tube. This phase is considered as a growth phase of the bubble, and the time associated with this phase is referred as the surface age. Further development of the bubble results in a decrease of the pressure as the radius of the bubble increases (Hunter 1993). The time of explosive growth and detachment represents dead time. The maximum pressure is converted to the surface tension using the Laplace equation (Adamson 1991).

$$\gamma = \alpha \frac{\Delta p \cdot r}{2} \quad (3-6)$$

3.1.1.4 *Comparison of surface tension methods*

Samples that need a well-defined time zero (very low surface ages) must be run by the maximum bubble pressure method (Chamberlain and Rulison 2011, Kruss technical report, TN307e/JC). This method could be used for samples that attain either a quick equilibrium value, or in cases of low surface ages.

Samples that do not need such quick data acquisition can be tested by the pendant droplet technique. This technique is used for surfactant solutions that do not attain an instantaneous

equilibrium surface tension, and for cases in which the adsorption kinetics of a surfactant at the gas-liquid interface needs to be followed.

Samples that do not exhibit changes in surface tension within a minute or so can be analyzed by the Wilhelmy plate or ring methods (Chamberlain and Rulison, Kruss technical report, TN307e/JC).

3.1.2 Turbidity measurements

Turbidity measurements on fatty acid solutions were performed with a Turbiscan Lab Expert (Formulation, France). The Turbiscan instrument and the relevant measurement principle are presented in Figure 3-6.

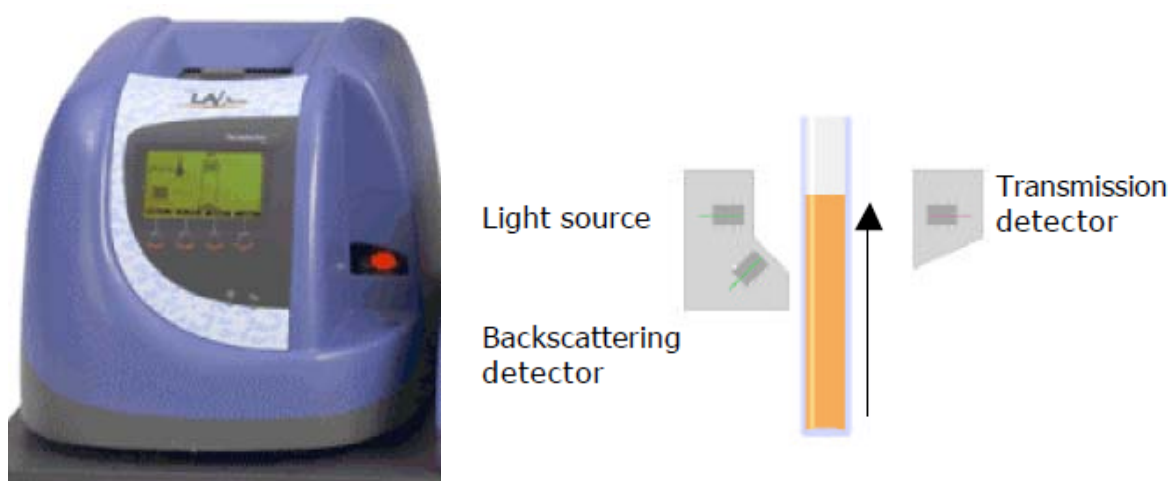


Figure 3-6. Turbiscan lab expert on the left and principle of Turbiscan measurement on the right

The turbidity data were used to assess the state of fatty acid in solution; whether the surfactant was completely dissolved or whether colloidal species (precipitates) were present under various experimental conditions. The Turbiscan uses light scattering to obtain a complete turbidity and light transmission profile of a solution along the entire height of the measuring cell (5-cm) in 45-micrometer height increments. A full scan takes about 40 seconds, so multiple transmission profiles can be obtained as a function of time, if necessary. The main part of the Turbiscan is a detection head, which is composed of a near-infrared light source ($\lambda = 880\text{nm}$) and two detectors. The transmission detector receives the light, which passes through the sample, while the backscattering detector receives the light reflected backward by the sample.

In this research, a single average transmission value (percentage of light transmitted) was measured from the entire profile since it was found that the tested solutions were very uniform, in terms of light transmission along the cell height and through time, even when precipitation of colloidal species was visually obvious. The effect of salt addition, temperature and pH variation on the transmission behaviour of fatty acid solutions could be also followed with the Turbiscan.

3.1.3 Foamability measurement methods

The measuring set up comprised of three glass columns, each 1-meter high and with an internal diameter of 4.3 cm. A picture of the complete foamability set up is included in appendix 5. Air was supplied to each column through a separate digital mass flow meter (ProStar PRS10FRC). Each flow meter was calibrated for airflow at a temperature of 25 °C and pressure of 0.1013 MPa (1 atm.). The airflow rates were controlled by a digital flow controller (ProStar CM4) and flow rate could be adjusted and maintained between 100-1000 cm³/min. In this way, three sample solutions could be tested simultaneously. This digital gas flow control system generated flow rates reproducible within 1% of the pre-set value. A schematic of one foamability column is demonstrated in Figure 3-7.

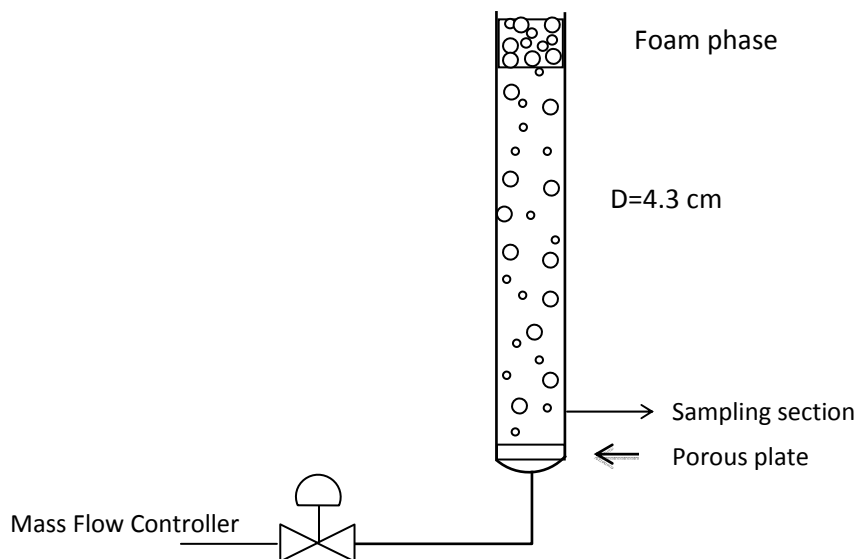


Figure 3-7. A single column of the foamability set up

3.1.3.1 Dynamic Foamability Index (DFI)

For characterizing foamability of fatty acid aqueous solutions, initially the standard procedure for the measurement of the dynamic foamability index (DFI) was employed

(Czarnecki et al 1982, Malysa 1992, Sweet et al 1997). The DFI test is normally performed by changing the volumetric gas flow rate and monitoring the resulting steady-state foam height. This final height value, which can easily be converted to foam volume, is recorded and then plotted as a function of the volumetric gas flow rate. Such a plot is a starting point for the graphical calculation of the retention time, rt , and subsequently of the DFI.

3.1.3.2 *Froth Growth Rate*

In the tests with oleic acid solutions, it was observed that a steady-state foam height was impossible to reach as the height increased continuously at a given air flow rate and fatty acid concentration. In other words, a retention time or a DFI value for oleic acid could not be defined following the standard procedure. This result is different from that usually reported for a typical frother like Methyl Isobutyl Carbinol (MIBC). An alternative approach is to report the foam volume at a fixed end point, which can be a given time or foam height (Novales et al 2010, Beneventi et al 2001, Aktas et al 2008).

A new approach was finally developed by the author which involved a continuous measurement of the foam height as a function of time at a given air flow rate. The procedure was to introduce 100 ml of a test solution into a column, and the air flow rate was adjusted to 400 cm³/min, equivalent to a superficial gas velocity, J_g , ca. 0.5 cm/s, i.e., as that used in the gas dispersion set up.

The first sets of data all showed a linear relationship between the foam height and time, and the slope of the line was used to measure the foam growth rate. When following this procedure another interesting observation was made, particularly for higher fatty acid concentrations. Although the growth of foam continued in a linear manner over a few minutes, at some critical height/time the foam quite rapidly collapsed so the time frame of this test had to be limited. The onset of foam collapse could be detected as a change in the slope of the foam height versus time plots. Therefore, only the initial linear part was considered for calculating the foam growth rate. A similar experimental result was described by Beneventi et al (2001) in their work on the foamability of surfactant solutions, and this behavior appears to be characteristic of long chain ionic surfactants.

Surfactants to be compared included a typical frother, such as MIBC, sodium salts of oleic acid, lauric acid and hexanoic acid as well as strong electrolyte surfactants, such as SDS

(sodium dodecyl sulfate) and ODS (octadecyl sulfate) whose speciation in solution is independent of pH.

3.1.4 Frother partitioning between bulk solution and foam phase (TOC analysis)

The preferential adsorption of surfactant molecules at the gas-solution interface leads to the gradual accumulation of the surface-active species within the generated foam. The rate of transfer of a surfactant by air bubbles and its gradual transfer from bulk to foam could be quantified by taking small samples of the bulk solution at different time intervals and determining the total organic carbon content of the sample, from which surfactant uptake to the foam could be estimated. To perform the test, a regular foamability test was carried out with 200 ml of sodium oleate solution at a predetermined concentration, pH and ionic strength, and 10 ml samples were taken from the bulk solution at 20, 50, 80 or 120 seconds of foaming, or up to a point when the foam collapse started to occur. The sampling of bulk solution was done with the help of a couple of syringes inserted through a plastic connection at the lowest position in the column near the porous glass frit. These samples together with the sample taken from the original solution were then analyzed for TOC to track the bulk concentration changes through time in the foamability test. This type of test was repeated for different concentrations, pH values and ionic strengths of sodium oleate solution. Finally, the surfactant concentrations were plotted as a function of time to present the rate and the amount of sodium oleate partition to the foam at different concentrations, pH, and ionic strength conditions. Analogous TOC data were also collected for the other tested surfactants.

The TOC method enables accurate detection of surfactants in the common range of surfactant concentrations encountered in mineral processing applications, which is on the order of 5-50 mg/L. The TOC technique is based on the complete combustion of organic molecules in the presence of a catalyst (platinum) to produce carbon dioxide. The amount of carbon dioxide released by the sample is then recalculated to the original organic carbon content and subsequently to the surfactant concentration. A TOC-V_{CPH} Analyzer (Shimadzu) was used in these tests. The TOC analyzer is equipped with an oxidation catalytic combustion chamber heated to 680°C, and a non-dispersive infrared (NDIR) gas analyzer where the resultant carbon dioxide is detected as it flows out from the combustion tube of the unit. The area under the generated peaks is measured by the equipment software. This area is linearly proportional to the

TOC concentration of the sample. A calibration curve using standard solutions with known TOC concentrations is however required in order to correlate the area under the peak to the TOC concentration of the sample. The instrument eliminates the issue of inorganic carbon presence in solution through its capability to separately measure the inorganic carbon (IC) thus enabling the determination of total carbon (TC). Acidification of samples with hydrochloric acid to pH below 3 evolves carbon dioxide from inorganic sources (mostly carbonate material and naturally dissolved CO₂). The TOC is then obtained as a difference (TC-IC). However, the equipment can directly determine the TOC by acidifying the sample to between pH 2-3 and purging out carbon dioxide with clean sparging gas before analysis yielding the so called non-purgeable organic carbon (NPOC). The natural amount of purgeable organics (volatiles) in the samples used in this study should be negligible and the NPOC value equals the TOC. This particular Shimadzu model has a wide TOC detection range from 4 µg/L to 30000 mg/L (Total Organic Carbon Analyzer (TOC-VCPH/CPN) User Manual).

In the measurements performed in this study TC-IC method was adopted and the samples were not acidified, as acidifying fatty acid samples leads to precipitation and makes sampling procedure inaccurate. Instead inorganic carbon was measured and subtracted from the TC.

3.1.5 Water recovery measurements

Water recovery was measured at concentrations well above CCC, or under conditions corresponding to the highest foamability for different reagents. These conditions were selected because the total gas volume in the foam phase was known and constant in these cases and equal to the gas volume supplied to the column. It was also important to compare the water recovery at concentrations over CCC, at which bubble sizes are relatively constant.

For this purpose, 1L of a surfactant solution was added to the column. After allowing air to flow into the column, a foam layer started to form and gradually overflowed into the launder installed at top of column specifically for the purpose of water recovery measurement. This overflowing foam was collected for 1 minute. According to the foamability results, at concentrations above the CCC of a surfactant, gas was not escaping from the foam so the foamability was at its maximum. Therefore, it was assumed that after a one-minute time interval the total volume of overflowing foam equaled to the volume of gas supplied to the column, which was 400 cm³. The collected foam was then left to destabilize and the volume of water was

measured. To calculate the volumetric water content in the foam, the volume of water in the foam was divided by the total volume of foam. Finally, the recovered solution was tested for TOC, and the amount of recovered water was correlated to the amount of recovered reagent. This measurement was repeated for sodium oleate, sodium dodecyl sulfate and sodium octadecyl sulfate at concentrations over CCC.

3.1.6 Gas dispersion measurements

3.1.6.1 Bubble size measurements

The ability of the tested surfactant to promote the dispersion of air into small bubbles was assessed using the sampling-for-imaging technique for bubble size distribution measurements (Gomez and Finch 2007 and Zhang et al 2009). The schematic of gas dispersion set-up and its control system is demonstrated in Figure 3-8.

The gas dispersion set up built at UBC is a column of 4-inch (10.16 cm) inner diameter and 2.5-meter height equipped with a porous plate sparger (nominal 5 μm pore size). As air bubbles formed and rose through the column, some were collected and directed to the viewing chamber through a sampling tube of 70 cm, made of PVC. On top of the column, a rectangular bubble-viewing chamber and a high-speed camera (Canon EOS Rebel T3i with EF-S 18-55 mm) are attached to aluminum brackets. The bubbles are directed from the bulk solution to the chamber filled with a surfactant solution when the tube valve is left open. The viewing chamber of the analyzer is filled with a solution of the same surfactant to prevent bubble coalescence and to preserve the bubble size distribution. The bubbles are exposed under pre-set backlighting conditions to be imaged using the camera. The sloping glass window of the chamber helps with arranging the moving bubbles into an ordered monolayer to facilitate bubble tracking and sizing. A superficial gas velocity, J_g , of 0.5 cm/s was employed and kept constant through all measurements. The typical superficial velocity range in flotation is 0.5-2.5 cm/s and the lower end was selected to get the lowest bubble size achievable under the experimental conditions. It should be remembered that higher volumetric gas flow rates at a fixed cross-sectional area of the column increase the probability of bubble collisions and thus enhance bubble coalescence and increase bubble sizes.

Extra dry air is supplied from a compressed gas cylinder. Air passes through three digital mass flow meters (ProStar PRS10FRC) with a maximum flow rate of 1000 cm^3/min in each. The

flow meters are connected in parallel to produce a total gas flow rate of 2400 cm³/min ($J_g=0.5$ cm/s). The airflow rate is controlled by a digital flow controller (ProStar CM4). A picture of complete gas dispersion set up at UBC is included in Appendix 5.

A large number of bubble images were captured at each condition giving a population of at least 3000 bubbles. Image samples are demonstrated in Figure 3-8.

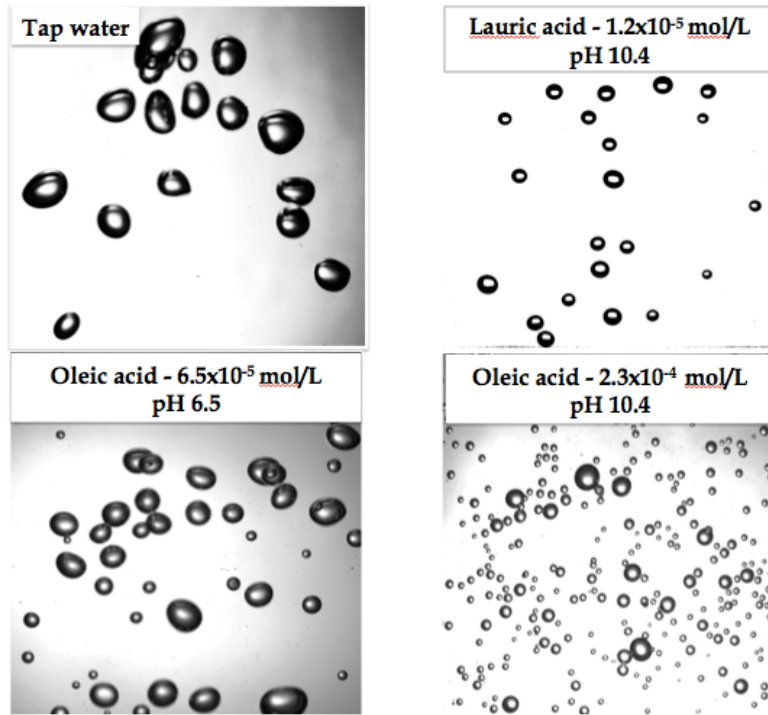


Figure 3-8. Sample images at different conditions

The bubble size distribution was obtained using the “ImageJ” image analysis software, and a macro was written to be used in line with ImageJ for analyses of all bubbles captured from 200-300 images. Bubbles larger than about 1mm start to lose their spherical shape and become ellipsoids. Ellipsoidal bubble diameters are computed by the software and are usually reported as equivalent spherical bubble diameters, d_i , calculated from the following expression (Hernandez-Aguilar and Finch 2005):

$$d_i = \sqrt[3]{d_{max}^2 \cdot d_{min}} \quad (3-7)$$

Where $d_{\min}$ and $d_{\max}$ are the minimum and maximum axes of the ellipse. For each bubble size distribution, the Sauter mean bubble diameter, d_{32} , is then calculated as follows:

$$d_{32} = \frac{\sum_{i=1}^n d_i^3}{\sum_{i=1}^n d_i^2} \quad (3-8)$$

The Sauter mean diameter is defined as the diameter of a sphere that has the same volume-to-surface area ratio as the bubble of interest. Although arithmetic means (e.g., d_{50}) could readily be obtained, the d_{32} parameter was of primary interest since froth flotation is driven by the surface area of gas bubbles available for particle-bubble attachment. For each set of testing conditions, the bubble size distribution and Sauter mean diameter were calculated.

Gas dispersion measurements in surfactant solutions should be performed under a continuous flow of fresh solution into the column to avoid frother depletion in the bulk solution and to ensure steady state conditions. This was done by pumping in fresh solution from a large tank to the column and pumping out the depleted solution from the bottom of the column. Variables in gas dispersion experiments are frother concentration, pH, and superficial gas velocity (J_g). Different frother concentrations allow the CCC to be determined, which is also a measure of frothing power. The effect of surfactant speciation in solution can be assessed by performing the measurements at different pH values while the effect of the gas flow rate can be evaluated by adjusting J_g .

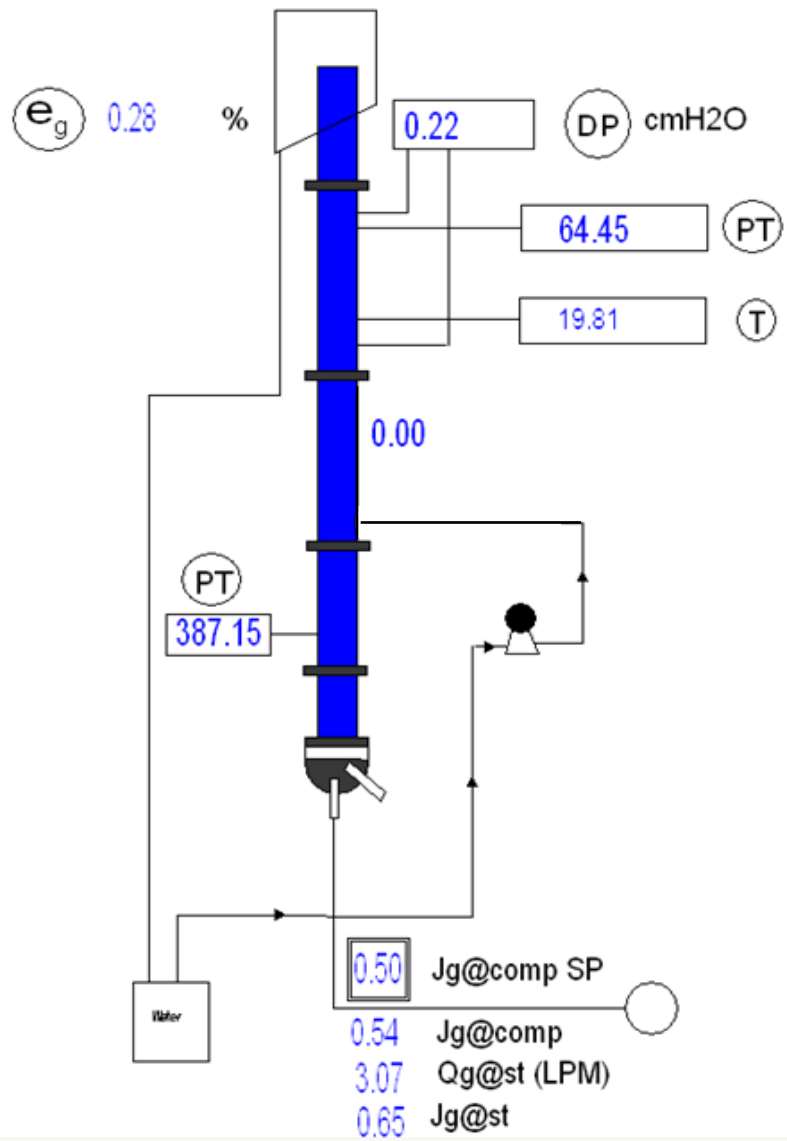


Figure 3-9. Material flow and control system on gas dispersion experimental set up

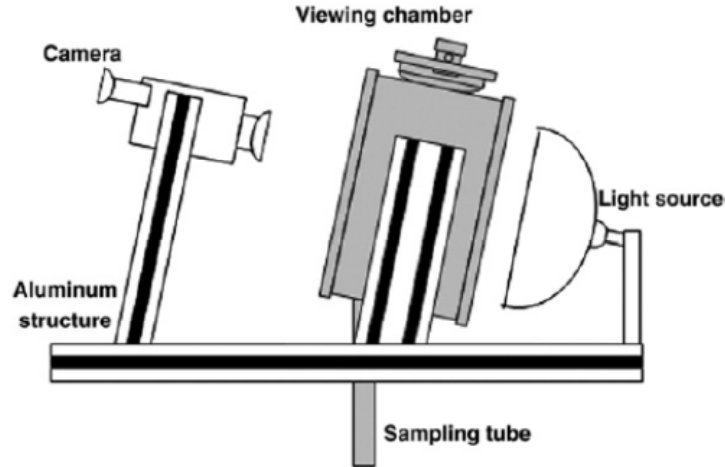


Figure 3-10. Schematic of McGill bubble viewer (Gomez and Finch 2007)

3.1.6.2 Gas hold-up measurements

Gas hold-up, which represents the volume fraction of gas in bulk solution, is determined simultaneously with bubble size measurements under the same experimental conditions using a differential pressure transmitter. The set-up is equipped with a 266DSH high performance differential pressure transmitter from ABB to determine gas hold-up as is demonstrated in Figure 3-11. It is measured automatically through the differential pressure reading (ΔP) between 2 points separated by a known distance ($h = 70$ cm) and calculated through the following equation:

$$\varepsilon_g = \frac{\Delta P}{h} \quad (3-9)$$

This parameter is an indication of the amount of gas available in the pulp at a given time for mineral recovery.

The column set up made at UBC is mounted on a wheeled cart (Figure 3-11) and comprises of 4 PVC pipe sections for flexibility; the sections could be removed to change height. The sections are comprised of two middle sections of 90 cm height, one top section of 40 cm height (attached to an acrylic launder of a 25.4 cm diameter) and a bottom section holding a porous plate sparger. The sections are all connected by flanges and isolated through gaskets. 40 L of surfactant solution is used in each test in the column.

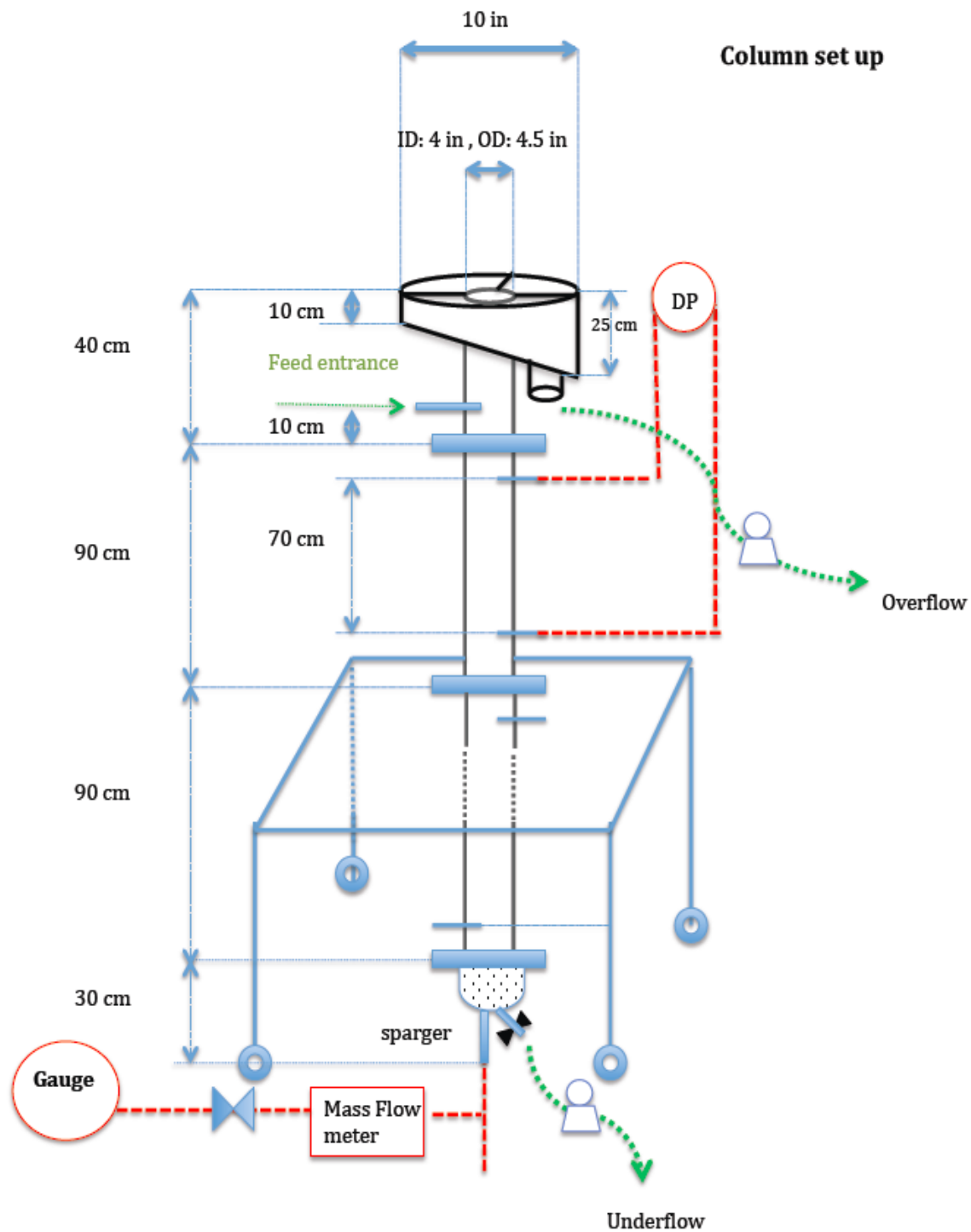


Figure 3-11. UBC gas dispersion set up

3.2 Reagents sources and preparation procedure

3.2.1 Fatty acids (oleate, laurate, hexanoate and tall oil)

- Oleic acid

Oleic acid, 99% (unsaturated cis-9-octadecenoic acid, $C_{18}H_{34}O_2$) was obtained in 25-ml ampoules from Sigma Aldrich. This reagent was used for turbidity measurements and some initial surface tension measurements. Oleic acid has a molecular weight of 282.46 g/mol and is an oily liquid with a melting point of 13-14° C and a density of 0.89 g/mL at 25° C. In order to solubilize it, a desired volume of oleic acid was taken with a micropipette, and was first neutralized with a stoichiometric amount of a sodium hydroxide (NaOH) solution. Then the solution was homogenized using an ultrasonic bath. The volume was increased to 1 liter, and the solution was mixed for 5 minutes.

- Sodium oleate

Sodium oleate, >82% fatty acids (as oleic acid) powder ($C_{18}H_{33}O_2Na$) was obtained from Sigma Life Science. Sodium oleate has a molecular weight of 304.44 g/mol.

This reagent was primarily used for large-scale gas dispersion measurements using the sampling-for-imaging technique since the technique required a large solution volume and so a large amount of oleic acid would also be needed. For this purpose, a desired amount of sodium oleate was first added to 1L of distilled water and mixed vigorously at room temperature. The solution was turbid at this stage due to the high concentration of the reagent. Then the volume was increased to 40 L in a mixing tank, as required to fill the column. The content of the tank was then well mixed for 5 minutes and pH was adjusted while mixing to reach steady state before initiating the test.

For foamability and surface tension measurements the desired concentration of sodium oleate was prepared in a 1L volumetric flask and the required amount used for the measurement.

- Tall oil

Tall oil is a mixture of fatty acids and a smaller proportion of resin acids (abietic acids) obtained as a by-product in the Kraft process of wood pulp treatment. The composition of tall oil obtained from different resources may vary. For the purpose of this research tall oil was obtained

from Arizona Chemical as a brown viscous liquid. The same reagent is used at Agrium - Kapuskasing Phosphate Operations as an apatite collector. As provided by the manufacturer, the reagent contained a total 93.2% of fatty acids distributed as follows: 34% non-conjugated linoleic acid, 9% conjugated linoleic acid, 44% oleic acid, 5% saturated fatty acids, and 8% other fatty acids. According to the manufacturer, at 25° C, tall oil has a specific gravity of 0.906 and a viscosity of 0.02 Pa*sec.

In the case of tall oil, the reagent was prepared as a 10% (wt.) emulsion by adding raw tall oil to a 1% NaOH solution in distilled water, mixing for 30 minutes, and then diluting the stock emulsion to the desired concentration. This preparation procedure is similar to the standard procedure employed at Agrium-Kapuskasing Phosphate Operations. It should be stressed that the stock solution in 1% sodium hydroxide was very turbid indicating that a substantial portion of tall oil was not dissolved under the preparation conditions. For solution preparation, distilled water was used.

- Sodium laurate

Lauric acid, sodium salt, 98% ($C_{12}H_{23}O_2Na$) was obtained from Acros Organics. It is a white powdery solid, and has a molecular weight of 222.3 g/mol.

- Sodium hexanoate

Sodium hexanoate, 99% ($C_6H_{11}O_2Na$) was obtained from Acros organics. The chemical has a molecular weight of 138.14 g/mol.

3.2.2 Sulfates (sodium dodecyl and octadecyl sulfate)

Dodecyl sulfate, sodium salt, 99% ($C_{12}H_{25}SO_4Na$) was obtained from Acros. Its molecular weight is 288.38g/mol. Sodium n-octadecyl sulfate ($C_{18}H_{37}SO_4Na$), 99% (dry weight), water content less than 7%, was obtained from Alfa Aesar. It has a molecular weight of 372.54 g.

3.2.3 MIBC

MIBC (methyl isobutyl carbinol, $C_6H_{14}O$) or 4-methyl-2-pentanol 98% pure, was obtained from Sigma Aldrich. Its molecular weight is 102.17 g. It is a branched hexyl alcohol and is a standard frother in flotation.

Oleic acid is a long chain (C18) anionic surfactant. It is also a weak electrolyte whose speciation in aqueous solutions is a strong function of pH. The additional surfactants were selected to investigate the effect of the hydrocarbon chain length and electrolyte type on the interfacial behavior of the reagents. Dodecanoic acid (C12) and hexanoic acid (C6) represented shorter chain weak electrolyte-type surfactants, while dodecyl (C12) and octadecyl (C18) sulfates were strong electrolyte-type surfactants of the same hydrocarbon chain lengths as those of the weak electrolyte homologues.

4. Interfacial properties of fatty acids

4.1 Equilibrium surface tension

4.1.1 Sodium oleate

The equilibrium surface tension of sodium oleate solutions was measured in the concentration range from 10^{-5} to 10^{-2} mol/L (3-3000 mg/L) using the Wilhelmy plate method. The results are demonstrated in Figure 4-1. Surface tension readings were taken under steady state conditions, and the time allowed to record the surface tension value was the time at which the standard deviation between two consecutive surface tension measurements was less than 0.05 mN/m.

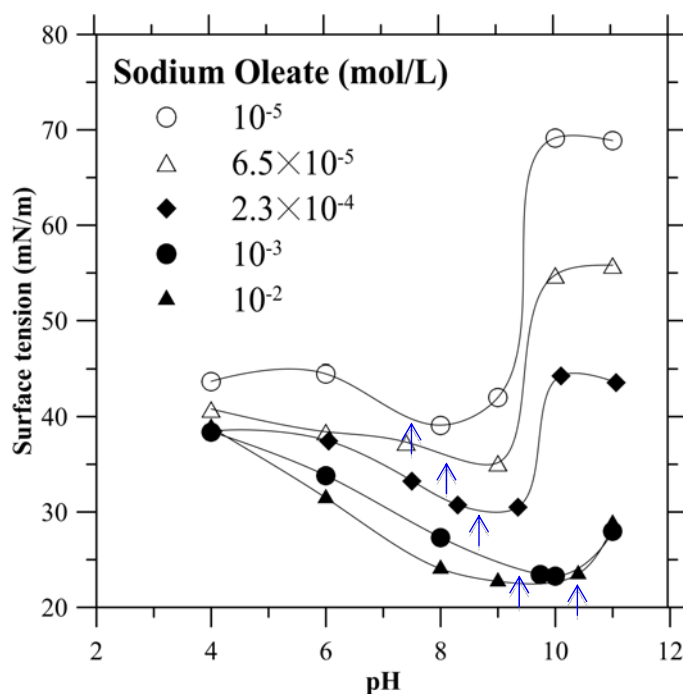


Figure 4-1. Surface tension as a function of pH at different concentrations of sodium oleate measured by Wilhelmy plate method (pH values of precipitation demonstrated by arrows are 7.5, 8.1, 8.7, 9.3 and 10.3 respectively)

Surface tension of sodium oleate solutions is affected by pH and surfactant concentrations. For all the tested concentrations a minimum surface tension value can be observed, although this minimum shifts slightly towards higher pH values as the concentration increases. As the concentration of oleate increases, the isotherm shifts towards lower surface tension values and the minimum value for surface tension shifts towards pH 9-10.

According to Pugh and Stenius (1985), this minimum in the surface tension data originates from the presence of the iono-molecular dimeric form $((\text{RCOO})_2\text{H}^-)$ in solution, whose maximum concentration coincides with the minimum in the surface tension. According to the speciation diagrams presented by Pugh and Stenius (e.g., Figure 2-2), the onset of the formation of precipitates also occurs at or near the pH of the minimum surface tension, and yet those authors focused only on the role of dimeric forms in solution. Moreover, the concentrations of non-ionic species and of monomeric ionic species are at their maximum at the onset of precipitation. The arrows in Figure 4-1 show the pH values of precipitation. What is also important to note is that at pH values lower than the pH of precipitation, the dominant form in solution is the undissociated acid whose concentration is constant and equal to the solubility limit (2.5×10^{-8} mol/L).

At pH values around 4, increasing the total concentration of oleate increases only the amount of precipitates, and yet all the surface tension data for various oleate concentrations tend to converge on the same surface tension value of around 40 mN/m. In other words, increasing amounts of precipitates do not affect the surface tension at low pH. In this pH range, the surface tension is relatively low suggesting that some surface-active species are still present in solution. According to speciation calculations, the undissociated acid is the only species in solution at pH 4, and this acid form seems to be responsible for the low surface tension at low pH even though the bulk of the reagent is in the form of a colloidal precipitate under these conditions.

At pH values higher than the pH of the minimum surface tension, which as noted earlier is very close to the pH of precipitation, the dominant soluble species in solution are acid dimers $(\text{RCOO})_2^{2-}$ and the oleate anions (RCOO^-) . It should also be noted that in comparison to low pH values – where the only soluble form is the undissociated acid - the concentrations of the soluble species at high pH are about 1000 times higher. These high levels of dissolved surfactant result in relatively low surface tension values at high pH. At the same time, the concentration of the very surface-active iono-molecular dimers decreases drastically. A decrease in the amount of molecular and iono-molecular complexes at alkaline pH leads to a relative increase in the surface tension values compared to lower pH values.

The surface tension of sodium oleate is illustrated as a function of concentration at a constant pH value in Figure 4-2. This type of graph allows one to determine the CMC value.

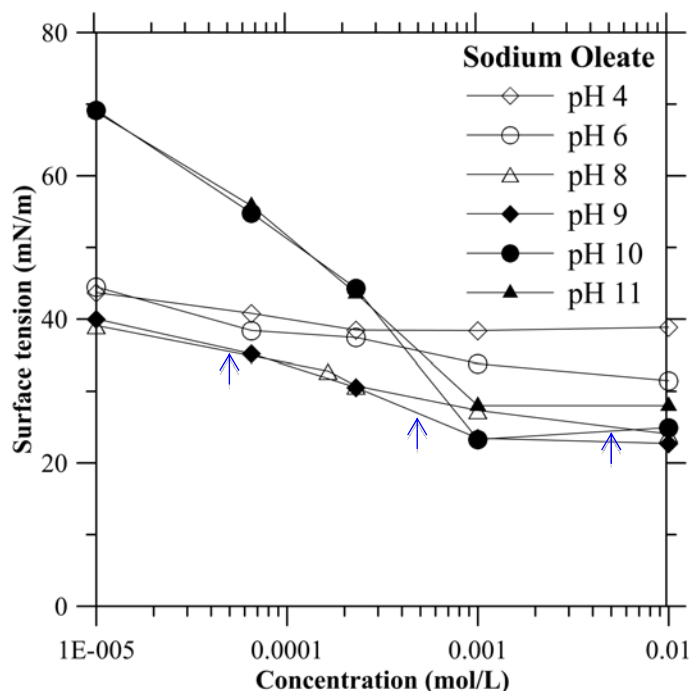


Figure 4-2. Surface tension as a function of concentration of sodium oleate at different pH values (precipitates form at pH 4 and 6 regardless of concentration and precipitation concentration is 5×10^{-5} at pH 8, 5×10^{-4} at pH 9 and 5×10^{-3} mol/L at pH 10)

At pH 4 the surface tension very weakly depends on concentration, and all the data points tend to fall on a single curve at about 40 mN/m in the tested concentration range from 10^{-5} to 10^{-2} mol/L. Precipitates are the dominant species at pH 4, and as a result, it is basically impossible to define the CMC of oleic acid under the conditions of extensive precipitation. The soluble RCOOH species are the only species in solution at this pH with a concentration of 2.5×10^{-8} mol/L in the whole concentration range.

Comparing the surface tension values at a low total concentration of 10^{-5} mol/L reveals that the surfactant is more surface-active at low pH than at higher pH. At pH 4, the soluble nonionic species are the dominant species in equilibrium with precipitates. In contrast, at a high pH around 10 or 11 all species are converted to the oleate anion and yet the surface tension at high pH is actually higher than at pH 4. This indicates that nonionic form appears to be quite surface active.

At pH 6, a precipitate appears at around a total oleate concentration of 5×10^{-7} mol/L, so the concentration of the undissociated acid is also constant at this pH and equal to the solubility limit. However, at pH 6, the combined concentrations of oleate and of the acid dimer are

significant (higher than the concentration of the undissociated acid) and the absolute surface tension values at pH 6 are lower than those at pH 4. At lower pH (4 and 6), the surface tension values do not seem to go through a well-defined CMC value although they tend to reach a plateau at higher oleate concentrations. According to Rosen (2004), if the CMC is higher than the solubility of the surfactant at a particular temperature, then the minimum surface tension will be achieved at the point of maximum solubility rather than at the true CMC, which is also observed in this case.

Even at pH 8, a precipitate appears in oleate solutions at a concentration of 5×10^{-5} mol/L, which is lower than an apparent CMC value at that pH. At pH 9, a precipitate appears at a concentration of 5×10^{-4} while at pH 10 a precipitate starts forming at a concentration of 5×10^{-3} mol/L. Whenever a precipitate forms, the key question is whether the concentration of all the soluble species in solution is sufficient to induce micelle formation, or whether the surface tension is constant above the apparent CMC value because the concentration of all the soluble species does not change due to the presence of a precipitate. The data at pH 10 and 11 suggest that oleate forms micelles at a concentration of 10^{-3} mol/L, which is below the corresponding concentrations for the onset of precipitation. For these two pH values, the surface tension data were essentially obtained under true solution conditions and therefore the CMC value could reliably be determined only at pH 10 and 11.

By taking a closer look at species distributions at pH 8 and 10 for low concentrations of oleic acid (Figure 2-2), the concentration of ionic species does not differ at these two pH values but the concentration of molecular species decreases between pH 8 and 10. Theander and Pugh (2001) concluded that there is an increase in the CMC value from pH 8 to 10. The reported CMC values increased from 4.7×10^{-5} mol/L at pH 8 to 5.7×10^{-5} mol/L at pH 10. The large number of data points they used for determination of CMC allowed those authors to notice the small difference in CMC as a function of pH. The much lower CMC value reported by Theander and Pugh compared to the value obtained in this thesis could originate from the use of a high ionic strength solution (0.1 kmol/m^3) as a background electrolyte in their work.

The equilibrium surface tension data provide a good understanding of the surface activity of the species present at each pH and concentration range, but since in the adsorption process

time is also important variable, dynamic parameters were looked at as well and some of the data are included in Appendix 1.

4.1.2 Sodium laurate

Equilibrium surface tension data measured with the Wilhelmy plate method for 10^{-5} to 10^{-2} mol/L of sodium laurate are presented in Figure 4-3 as a function of pH. pH values of precipitation are demonstrated by arrows at each concentration of sodium laurate.

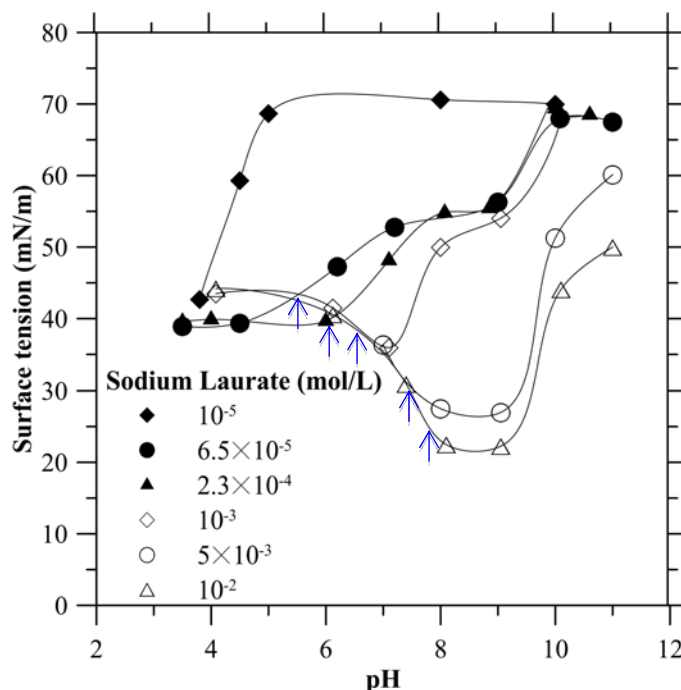


Figure 4-3. Surface tension as a function of pH at 10^{-5} to 10^{-2} mol/L sodium laurate measured by Wilhelmy plate method (there is no precipitate at 10^{-5} mol/L and pH of precipitation at the subsequent tested concentrations are 5.4, 6.0, 6.6, 7.3 and 7.6)

The data show that at low pH below the pH of precipitation the surface tension is quite low suggesting that undissociated acid strongly adsorbs at the gas-liquid interface. Below the pH of precipitation, solutions are saturated with respect to the undissociated acid and the concentration of the acid is equal to the solubility limit (1.2×10^{-5} mol/L). At the same time, the amount of precipitates increases as the total laurate concentration increases, and yet the data seem to fall on the same point. This observation suggests that the precipitate does not significantly contribute to the measured surface tension and that the undissociated acid is responsible for the low surface tension values in the pH range below the pH of precipitation. It

should be noted that at low pH and in the presence of precipitates the surface tension values are much lower than the surface tension of water (72 mN/m).

As the pH of solution increases and exceeds the pH of precipitation, the surface tension values start increasing at intermediate laurate concentrations (6.5×10^{-5} and 2.3×10^{-4} mol/L) reaching values very close to the surface tension of the background electrolyte (~ 72 mN/m) as if no surfactant adsorption took place. As pH increases, the precipitate disappears and the dissociated laurate anion becomes the dominant species in solution. These results strongly suggest that laurate anion is less surface-active than undissociated lauric acid. At even higher total surfactant concentrations, the surface tension data go through a minimum in a very similar fashion to the behavior of sodium oleate. Assuming that this minimum results from the presence of dimeric species in oleic acid solutions (Pugh and Stenius 1985), it appears that similar complexes form in lauric acid solutions at sufficiently high surfactant concentrations. Rosano et al. (1966) referred to the inflection points detected at higher concentrations of potassium laurate solutions as formation of acid soap complex. As the surface tension data for lauric acid suggest, the presence of dimers may probably be neglected for dilute lauric acid solutions (total concentration of less than 10^{-3} mol/L), but for more concentrated solutions complex surfactant species should probably be considered, although at present no thermodynamic data on such species of lauric acid has been reported in the literature.

A very important set of results is shown in Figure 4-3 for a total concentration of 10^{-5} mol/L of sodium laurate. This concentration is lower than the solubility limit of the undissociated acid and therefore a precipitate does not form at this concentration regardless of pH. In other words, it now becomes possible to directly compare the surface activity of the laurate anion (RCOO^-) with the surface activity of undissociated lauric acid (RCOOH). It can be seen that the surface tension is much lower at low pH while the surface tension values are basically equal to that of pure water at higher pH. This trend shows that undissociated acid is much more surface-active than laurate anion at the gas-liquid interface

The results in Figure 4-4 show qualitatively a very similar trend to the results for oleic acid given in Figure 4-2. For each pH value, a surfactant concentration can be found at which a precipitate will form which is shown by arrows in figure. At pH 4, the data point at a concentration of 10^{-5} mol/L is the only experimental point without a precipitate since the

concentration is below the solubility limit of the surfactant. As the concentration increases, the amount of precipitate also increases and yet the surface tension data remain constant. This result again shows that the precipitate is not surface-active.

At pH 6, a precipitate appears at a concentration of 2.5×10^{-4} mol/L and the solution becomes saturated with respect to the undissociated acid. Below that concentration, the concentration of the undissociated acid decreases and the concentration of laurate anion increases in solution. Comparing the data at a concentration of 10^{-5} and at pH values 4 and 6, i.e. in the absence of a precipitate, it is again clear that the undissociated acid is more surface-active than the laurate anion. At pH 7, a precipitate forms at a concentration of 2.5×10^{-3} mol/L, while at pH 8 precipitation starts occurring at a concentration of 2.5×10^{-2} mol/L. In other words, in the studied surfactant concentration range, a CMC value of lauric acid cannot be reached/identified before inducing precipitation.

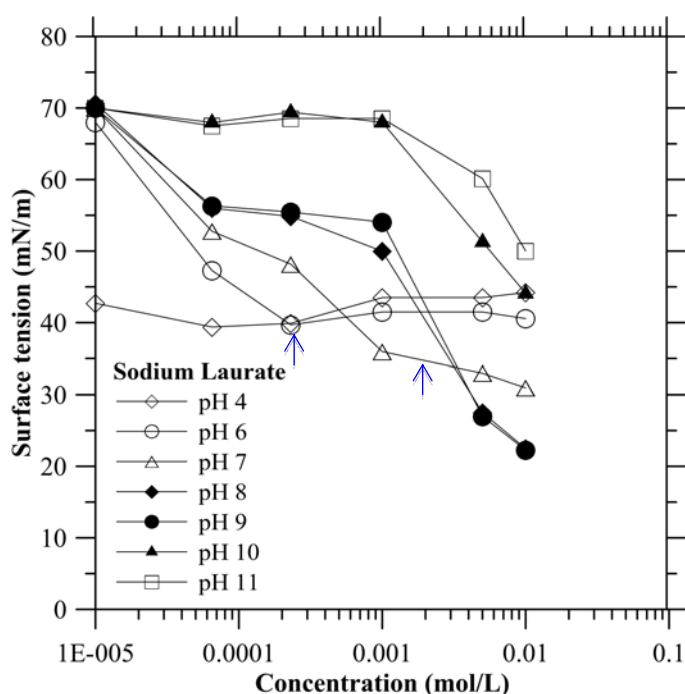


Figure 4-4. Surface tension of sodium laurate as a function of concentration at different pH values (precipitates form at pH 4 regardless of concentration and precipitation concentration is 2.5×10^{-4} at pH 6, 2.5×10^{-3} at pH 7, 2.5×10^{-2} at pH 8 and 0.25 mol/L at pH 9)

A similar analysis of precipitation and dissolution phenomena and the detection of the CMC value was presented by Laskowski et al (2007) for dodecyl amine solutions. These authors concluded that true CMC values can only be obtained for true amine solutions in the absence of

precipitates. Otherwise, the surface tension measurement detects precipitation rather than micellization. Dynamic surface tension data for sodium laurate at 6.5×10^{-5} and 2.3×10^{-4} mol/L are included in Appendix 1.

4.1.3 Sodium hexanoate

In the case of hexanoate, it can be observed in Figure 4-5 that concentrations lower than 10^{-3} - 10^{-2} mol/L do not have a significant effect on the surface tension. The surface tension remains constant regardless of pH. At higher concentrations, it is clear that low pH conditions lead to enhanced surface activity of the surfactant, and this result can again be attributed to the presence of the undissociated hexanoic acid. At pH values lower than 4.5-5.0 (pK_a for carboxylic acids) the acidic form dominates over the anionic form and the surface tension decreases.

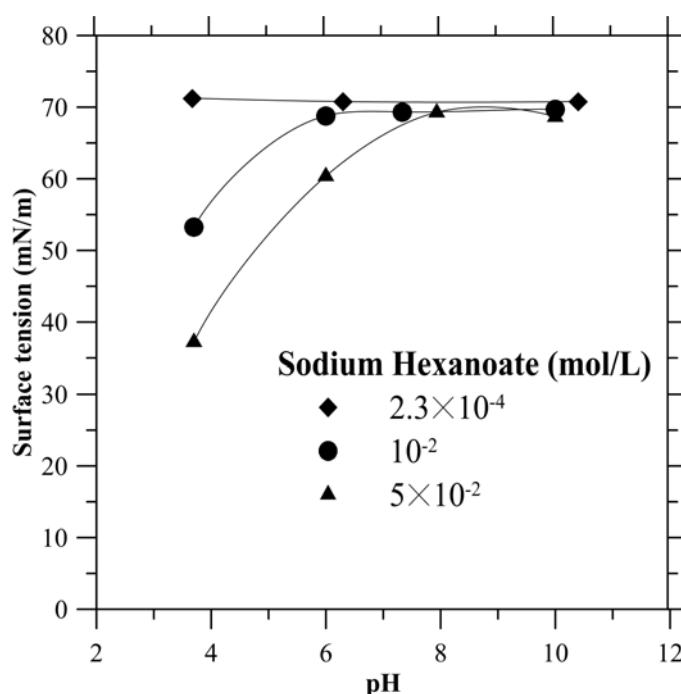


Figure 4-5. Surface tension as a function of pH at 2.3×10^{-4} to 5×10^{-2} mol/L of sodium hexanoate measured by Wilhelmy plate method

When the surface tension data for sodium hexanoate are presented as a function of concentration at a fixed pH value in Figure 4-6, the surface tension is more sensitive to changes in concentration at lower pH compared to high pH. In fact, at pH 7.5 or higher no effect of the surfactant concentration on the surface tension of water was observed in the studied concentration range. This trend again shows the higher surface activity of undissociated acid compared to the anionic form.

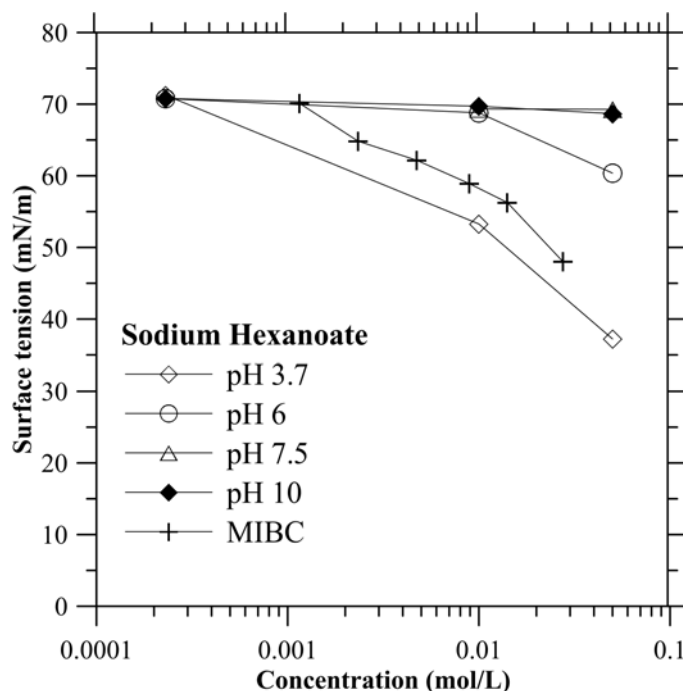


Figure 4-6. Surface tension of sodium hexanoate as a function of concentration at different pH values (MIBC data was obtained from Sweet et al 1997)

Comparing sodium hexanoate to the longer chain reagents, it is such a short chain reagent that it cannot affect surface tension in the low concentration range from 10^{-4} to 10^{-3} mol/L. Overall, the surface tension data show that undissociated acids are more surface-active at the gas-liquid interface compared to their dissociated anions. This enhanced surface activity of the acids can be explained by a higher ability of the acids to adsorb at the air-solution interface. In the case of surfactant anions, the dense adsorption of the anions at the gas-liquid interface is inhibited by lateral electrostatic repulsive forces. In contrast, electrostatic repulsion between the adsorbed surfactant molecules is insignificant and such uncharged molecules can more densely adsorb at the interface. Also, as the chain length of the surfactant molecule increases, attractive van der Waals interactions between the chains of adjacent molecules increase, bringing these molecules closer to each other. According to the Gibbs equation (equation 2-18), higher adsorption of uncharged molecules at the gas-liquid interface should result in lower surface tension.

4.1.4 Sodium dodecyl and octadecyl sulfate

The surface tension of sodium dodecyl sulfate (SDS) solutions only slightly decreased at lower pH but the behavior is not a strong function of concentration and pH in the tested

concentration and pH ranges. This was expected from SDS as a strong electrolyte surfactant. The value of CMC for sodium dodecyl sulfate in water (no other additives or salts) at 25 °C and atmospheric pressure was reported as 8×10^{-3} mol/L by Dominguez et al 1997.

Since sodium octadecyl sulfate (SOS) is not completely soluble at room temperature, it was necessary to perform the tests at higher temperature (50°C). SOS decreases the surface tension to a large extent at the two tested concentrations and its behavior is not a function of pH. It should be noted that there is no minimum in the surface tension data for SOS, which is contrast to the results for oleic acid. This result indicates that dimeric complexes either do not form in octadecyl sulfate solutions or that they are not surface active.

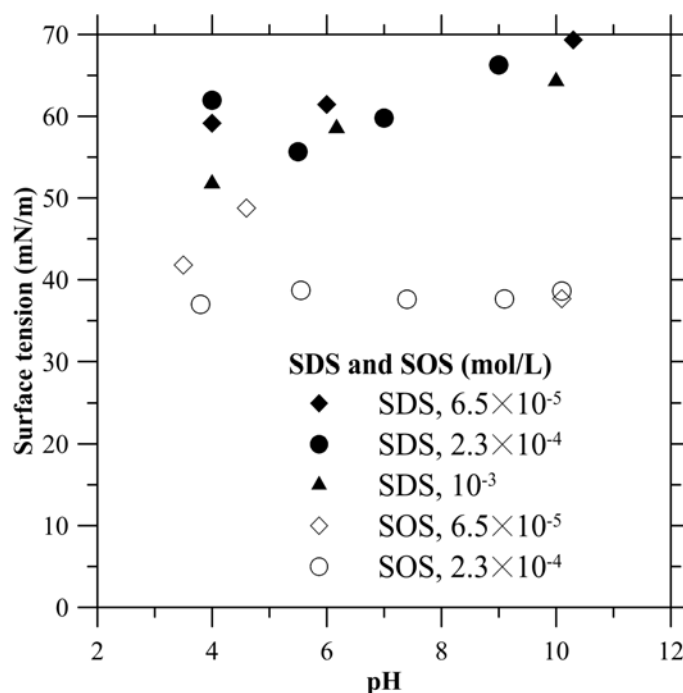


Figure 4-7. Surface tension as a function of pH at different concentrations of sodium dodecyl and octadecyl sulfate measured by Wilhelmy plate method

4.1.5 Comparison of different reagents

Equilibrium surface tension data measured with the Wilhelmy plate method for 2.3×10^{-4} mol/L solutions of different reagents are presented in Figure 4-8 as a function of pH for comparison. An intermediate concentration of 2.3×10^{-4} mol/L was selected since the majority of gas dispersion measurements were also carried out at that concentration.

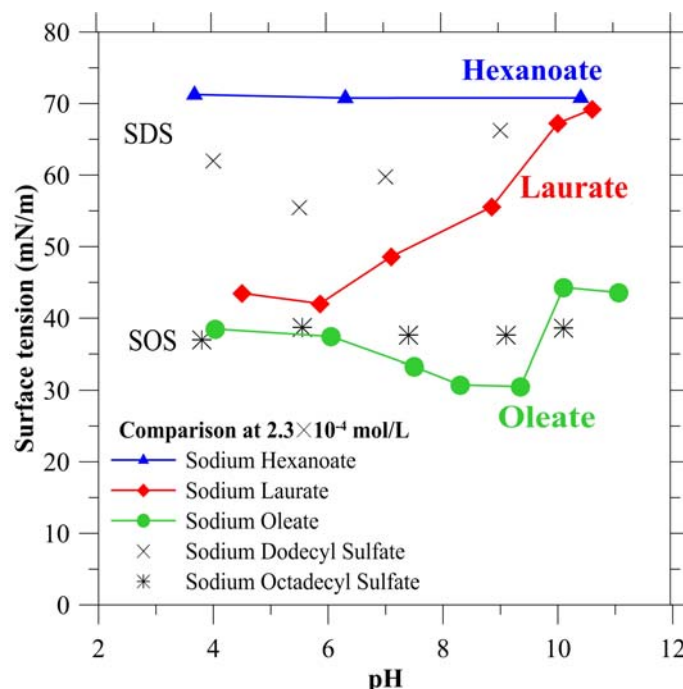


Figure 4-8. Surface tension as a function of pH at a concentration of 2.3×10^{-4} mol/L of different anionic reagents measured by Wilhelmy plate method

The data shown in Figure 4-8 can be categorized into three types of responses:

- 1) High surface tension values independent of pH: hexanoate and sodium dodecyl sulfate belong to this group.
- 2) Low surface tension values: sodium oleate and sodium octadecyl sulfate – both are C18 surfactants – behave in this way.
- 3) Transition data between low and high surface tension that are a strong function of pH. Sodium laurate represents this response.

It is noteworthy that the surface tension data for laurate are a strong function of pH, while the data for oleate relatively weakly change with pH – all the data for oleic acid range from 30 mN/m to 45 mN/m. When directly compared, the difference between sodium octadecyl sulfate (strong electrolyte) and sodium oleate (weak electrolyte) is not large, while the difference between the C12 homologues (sodium laurate and sodium dodecyl sulfate) is more pronounced. In other words, the effect of pH in Figure 4-8 is not independent of the effect of the chain length of the surfactant, and reagents with quite different chain lengths may actually give the same surface tension results depending on pH. In the case of the C18 surfactants, the effect of chain

length seems to dominate over the effect of electrolyte type. Lauric acid behaves just like a C18 surfactant only at low pH values when the undissociated lauric acid is the dominant form in solution even when a precipitate is present. However, lauric acid behaves just like sodium dodecyl (C12) sulfate at high pH when laurate anion is the dominant species in solution. Under high pH conditions the surface activity of laurate anions appears to be very low since the surface tension values are not very different from that of pure water. Finally, hexanoic acid does not affect the surface tension at the tested concentration, and speciation (or the effect of pH) is not a factor in the presented results. It seems that the relatively short chain length is insufficient to impart significant surface activity to hexanoate at this concentration. Overall, however, it appears that the effect of speciation of fatty acids on the equilibrium surface tension is most visible only for reagents with intermediate chain lengths between C6 and C18. Also, in the case of lauric acid, the data suggest that undissociated lauric acid is more surface-active than dissociated laurate anion. In this context, it should be highlighted that a C12 strong electrolyte (SDS) is only weakly surface active regardless of pH.

4.2 Turbidity

Turbidity of oleic acid solutions was measured as a function of concentration and pH. According to Figure 2-3, different concentrations of sodium oleate solution precipitate at different pH values. Since that diagram is based on thermodynamic equilibrium calculations, and to further investigate the state of oleic acid in solution, the transmission values of different concentrations of oleic acid in the concentration range from 10^{-5} to 10^{-2} mol/L (3-3000 mg/L) were directly measured as a function of pH with the Turbiscan instrument. The results are demonstrated in Figure 4-9. The data show that a colloidal phase starts appearing in sodium oleate solutions below a certain pH depending on concentration. It can also be seen that the transition between completely clear and fully opaque solutions is in fact not as sharp as thermodynamic calculations may suggest. The change in transmission values is gradual and takes place over a few pH units, and all solutions reach the same transmission level above pH 10. As a reference, the transmission of distilled water was found to be 90%.

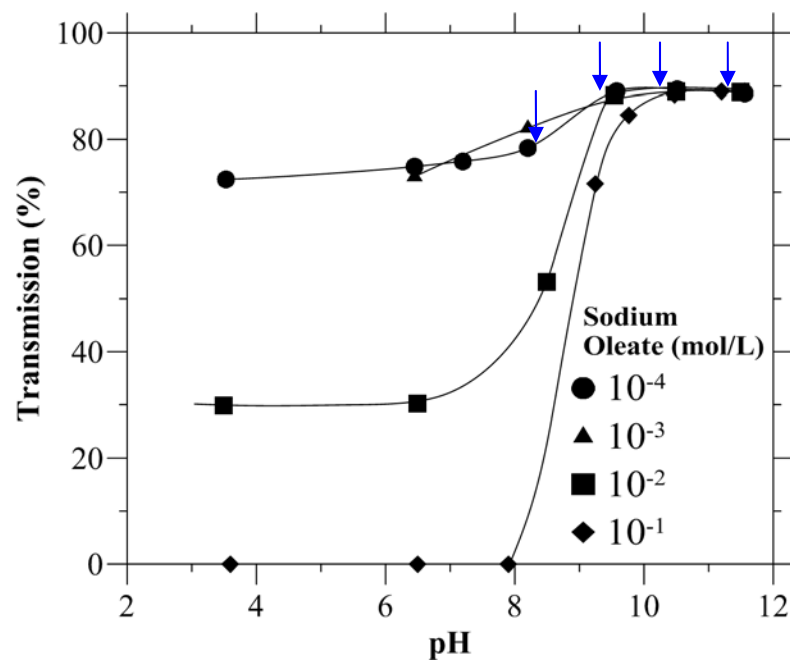


Figure 4-9.Transmission of oleic acid solutions of various concentrations as a function of pH (pH values of precipitation are 8.3, 9.3, 10.3 and 11.3 respectively, shown by arrows)

5. Gas dispersion properties of fatty acids

5.1 Bubble size measurements

5.1.1 Sodium oleate

Gas dispersion measurements for determining the bubble size distribution, CCC, and gas hold up values were performed for a number of flotation frothers in literature. For MIBC the minimum bubble size of around 1 mm was reported at a CCC value of 8.9×10^{-5} mol/L (Castro et al 2013). Gas dispersion measurements for sodium oleate were performed using the column constructed at UBC over a wide pH range. Sauter mean bubble diameters for sodium oleate at natural pH and pH 10.4 measured in gas dispersion column set up are demonstrated in Figure 5-1.

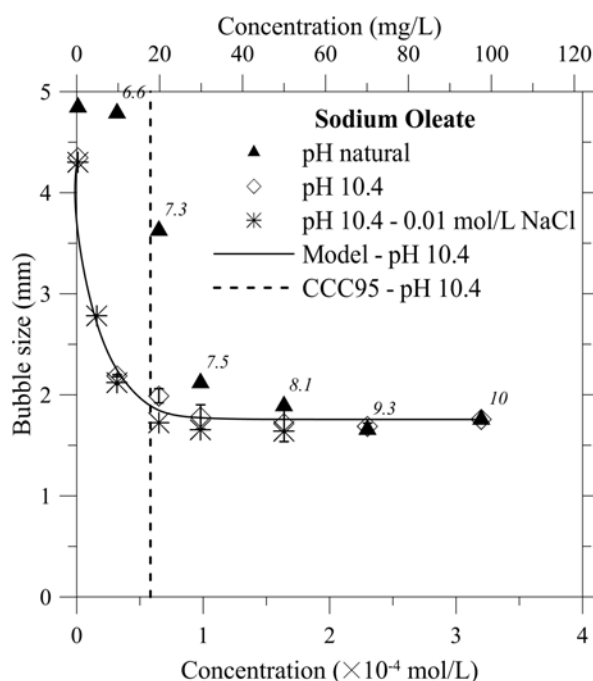


Figure 5-1. Sauter mean bubble diameter in sodium oleate solutions at natural pH and pH 10.4

The natural pH varied quite widely at different concentrations of sodium oleate due to variation in concentration of species - the corresponding pH values are given above the data symbols in the figure. The mean bubble size decreases with oleate concentration due to coalescence prevention or bubble break up phenomena, and above a critical concentration (CCC95) bubbles are dispersed and no coalescence takes place. Since sodium oleate is an ionic

and weak electrolyte surfactant, its species distribution changes as a function of pH. Sodium oleate forms colloidal precipitates below a certain pH value depending on the surfactant concentration. These pH values can be calculated from thermodynamic data (Pugh and Stenius 1985) and are given in Table 5-1.

Table 5-1. Precipitation boundary for different concentrations of sodium oleate

Sodium oleate concentration (mg/L)	Sodium oleate concentration (mol/L)	pH of precipitation (from thermodynamic calculations)
5	1.6×10^{-5}	7.5
10	3.2×10^{-5}	7.8
20	6.5×10^{-5}	8.1
30	9.8×10^{-5}	8.3
50	1.6×10^{-4}	8.5
70	2.3×10^{-4}	8.6
100	3.2×10^{-4}	8.8

As a result of variation in species distribution at each pH value, the mean bubble size is also strongly affected by pH. At pH 10.4, at which sodium oleate is fully dissolved and dissociated in the whole concentration range, this reagent exhibits a strong ability to prevent bubble coalescence. The CCC95 was calculated using the empirical model described by equations 2-12 through 2-14.

At natural pH, bubble sizes are large at a concentration lower than 1.6×10^{-4} mol/L (50 mg/L). As soon as the concentration and consequently pH becomes high enough to exceed the pH of precipitation, the average bubble size decreases to its minimum value. The larger bubble sizes at pH values corresponding to the presence of colloidal species are an indication of lower ability of sodium oleate to prevent coalescence in colloidal systems compared to true solutions. Since the concentration of insoluble RCOOH precipitates increases in the colloidal pH range at

the expense of other species, it could be concluded that these precipitates are inactive species in terms of their ability to reduce bubble sizes.

The effect of addition of 0.01 mol/L NaCl as background electrolyte was also investigated. As is demonstrated in Figure 5-1, 0.01 mol/L NaCl also did not have a significant effect on the CCC95 at pH 10.4 and the CCC95 value was calculated to be at 5.7×10^{-5} mol/L (17.37 mg/L) under these conditions.

Bubble size distributions for sodium oleate at different concentrations and at natural pH are demonstrated in Figure 5-2.

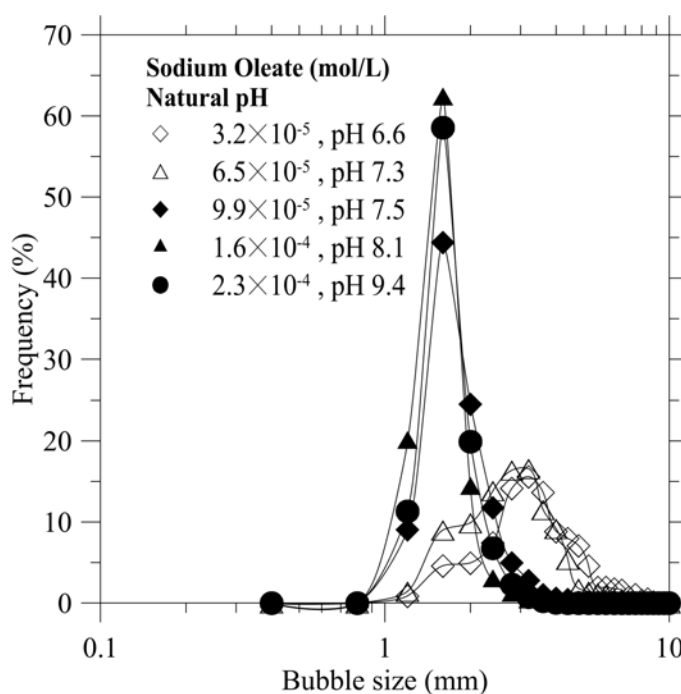


Figure 5-2. Bubble size distribution of different concentrations of sodium oleate solutions at natural pH

At lower concentrations and pH values, or when a significant amount of colloidal precipitates is present in the tested solutions, the bubble size distribution is wider and exhibits pronounced bimodality. At higher concentrations and pH values, or in the absence of colloidal precipitates, the bubble size distribution becomes monomodal and symmetrical around the mean value. The monomodality of the bubble size distribution is an indication of coalescence prevention, which leads to a narrower distribution of bubble sizes. The standard deviation of bubble size distributions at natural pH decreases with increasing solution concentration, as is shown in Table 5-2, which is also an indication of coalescence prevention.

Table 5-2. Standard deviation of bubble size distributions at natural pH

Concentration (mol/L)	Standard deviation
3.2×10^{-5}	1.36
6.5×10^{-5}	1.03
9.9×10^{-5}	0.45
1.6×10^{-4}	0.27
2.3×10^{-4}	0.35

Figure 5-3 demonstrates the bubble size distributions at different concentrations of sodium oleate at pH 10.4. All distributions are monomodal as they were all obtained in true solutions although by increasing the concentration the peak value slightly increases while the frequency of larger bubbles gradually decreases.

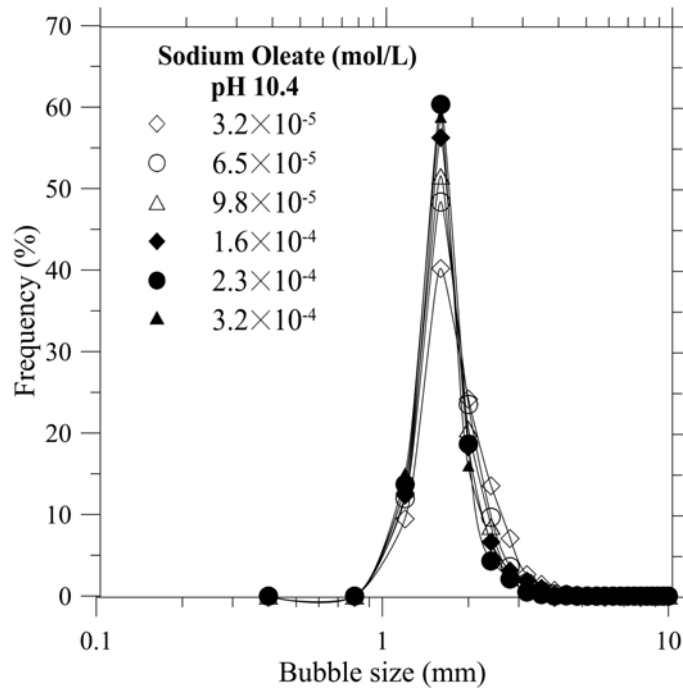


Figure 5-3. Bubble size distribution of sodium oleate at pH 10.4

The Sauter mean bubble diameter in sodium oleate solutions as a function of pH is presented in Figure 5-4.

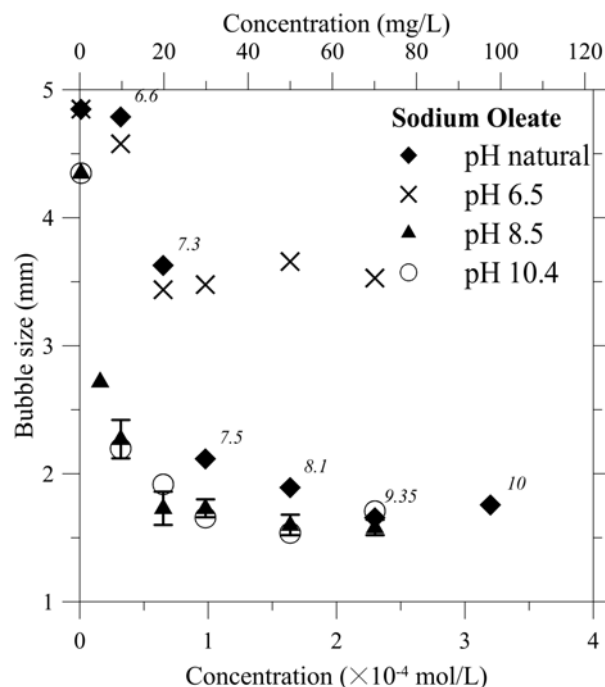


Figure 5-4. Bubble size as a function of concentration of sodium oleate at different pH

At pH 6.5, increasing the total surfactant concentration results in a gradual increase of the amount of precipitate since the solution is basically saturated with respect to the soluble species. Even though the amount of precipitate increases, the average bubble size quickly stabilizes and does not seem to be affected by increasing concentration of the precipitate.

In the case of natural pH, when a large amount of precipitates are present at 3.2×10^{-5} mol/L and 6.5×10^{-5} mol/L (10 and 20 mg/L), the two curves for natural pH and pH 6.5 overlap. At higher concentrations and as pH increases, precipitates convert to more active species and bubble sizes become much smaller. The precipitation boundary for the concentration range studied is in the pH range 7.5-8.8, as was shown in Table 5-1, and it seems that the effect of sodium oleate on bubble size is also enhanced over this pH range. Therefore, when sodium oleate starts precipitating, its effect on bubble size is much weaker than when the reagent forms a true solution, and it appears that the precipitates are not able to reduce bubble sizes to the same extent as can dissolved molecules.

It should be noted that oleic acid solutions containing precipitates could be characterized by low surface tension values (Figure 4-1), when compared to the MIBC data. At pH 4 and regardless of concentration, the surface tension of oleic acid solutions is on the order of 40 mN/m, which is significantly lower than the surface tension of water. Interestingly, true solutions

of oleic acid at high pH also exhibit low surface tension values. This very important fundamental observation is in strong contrast to the MIBC results, which suggests that the mechanism of bubble size reduction in oleate solutions is quite different from that in MIBC and other frother solutions. According to the work published by Sweet et al (1997), MIBC and some other alcohol-type frothers affect bubble sizes at concentrations that are approximately 100 times lower than the concentrations required to just start decreasing the surface tension of water. In other words, typical frothers decrease bubble sizes at concentrations at which the surface tension is high and equal to the surface tension of water. The ability of such frothers to affect bubble sizes at such low concentrations was explained in terms of the surface tension gradient induced at the bubble surface as the surfactant molecules rearrange and accumulate at the rear end of the bubble when the bubble rises through the bulk solution (Finch et al 2008). In other words, changes in the surface tension of oleic acid solutions may be responsible for the observed small decrease in bubble sizes at low pH.

The common starting point for calculating the size of a bubble detached from a single orifice is to balance the buoyancy and surface tension forces leading to an equation referred to as Tate equation. Based on the Tate equation as reported by Rubinstein (1995), for a capillary of a given diameter, d_c , immersed in a solution with the surface tension γ , the diameter of a gas bubble (d_b) generated from the capillary is related to the surface tension of the solution:

$$d_b = \left(\frac{6d_c\gamma}{g(\rho_l - \rho_g)} \right)^{1/3} \quad (5-1)$$

Although the above equation is strictly applicable to calculating bubble sizes generated from a single capillary, the sparger system of the gas dispersion column can be viewed as consisting of a large number of individual capillaries with some average diameter, d_c . Although the individual capillary diameters are not known the above equation can still be re-arranged to give a relative measure of changes in bubble sizes as a result of changes in the surface tension of the solution. In the above equation, all parameters are basically constant for a given sparger system, and the only variable is the surface tension. The equation can thus be written as:

$$d_b = C \gamma^{(1/3)} \quad (5-2)$$

C is a constant including all the parameters from equation 5-1 except the surface tension. Since the surface tension of water is 72.5 mN/m and the lowest surface tension of a sodium oleate

solution at the concentration of interest and pH 6 (Figure 4-1) is 34 mN/m, and using bubble sizes from Figure 5-4, the following two expressions can be given:

$$d_{b1} = C \cdot \gamma_1^{(1/3)} \quad \text{for water} \quad (5-3)$$

$$d_{b2} = C \cdot \gamma_2^{(1/3)} \quad \text{for oleate solution at pH 6} \quad (5-4)$$

Where d_{b1} and d_{b2} are the bubble diameters measured in water and in oleate solution (pH 6), respectively. The surface tension of oleate solution, γ_2 , can also be expressed as $\gamma_2 = 0.469 \cdot \gamma_1$, where γ_1 is the surface tension of water (72.5 mN/m) while 0.469 is the ratio of γ_2 to γ_1 (or 34 mN/m / 72.5 mN/m).

After substituting $\gamma_2 = 0.469 \cdot \gamma_1$, equation 5-4 becomes:

$$d_{b2} = C (0.469 \cdot \gamma_1)^{(1/3)} = 0.469^{(1/3)} C \gamma_1^{(1/3)} = 0.469^{(1/3)} d_{b1} = 0.778 d_{b1} \quad (5-5)$$

This calculation shows that by reducing the surface tension from 72.5 mN/m in water to 34 mN/m in oleate solutions, the average bubble size in oleate solutions at pH 6 should approximately be reduced to about 78% of the bubble size in water. The average bubble size measured in water was 4.8 mm so the calculated bubble size based on the above considerations should be $4.8 \cdot 0.778 = 3.7$ mm. It is intriguing to note that the experimental results in Figure 5-4 at pH 6.5 are very close to this approximate prediction. This comparison, however, strongly suggests that the small reduction in bubble sizes at pH 6.5 for sodium oleate solutions is driven by the relatively low surface tension of those solutions. Using the above expressions it can also be shown that for very low surface tension values, such as those seen for more concentrated oleate solutions at pH 10 (e.g., 22 mN/m), this change in bubble sizes due to surface tension alone would be only about 70% of the original bubble size (or down to 3.4 mm for our system). Therefore, reduction in bubble sizes to about 1.5-1.8 mm is caused by other phenomena.

According to the bubble break-up model of Finch et al (2008), non-equilibrium distributions of surfactant molecules on the bubble surface introduce forces and flows that cause instability on the bubble surface. As discussed in the literature review section, this surface instability due to generated surface tension gradients is believed to play a key role in initiating bubble break-up to form bubbles of smaller sizes. Most importantly, it should be recalled that the bubble break-up model was developed for surfactant solutions in which changes in bubble sizes occur at surfactant concentrations at which the surface tension is not affected, as highlighted by the systematic bubble size and surface tension data published by Sweet et al (1997). In the bubble break-up model, the total adsorption density of a surfactant on the bubble surface does not have to be high (i.e. the surface tension remains high), but re-arrangement of the molecules at the interface results in local accumulation of the surfactant which induces large surface tension gradients.

The main conclusion from the analysis of the results for oleate solutions is that under conditions of precipitation (with low surface tension), the surface tension seems to be primarily responsible for bubble size reduction since most likely the amount of soluble species is insufficient to generate surface tension gradients. In the absence of precipitates at high pH (and also with low surface tension), the concentration of oleate in solution is sufficiently high to induce gradients although the low surface tension is also probably a factor. In other words, although the steady state surface tension at low pH is lower than the surface tension at high pH at lower concentrations, the mobility of surfactant molecules and the kinetics of adsorption are inhibited by the presence of colloidal precipitates at the interface.

The effect of pH 8.5 and pH 10.4 on the average bubble size in Figure 5-4 is very similar. It should be noted that species distributions at these two pH values are also quite similar, especially at lower oleate concentrations. According to thermodynamic calculations (Pugh and Stenius 1985), at pH 10.4, 100% of acid is dissociated to RCOO^- in the tested concentration range. At pH 8.5, 99.98% of species are in the ionic form (RCOO^-), and only 0.01-0.02% of acid is in the associated form (RCOOH) up to a concentration of 9.8×10^{-5} mol/L. At pH 8.5, by increasing concentration to 1.6×10^{-4} and 2.3×10^{-4} mol/L, although 4% and 31% of acid convert into precipitates respectively, the concentration of the soluble species in solution still increases. Moreover, these concentrations of soluble species are already above the CCC95 (5.7×10^{-5} mol/L)

and small changes in speciation do not affect the results. In other words, this change in speciation between pH 8.5 and 10.4 does not seem to affect the bubble size. Overall, the strongest effect of pH on bubble sizes is observed near the precipitation range, where the concentration of soluble surface-active species is the highest, but once the system becomes a true solution at higher pH, the effect of pH is no longer significant.

According to Figure 5-5, the bubble size distribution for sodium oleate at pH 6.5 shows some evidence of bimodality while in the case of true solutions at pH 10.4 (Figure 5-3) and at pH 8.5, the bubble size distribution is mono-modal. Bubble size distributions for sodium oleate solutions at pH 6.5 are also compared with water alone in Figure 5-5. In the case of sodium oleate at pH 6.5, the distribution shifts slightly towards smaller bubble sizes as the concentration increases, although only a small difference was detected in the average bubble size between water alone and oleate at pH 6.5 at which precipitates are present.

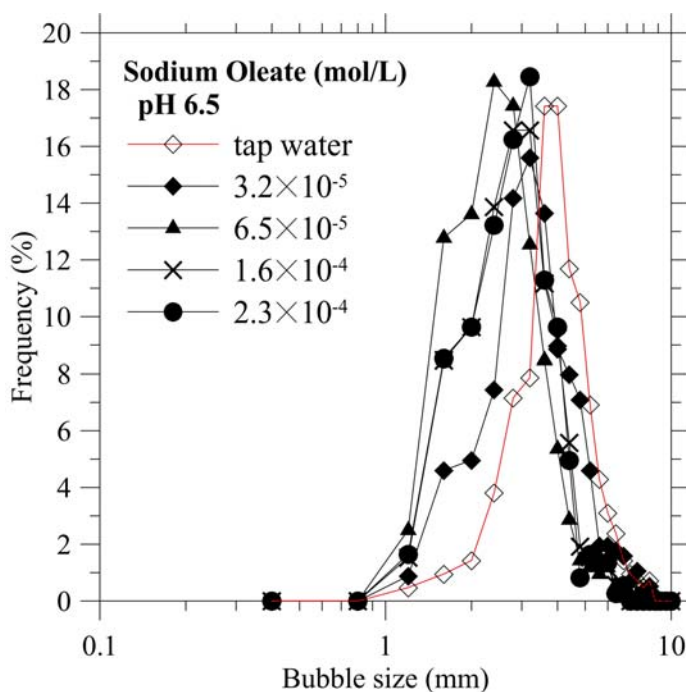


Figure 5-5. Comparison of bubble size distribution in sodium oleate solution at pH 6.5 with water alone

It should be noted that even in the colloidal region, when precipitates are the dominant species, there are still small equilibrium concentrations of soluble species. Speciation calculations at pH 6.5 indicate that up to 10% of the reagent is soluble (ionic and molecular form) at a total concentration of 1.6×10^{-5} mol/L (5 mg/L), and only 0.7% of the reagent is

dissolved at 2.3×10^{-4} mol/L (70 mg/L). In both cases, the total concentrations of soluble species are on the order of 1.6×10^{-6} mol/L. Equilibrium surface tension measurements for sodium oleate in Figure 4-2 show a considerable decrease in surface tension at pH 6.5 compared to the surface tension of water, which is an indication of the presence of surface active species at the gas-liquid interface. However this concentration is probably not high enough to induce the surface tension gradient.

Although it is difficult to identify which species are responsible for the low surface tension values in oleate solutions at pH 6.5, the validity of the earlier calculations of bubble sizes based solely on changes in the surface tension are further supported by the size and shape of the bubble size distributions shown in Figure 5-5. The bubble size distributions in the tested range of oleic acid concentrations are very similar, in terms of the shape and the occurrence of the main frequencies, to the bubble size distribution in water. At the same time, the distributions in the presence of oleic acid are shifted towards lower bubble sizes, as if each size in water was reduced by a constant factor after adding oleic acid, and this constant factor is equal to the value calculated from equation 4-7. In other words, knowing the bubble size distribution in water, the bubble size distribution in oleic acid solutions in the presence of a precipitate can accurately be calculated based on the corresponding change in the surface tension value. In this context, it is also important to highlight that the general shape of bubble size distributions in oleic acid solutions at high pH values (Figure 5-3) is very different than the bubble size distribution obtained in water. These high-pH distributions are dominated by a single high peak centered around a small average bubble size of about 1.5-1.6 mm. These observations in turn indicate that the mechanism of reduction of bubble sizes by oleate is different at pH 6.5 than at say pH 8 or higher.

It can therefore be argued that oleate solutions at pH 6.5 primarily affect bubble sizes through changes in the surface tension – this mechanism produces only a small change (by about 20-30%) in bubble sizes. However, alkaline solutions of oleic acid appear to additionally reduce bubble sizes to very small values through the bubble break-up and coalescence prevention mechanisms.

It is difficult to imagine that colloidal oleic acid precipitates alone are capable of reducing the surface tension of water. Although past research suggested that such precipitates are

hydrophobic and should readily attach themselves to air bubbles, the results presented in this thesis strongly indicate that, in general, there seems to be very little interaction between colloidal precipitates and bubbles. For example, the average bubble size is much larger when precipitates appear in solution compared to bubble sizes in true solutions at the same concentration. Even at a high surfactant concentration, where there is a large amount of precipitates, the bubble size distribution is not significantly affected. To test the contribution of precipitates, pH was fixed and the concentration of precipitates was increased by increasing total oleate concentration. The bubble size tests were performed at 3.2×10^{-4} , 6.4×10^{-4} and even 3.2×10^{-3} mol/L of sodium oleate at pH 8.5, where between 50% and 90% of the reagent was precipitated. These different concentrations resulted in a small Sauter mean bubble diameter of 1.61-1.48 mm. It should be noted that in all these cases, the concentration of soluble species was above the CCC95 value even though the amounts of precipitate were very high. Under these conditions, precipitates did not seem to play any role in reducing bubble sizes. It is also worth mentioning at this point that the TOC transfer measured during foamability experiments for sodium oleate at low pH (discussed in more detail in chapter 6) suggests that there is not much transfer of the surfactant to the foam phase when precipitates are present, which strongly suggests that precipitates do not adhere to air bubbles and therefore are not carried to the foam by the bubbles.

5.1.2 Sodium laurate

Gas dispersion studies on sodium laurate solutions as 12-carbon carboxylic acid provide further insight into the effect of different species on interfacial properties of fatty acids. The Sauter mean bubble diameter of sodium laurate solutions is shown in Figure 5-6 as a function of concentration for two pH values: 4.5 and 10.4.

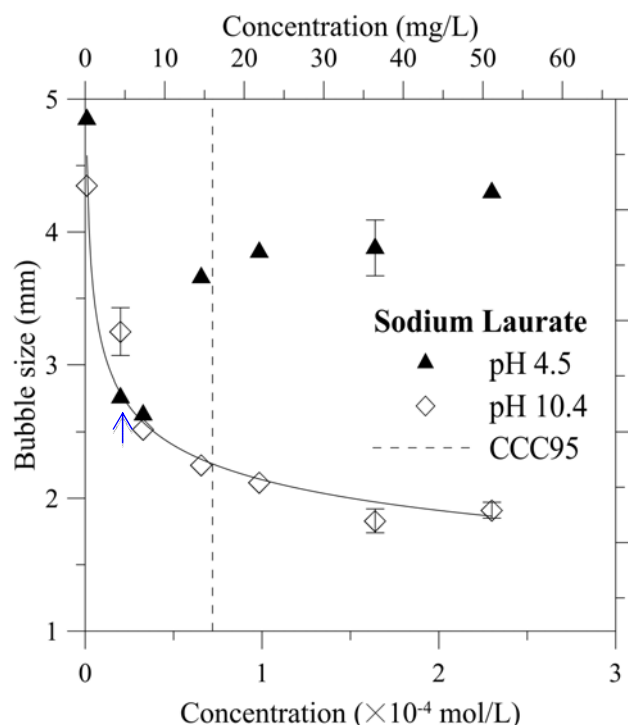


Figure 5-6. Sauter mean diameter for sodium laurate at pH 4.5 and 10.4 (precipitate appears over a concentration of 2×10^{-5} mol/L at pH 4.5)

The values of the pH of precipitation for lauric acid solutions in the tested concentration range are listed in Table 5-3. These values are based on thermodynamic calculations.

Table 5-3. Precipitation boundary for different concentrations of lauric acid

Lauric acid concentration (mg/L)	Lauric acid concentration (mol/L)	pH of precipitation
7.3	3.2×10^{-5}	4.9
14.6	6.5×10^{-5}	5.4
21.9	9.8×10^{-5}	5.6
36.5	1.6×10^{-4}	5.8
51.1	2.3×10^{-4}	6.0

At pH 4.5, in the presence of precipitates at concentrations higher than 2×10^{-5} mol/L (marked with an arrow in Figure 5-6), the undissociated acid is the only species in solution with a concentration of 1.2×10^{-5} mol/L, equal to the solubility limit of lauric acid. As the surface tension results show, this amount of lauric acid is sufficient to significantly reduce the surface tension of water. However, the average bubble size measured at pH 4.5 at a concentration of

1.2×10^{-5} mol/L (the first data point on each pH curve in Figure 5-6) is significantly lower than what could be expected from the theoretical calculations based on changes in the surface tension alone. In contrast to oleic acid, the bubble size distribution at pH 4.5 for a concentration of 1.2×10^{-5} mol/L (Figure 5-7) does not resemble the distribution in water. These observations suggest that at a concentration of 1.2×10^{-5} mol/L at pH 4.5, the surface tension is not the only factor responsible for the resulting reduction in bubble sizes. Considering that this concentration is about 1000 times higher than the solubility limit of oleic acid, it seems that this amount of lauric acid is also sufficient to generate surface tension gradients around gas bubbles. Therefore, at pH 4.5 and in the absence of precipitates a combination of surface tension effects and of surface tension gradients affect the bubble sizes. Most interestingly, when a precipitate appears at higher lauric acid concentrations at pH 4.5, the average bubble sizes increase to the levels predicted by equation 5-5. In the presence of precipitates, the surface tension is also low, but in this case the surface tension appears to be the only mechanism of reduction of bubble sizes despite the presence of 1.2×10^{-5} mol/L of lauric acid in equilibrium with the precipitates. This very interesting trend at pH 4.5 strongly suggests that colloidal precipitates of lauric acid prevent the formation of surface tension gradients around gas bubbles.

Following the arguments discussed by Parkinson and Ralston (2011) about interactions between bubbles and hydrophilic mineral particles, very fine colloidal precipitates of fatty acids can accumulate near the bottom end of a rising bubble by hydrodynamic drag forces and can therefore occupy the same volume that would otherwise be available to surfactant molecules. With the surfactant molecules now displaced from that zone, surface tension gradients cannot be generated and the bubble size cannot be reduced through the bubble-break up mechanism. It is also possible that the presence colloidal precipitates at the gas-liquid interface affects the diffusion of surfactant molecules around the bubble surface thus further limiting the formation of surface tension gradients. This type of volume exclusion effect appears to be the most likely mechanism of action of colloidal precipitates. This mechanism closely resembles one that causes the entrainment of hydrophilic particles in the froth layer during froth flotation.

At pH 10.4, when precipitates disappear and the system forms a true solution, there is a very strong effect of laurate anions on average bubble sizes especially at higher laurate concentrations. The CCC95 of laurate can be identified at a concentration of 7.2×10^{-5} mol/L. In

the case of laurate solutions at high pH, the surface tension is high (see Figure 4-4) and equals to the surface tension of water even at a highest tested concentration of 2.3×10^{-4} mol/L, which is well above the critical coalescence concentration. However, bubble sizes still decrease rapidly with concentration to very low levels. At the same time, bubble size distributions at pH 10.4 are very different than those in water in the absence of lauric acid. These observations indicate that the most plausible mechanism of bubble size reduction at pH 10.4 involves surface tension gradients around gas bubbles. The tested concentrations of lauric acid are most likely sufficient to generate those gradients. From this point of view, the mechanism of gas dispersing action of lauric acid at pH 10.4 is very similar to the behavior of MIBC: even though there is no change in the surface tension of surfactant solutions, a large decrease in bubble sizes is usually observed in the same surfactant concentration range. The value of CCC95 for sodium laurate at pH 10.4 was found to be 7.2×10^{-5} mol/L, which is a little higher than the CCC95 of sodium oleate at pH 10.4 (5.7×10^{-5} mol/L).

Since the pK_a of lauric acid is at pH 4.7, it is also reasonable to assume that at pH 4.5, there are roughly equal amounts of ionic and nonionic species. At a concentration as low as 1.2×10^{-5} mol/L, which is the solubility of lauric acid, there is no precipitation regardless of pH. At pH 10.4 the reagent is fully ionized while at pH 4.5 a half of the reagent is ionized. According to Figure 5-6, at a concentration of 1.2×10^{-5} mol/L, the difference in the measured bubble sizes at these two pH values is small and the average bubble size at this concentration is even lower at pH 4.5 compared to pH 10.4, so lauric acid at pH 4.5 is actually a little more effective in reducing bubble sizes. This additional observation is another indication of higher surface activity of the undissociated lauric acid species compared to the laurate anion. Similarly to the trends observed in the surface tension data (Figure 4-4), it seems that at a lower chain length the difference between ionic and nonionic species is more significant, but the contribution of the chain length may become more important for longer chain surfactants.

Bubble size distributions for sodium laurate at the solubility limit (1.2×10^{-5} mol/L) are given as a function of pH in Figure 5-7. The frequency of smaller bubbles is higher at pH 4.5 with a narrower size distribution. Bubbles coalesce at higher pH, larger bubbles are formed and distribution becomes wider. It should again be stressed that colloidal precipitates do not form at this concentration in the tested pH range so the data effectively present the effect of dissociated and associated species on the bubble size distributions.

On the other hand, Figure 5-8 demonstrates the bubble size distribution at a selected concentration of sodium laurate higher than the solubility limit, 1.6×10^{-4} mol/L (36.51 mg/L). It could be observed that as pH increases, the distribution becomes narrower, which is due to increasing concentrations of soluble surface-active species. Based on the earlier discussion of the data for laurate and oleate solutions at high pH, such monomodal distributions are indicative of bubble size reduction through bubble break-up and coalescence prevention mechanisms.

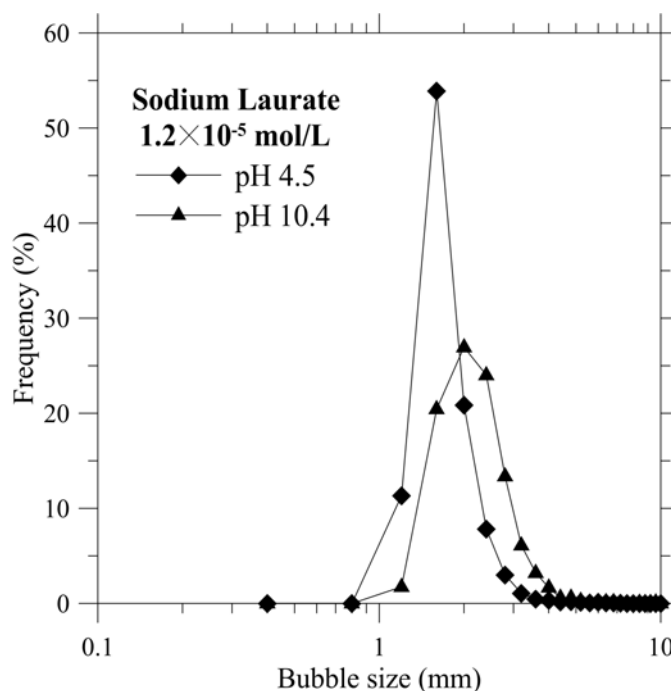


Figure 5-7. Bubble size distribution of 1.2×10^{-5} mol/L (2.67 mg/L) sodium laurate at pH 4.5 and pH 10.4

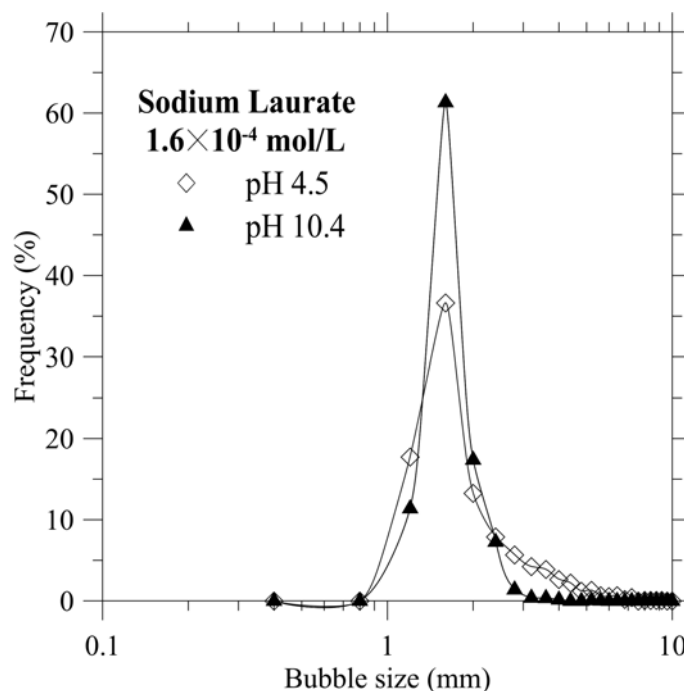


Figure 5-8. Bubble size distribution of 1.6×10^{-4} mol/L (36.51 mg/L) sodium laurate at pH 4.5 and pH 10.4

For sodium laurate no sign of bimodality is observed even at pH 4.5 for a concentration of 1.6×10^{-4} mol/L (36.51 mg/L) at which precipitates are present, instead there is a tail (skewness) towards the larger bubble sizes in the distribution. While in the case of sodium oleate bimodality is quite evident in the presence of precipitates. This difference could be attributed to the difference in the solubility of lauric acid and oleic acid. As speciation diagrams show, a small amount of the surfactant is always present in equilibrium with the precipitate, and this constant concentration is equal to the solubility of the undissociated acid species. From this point of view, lauric acid is much more soluble than oleic acid even when precipitates appear. There is always 1.2×10^{-5} mol/L of dissolved free surfactant in equilibrium with precipitate for lauric acid solutions, while for oleic acid this equilibrium concentration is 1000 times lower and equals to about 2.5×10^{-8} mol/L of the surfactant. This amount in solution is sufficient to change the bubble size distribution even in the presence of precipitates. Investigating lauric acid at a very low concentration, close to 1.2×10^{-5} mol/L, revealed the effect of soluble surfactant molecules on the bubble size distribution. At this low concentration, all lauric acid is soluble and there is no precipitation regardless of pH. In this case, a change in pH only results in a change in the concentration of anionic versus non-ionic species. The lowest concentration tested for sodium laurate was 1.2×10^{-5} mol/L, or 2.7 mg/L. Figure 5-9 compares bubble size distributions at this

concentration and at higher concentrations, all at a low pH of 4.5. A substantial shift of the distribution towards lower bubble sizes in the presence of 1.2×10^{-5} mol/L (2.7 mg/L) sodium laurate can be found in comparison to the distribution in water only. Since the entire amount of laurate is completely dissolved at this concentration, it could be concluded that this soluble amount is responsible for the change in the bubble size distribution. A very small amount of this reagent changes the location of this peak.

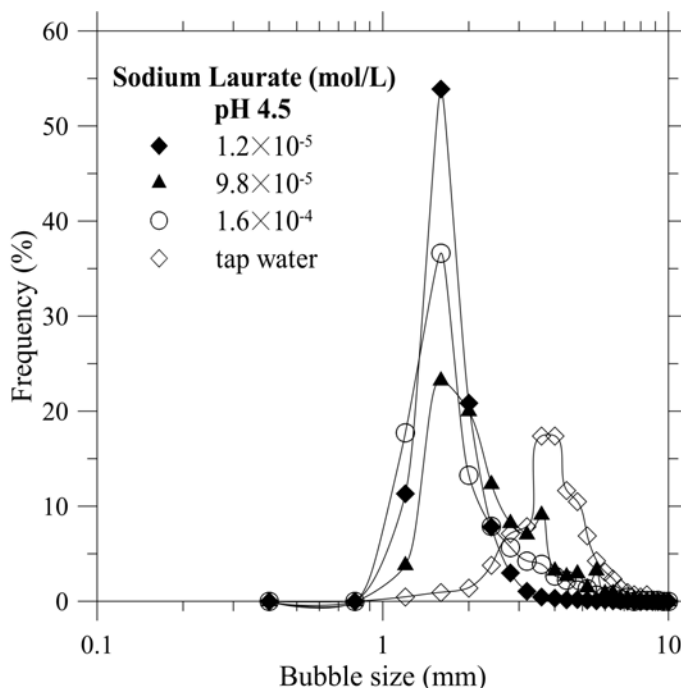


Figure 5-9. Comparison of bubble size distribution at different concentrations of sodium laurate solution at pH 4.5 with water only case

At higher concentrations, the frequency of small bubbles decreases. While sodium laurate is completely soluble in water at pH 4.5 at a concentration of 1.2×10^{-5} mol/L (2.7 mg/L), the fraction of soluble species decreases to 20% and 12% at concentrations of 9.8×10^{-5} mol/L (21.9 mg/L) and 1.6×10^{-4} mol/L (36.5 mg/L) and the amount of soluble species (ionic plus soluble molecular) equals to 2×10^{-5} mol/L (4.4 mg/L) as calculated from thermodynamic calculations, by adding the amounts of ionic and soluble molecular species. At pH 4.5, as the total concentration of laurate is increased, the main factor changing is the amount of precipitate, while the soluble amount in solution is constant and equal to the solubility of laurate. In other words, since the mean bubble size increases and the bubble size distribution becomes wider by increasing concentration at pH 4.5, it seems that lauric acid precipitates actually induce coalescence.

Overall for sodium laurate, the strongest effect of concentration (understood as total concentration: soluble species plus any precipitate) occurs at higher pH, when all lauric acid is in the form of soluble species and there is no precipitate. As soon as precipitates appear in solution, and since they do not exhibit significant surface activity, the average bubble size increases, and the bubble size distribution becomes wider and still monomodal. In the case of sodium oleate the response is slightly different due to lower solubility: as soon as precipitates appear, the bubble size distribution becomes bimodal as the concentration of soluble species in equilibrium with the precipitate becomes too low to induce surface tension gradients, and consequently to make the distribution narrower and monomodal.

5.1.3 Sodium hexanoate

Sodium Hexanoate as a 6-carbon fatty, which has a much higher solubility (0.084 mol/L according to Fuerstenau et al 1985) than the longer chain fatty acids (C12, C18), was also tested in gas dispersion studies. Since no precipitate is forming in the case of sodium hexanoate in the tested concentration and pH ranges, the effect of ionic and molecular species on gas dispersion properties could be illustrated more clearly.

The surface tension values for sodium hexanoate do not differ from the surface tension of water in the concentration range of gas dispersion measurements. In other words, surface tension effects do not play a role in bubble size reduction in hexanoate solutions, just as in the case of an alcohol frother such as MIBC. Reduction in bubble sizes most likely proceeds through generation of surface tension gradients. It is still noteworthy that the undissociated acid species is more powerful than the hexanoate anion in reducing bubble sizes. This effect was also observed for lauric acid. It seems that hexanoic acid is capable of more densely adsorbing on bubble surfaces compared to the anion, which should also lead to an enhanced ability to generate surface tension gradients.

The Sauter mean bubble diameters of sodium hexanoate are shown in Figure 5-10 as a function of concentration at pH 3.7 and pH 10.4. The surfactant was tested at a sufficiently low pH, below the pK_a , at which almost all the reagent was converted to the associated acid form. Interestingly, sodium hexanoate at a pH as low as 3.7 prevents bubble coalescence to a much higher degree than at pH 10.4. The effect of speciation could still be detected for lauric acid for which it is rather clear that undissociated acid is more effective in reducing bubble sizes than the

dissociated laurate anion in absence of precipitates. For oleic acid, however, such a comparison was impossible due to the very low solubility of the undissociated acid. The CCC95 of sodium hexanoate was found to be 1.9×10^{-4} mol/L (26 mg/L) at pH 3.7. Hexanoate did not show an equally strong effect on bubble sizes at pH 10.4, at which the reagent was fully ionized, even at a relatively high concentration of 6.5×10^{-4} mol/L.

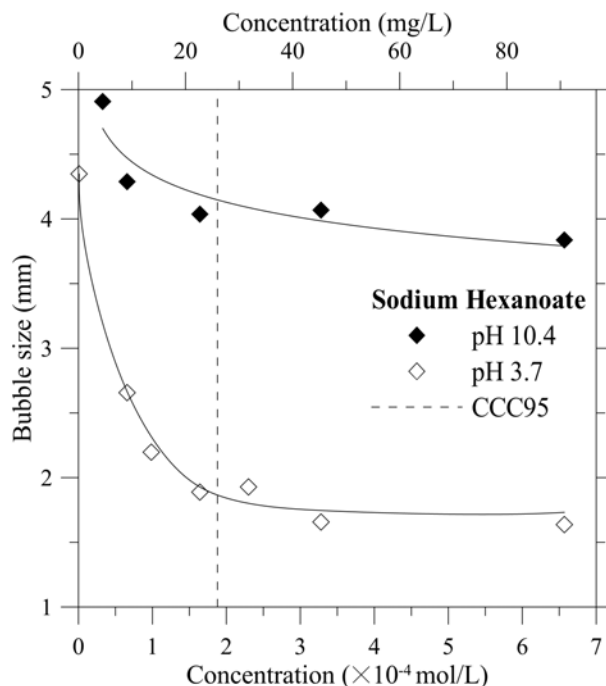


Figure 5-10. Bubble size of sodium hexanoate at pH 3.7 and 10.4

Considering the results for hexanoate, the difference in the behavior of short and long chain fatty acids could be explained by the much lower solubility of longer chain carboxylic acids.

Overall, the results for sodium hexanoate show that among the soluble species, the undissociated hexanoic acid ($R\text{-COOH}$) is far more capable of reducing bubble sizes than the fully ionized form $R\text{-COO}^-$. In fact, the results for hexanoic acid are very similar to the published bubble size data for many standard alcohol-type frothers, such as MIBC or hexanol. Hexanoic acid, as a nonionic surfactant, behaves in the same way as short chain C6 alcohols.

5.1.4 MIBC and reagent comparison

Sauter mean bubble diameter for MIBC measured as a function of concentration under the same experimental conditions as for anionic reagents is shown in Figure 5-11 for reference.

The CCC95 value for MIBC was calculated to be at 8.0×10^{-5} mol/L (8.18 mg/L), which is not very different from the CCC95 values of the anionic reagents. The CCC of MIBC was reported as 8.9×10^{-5} mol/L by Castro et al (2013) as measured by bubble size analyzer developed by UCT, which is very close to the value measured in this thesis.

Figure 5-11 also shows mean bubble diameters in fatty acid solutions of different chain lengths and compares those to bubble size data for MIBC. All the data are remarkably similar. There is only a slight decrease in bubble sizes with increasing alkyl chain lengths, and sodium oleate at pH 10.4 shows bubble sizes very similar to those of MIBC at the same molar concentration. Comparing the CCC95 value of sodium hexanoate (1.9×10^{-4} mol/L - 26 mg/L - pH 3.7) with sodium laurate (7.2×10^{-5} mol/L - 15 mg/L - pH 10.4) and sodium oleate (5.8×10^{-5} mol/L - 17.76 mg/L - pH 10.4), it seems that the CCC95 values decrease slightly by increasing chain lengths of fatty acids but overall does not dramatically change in the case of carboxylic acids. There exists a limiting minimum bubble size, which cannot be further reduced by surfactant addition. The alcohol frothers reported in literature also approach a limiting bubble size but their CCC95 values decrease by 2 orders of magnitude by increasing chain length from propanol to octanol (Zhang et al 2012).

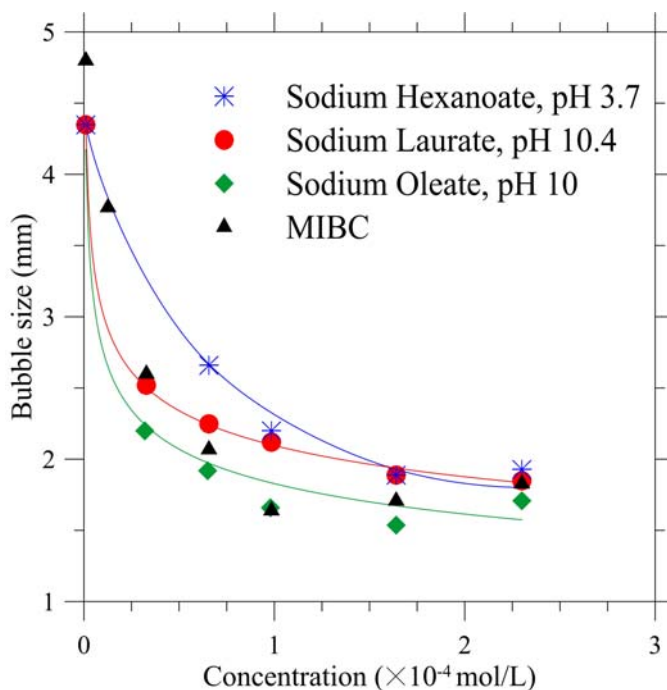


Figure 5-11. Sauter mean diameter of fatty acids of different chain lengths and MIBC as a function of concentration

Bubble size distributions for different concentrations of MIBC are given in Figure 5-12. The bubble size distribution is wider at low concentrations of MIBC and becomes narrower and monomodal at higher concentrations.

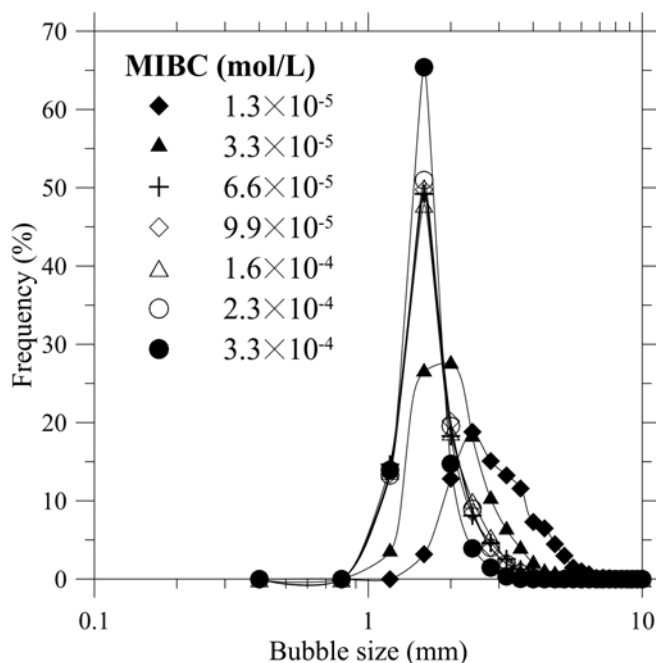


Figure 5-12. Bubble size distribution at different concentrations of MIBC

The effect of MIBC, sodium hexanoate, laurate and oleate on the normalized bubble size and surface tension are compared in Figure 5-13. It could be observed that the behavior of sodium hexanoate and laurate solutions are very similar to MIBC in a sense that they affect bubble sizes at a concentration 100 times lower than the range at which surface tension is affected. While in the case of sodium oleate these two concentration ranges are much closer. In other words, comparing CCC95 to CMC values, for MIBC these values are 100 times different, but they are very close for oleate at pH 10.

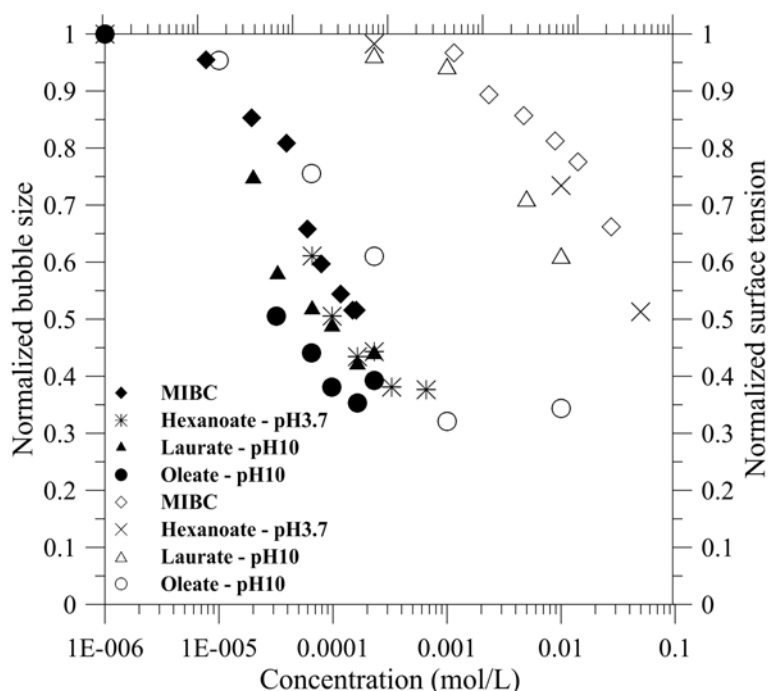


Figure 5-13. Bubble size versus surface tension of MIBC, sodium laurate and oleate at pH 10.4 and sodium hexanoate at pH 3.7 (filled symbols represent bubble size data and empty symbols represent surface tension data)

5.1.5 Sodium dodecyl sulfate

Alkyl sulfates are strong electrolytes and remain fully ionized in solution regardless of pH. Sodium dodecyl sulfate was used in this research as a reference C12 surfactant that does not form colloidal precipitates. In a sense, the reagent simulates the behavior of fatty acids at high pH, without colloidal species.

Sodium dodecyl sulfate is fully dissociated in the whole pH range and no effect of pH is observed on bubble sizes as is shown in Figure 5-14. The final average bubble size is not significantly different from the final bubble size in sodium oleate. Low dosages, close to 3.2×10^{-5} mol/L (10 mg/L), sharply decrease bubble sizes.

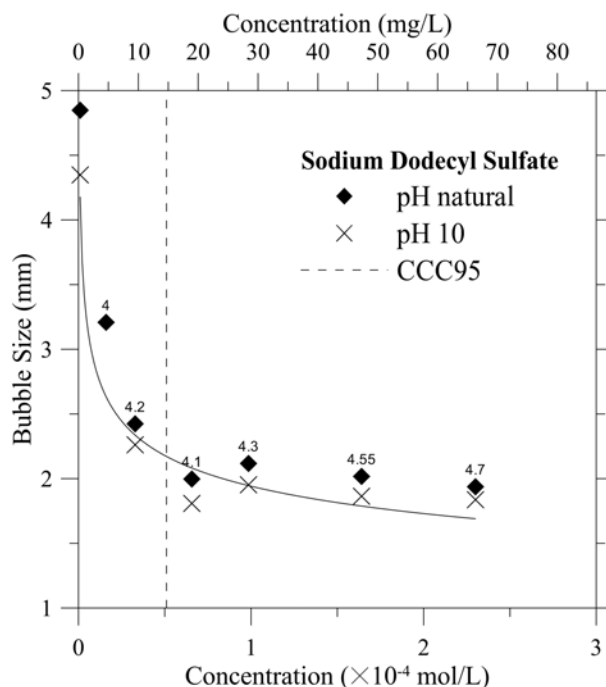


Figure 5-14. Sauter mean bubble diameter of sodium dodecyl sulfate at natural pH (4.1-4.7) and pH 10

Overall it could be concluded that the gas dispersion properties of surfactants are defined by the amount of soluble surfactant in solution. In the case of strong electrolytes, for which the effect of pH is eliminated and the entire amount of surfactant is available for adsorption at the bubble surface, bubble sizes are reduced regardless of pH. For weak electrolyte surfactants, bubble sizes are reduced to a minimum at a pH value at which the concentration of surface-active species is sufficiently high to induce surface tension gradients.

Sauter mean bubble diameter of sodium dodecyl sulfate is compared to sodium oleate, and sodium laurate at pH 10.4 in Figure 5-15. It could be observed that at high pH, when the surfactants are all dissolved in solution, there is only a slight difference in Sauter mean bubble diameters. At pH 10.4, the CCC95 of SDS is 5.1×10^{-5} mol/L (14.8 mg/L), which is not very different from CCC95 of sodium oleate, and laurate, which are determined to be 5.7×10^{-5} mol/L (17.8 mg/L) and 7.2×10^{-5} mol/L (16 mg/L). All three values are quite similar.

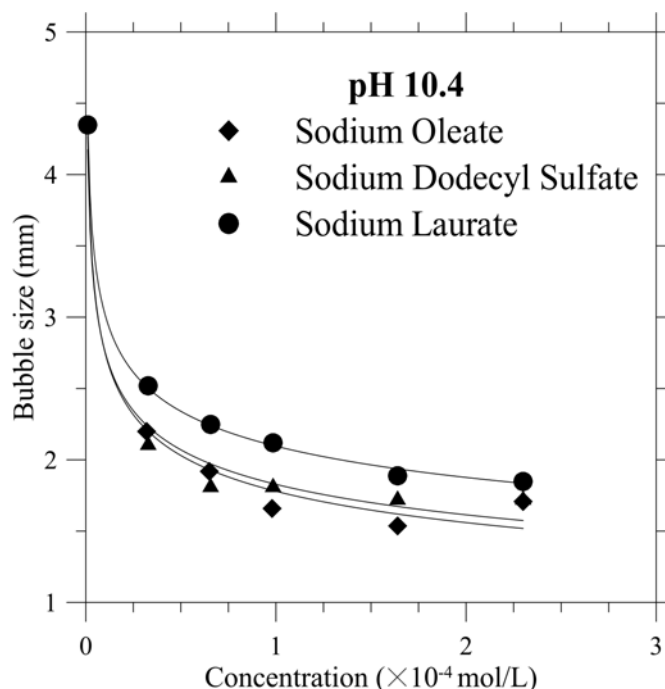


Figure 5-15. Sauter mean bubble diameter of sodium oleate, sodium dodecyl sulfate and sodium laurate at pH 10.4

- Hydrophobic-Lyophobic balance

In literature the gas dispersion properties of alcohol-type frothers are correlated to their hydrophobic-lyophobic balance (HLB) (Zhang et al 2012). For the same purpose, the HLB of the anionic reagents used in this study were calculated according to the Davis method (Equation 2-15) (Davies and Rideal 1961). The HLB of sodium oleate, laurate, hexanoate, octadecyl sulfate and dodecyl sulfate are calculated to be 18.0, 20.9, 23.7, 37.15 and 40.0 respectively.

According to Zhang et al (2012), as described in literature section, the CCC95 increases as HLB increases in the case of aliphatic alcohols and polyglycols, they also indicated that CCC95 tended to level off above 6 carbons in the molecule. In the case of the tested anionic reagents, their gas dispersion properties do not seem to be a strong function of HLB as in the case of alcohols and polyglycols; CCC95 increases only slightly with the chain length and with the HLB values of carboxylic acids. Although the HLB of SDS is nearly twice as high as the HLB of the carboxylic acids, the CCC95 does not proportionally increase for SDS. It should be highlighted that HLB is not a good parameter for correlating with gas dispersion for anionic weak electrolyte type surfactants. The concept is perhaps more applicable to short chain alcohols and polyglycols, which are all fully soluble in water and their speciation does not change with

pH, but for fatty acids of above 6 carbon atoms this relationship between HLB and bubble sizes is not clear at all.

Gas hold-up measurement results performed along with bubble size measurements are included in Appendix 2.

6. Foamability and partition of anionic surfactants

6.1 Sodium oleate

The foamability characteristics of 100-ml sodium oleate solutions were assessed in the foamability set up following the method described in the experimental section. The total gas volume contained in the system (in the solution phase plus in the foam phase) is presented in Figure 6-1 as a function of time for different concentrations of sodium oleate. These results were obtained at natural pH, similarly to the bubble size data at natural pH in Figure 5-1. A set of results for a relatively high concentration of MIBC solution is also shown for comparison.

It is important to note that no significant foaming was observed at oleate concentrations below 6.5×10^{-5} mol/L (10-20 mg/L). At 9.8×10^{-5} mol/L (30 mg/L), a substantial increase in foam growth rate and volume was suddenly obtained. Increasing oleate concentration to 50 mg/L (1.6×10^{-4} mol/L) resulted in a further increase in both parameters, but higher concentrations did not have a significant effect. The slopes of the lines remained constant at concentrations of 2.3×10^{-4} to 3.2×10^{-4} mol/L (70 mg/L-100 mg/L) compared to the data at 1.6×10^{-4} mol/L (50 mg/L). At aeration times of 80-100 seconds, the onset of froth collapse was observed and the curves continued in a downward manner at longer times. The results show that the total gas volume increases faster at higher concentrations of sodium oleate but the growth rate does not increase at concentrations higher than about 1.6×10^{-4} mol/L (50 mg/L).

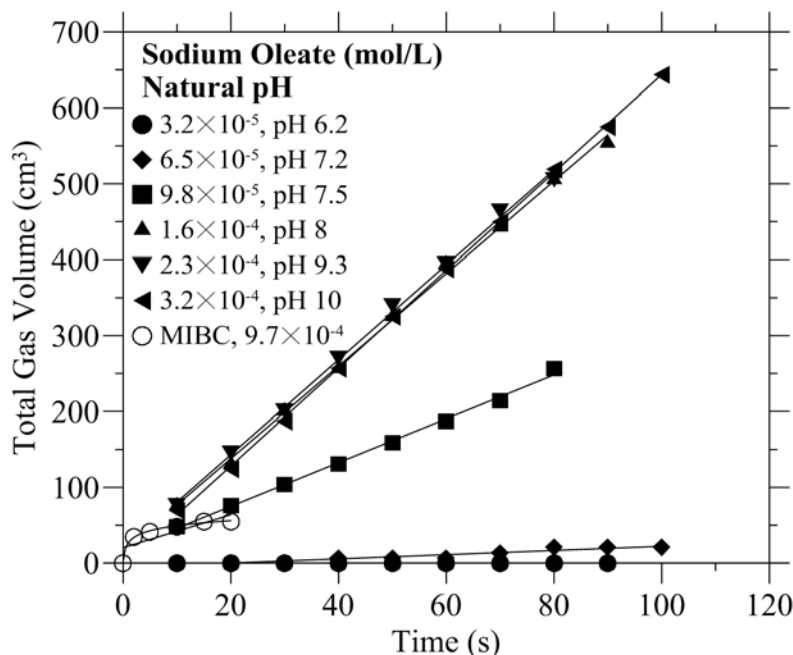


Figure 6-1. Total gas volume as a function of time at $J_g = 0.5\text{cm/s}$ and natural pH for different concentrations of sodium oleate solution, initial solution volume is 100 mL

At sufficiently high oleate concentrations, the resulting foam grew continuously without reaching steady state conditions. Instead, the foam underwent an irreversible collapse when the amount of air contained within the foam phase exceeded a critical level.

An interesting observation can be made when one notes that after 60 seconds of foam growth the total gas volume in the system is about 400 cm^3 for oleate concentrations of at least $1.6 \times 10^{-4}\text{ mol/L}$ (50 mg/L). Considering that the volumetric gas flow rate of this test was $400\text{ cm}^3/\text{min}$, it is quite clear that all the air supplied to the column was retained within it, either in the bulk solution (gas hold-up) and/or within the foam. In other words, at higher oleate concentrations air does not escape from the system and no foam breakage is observed. After a critical time, when the foam cannot hold any additional air, the foam layer starts to burst and irreversibly collapse. As far as visual observations permit to conclude, up to this collapse point, there is in fact very little bubble coalescence occurring within the foam phase. For typical frothers like MIBC, simultaneous froth growth and collapse are usually observed, so the gas volume never reaches the volume of air supplied to the column, and these two competing processes lead to establishment of a steady-state froth volume/height. Clearly, the behavior of sodium oleate is very different as only net foam growth with time manifests itself in the

presented data, and these observations illustrate well the difficulty of analyzing the foaming power of sodium oleate using the DFI approach. This steady froth building capacity of sodium oleate may lead to froth stability issues since under operating conditions the froth is expected to collapse as soon as it leaves the flotation cell.

As the data for MIBC demonstrate, a concentrated MIBC solution produces an equilibrium foam volume within the first 10-20 seconds of the test, and the resulting total gas volume is several times lower than the maximum volume achievable under the experimental conditions.

An analysis of foamability data for short chain fatty acids reported by Malysa et al (1991) shows that short-chain fatty acids (up to C8) behave similarly to MIBC and for these reagents the retention time can be obtained from the DFI test. Malysa et al (1991) also reported a dramatic decrease in the retention time for C9 and C10 fatty acids, which is equivalent to very small foam volumes produced at a given volumetric gas flow rate. It should be noted that all the data in Malysa et al (1991) were obtained in 0.005mol/L hydrochloric acid as the background electrolyte so all the fatty acids were in their associated forms. As will be presented later, at sufficiently low pH of the tested solution, oleic acid may give a similar result to that reported by Malysa et al (1991) for C9 and C10 homologues.

By plotting the foam growth rate, or the slope values of the linear sections of the curves from Figure 6-1, and also the total gas volume obtained after 70 seconds of aeration as a function of oleate concentration, it can be seen from Figure 6-2 that the two parameters approach a constant value at oleate concentrations at which the average bubble size at natural pH approach its minimum limiting value (CCC).

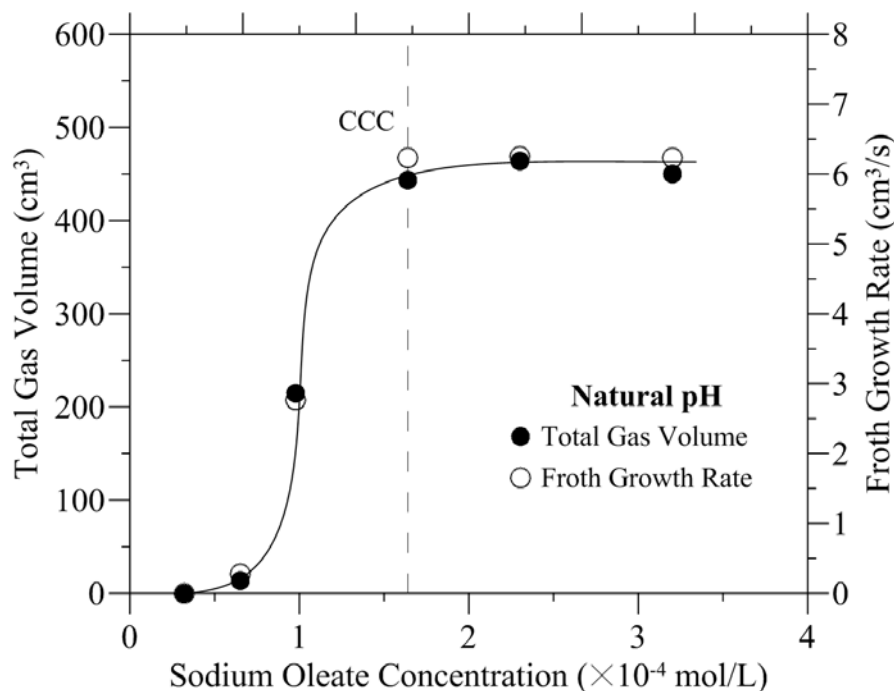


Figure 6-2. Foam growth rate and total gas volume at different concentrations of sodium oleate solutions

6.1.1 Effect of solution volume

A set of additional foamability tests at natural pH was also performed using oleate solutions with an initial volume of 200 mL. This was done to check the reproducibility of foamability results and observe the effect of solution volume. The data in Figure 6-2 suggest that maximum foamability coincides with the CCC at natural pH, and the concern was that a smaller initial volume of 100 mL was insufficient to show differences between the foamability (total gas volume) of oleate solutions at higher concentrations particularly around the CCC. Therefore a series of tests with an initial volume of 200 ml was performed. The total gas volume contained in the system is presented in Figure 6-3 as a function of time for different concentrations of 200 ml sodium oleate solution at natural pH.

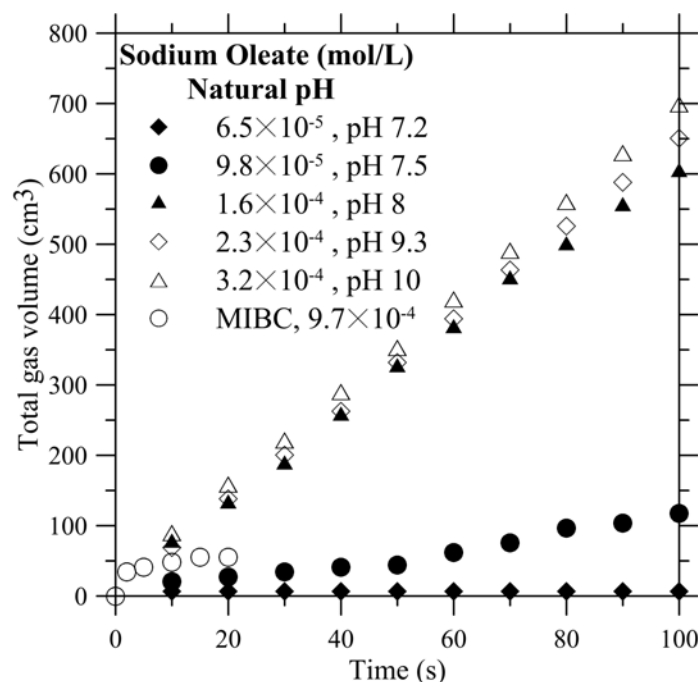


Figure 6-3. Total gas volume as a function of time at $J_g = 0.5\text{cm/s}$ and natural pH for different concentrations of sodium oleate solution, initial solution volume is 200 mL

The general trends are very similar to those shown in Figure 6-1 and the data indicate that the ratio of the airflow rate to the solution volume is not a significant factor in the foamability test although small detectable differences can now be seen for higher oleate concentrations.

6.1.2 Effect of pH

A 100 ml of 6.5×10^{-5} mol/L (20 mg/L) and 2.3×10^{-4} mol/L (70 mg/L) sodium oleate solutions were selected for these measurements. Based on Figure 5-1, the lower concentration was chosen such that its effect on the mean bubble size was not very pronounced at natural pH. The second concentration was higher than the proposed CCC value for sodium oleate at natural pH.

The foamability of a 6.5×10^{-5} mol/L (20 mg/L) sodium oleate solution is shown in Figure 6-4 at different pH values. In the foamability measurements the standard deviation of three total gas volume readings at a given time ranged from 5 cm^3 to 20 cm^3 , and the size of the data symbols in the subsequent figures is basically equal to the largest error involved.

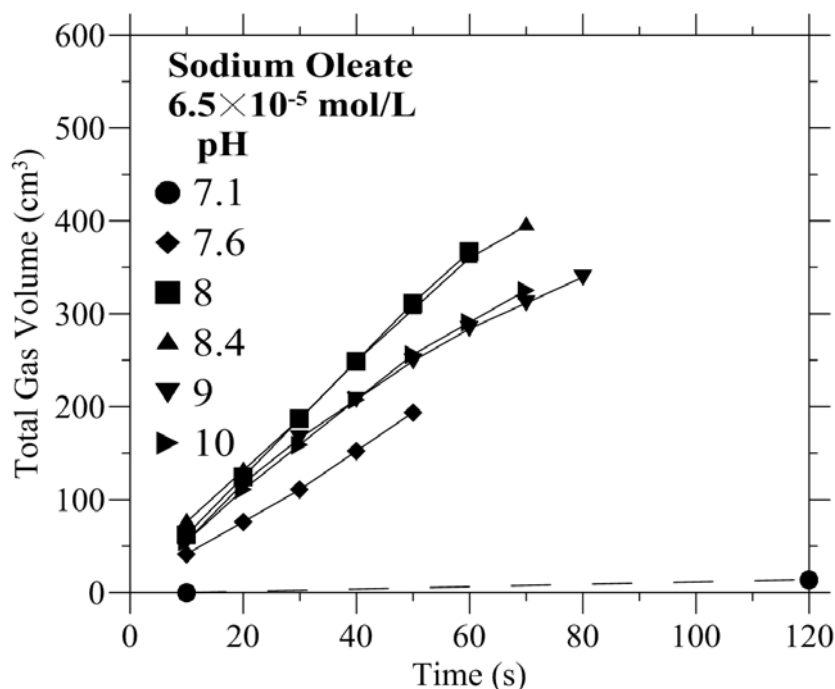


Figure 6-4. Total gas volume versus time at $J_g = 0.5 \text{ cm/s}$ at different pH values for $6.5 \times 10^{-5} \text{ mol/L}$ (20 mg/l) sodium oleate solution (pH of precipitation is 8.1)

The pH of bulk precipitation of oleic acid is 8.1 at this oleate concentration according to the thermodynamic data illustrated in Figure 2-3 and Table 5-1. As can be seen from the results in Figure 6-4, pH as low as 7.1 (natural pH) completely prevents any foaming in this solution. As pH increases, the foaming of oleic acid solutions is significantly enhanced, although a small decrease can be seen at pH 9 and 10. It is also interesting to note that even at $6.5 \times 10^{-5} \text{ mol/L}$ (20 mg/L) of sodium oleate at higher pH the experimental points fall on a line whose slope is almost equal to the maximum foam growth rate at this volumetric flow rate of air ($\sim 400 \text{ cm}^3/\text{min}$). This is also in line with the fact that a concentration of $6.5 \times 10^{-5} \text{ mol/L}$ is over CCC95 of sodium oleate at pH 10. The fact that sodium oleate solutions completely lose their foaming power at lower pH is entirely in line with the earlier mentioned results of Malysa et al (1991) for C9 and C10 fatty acids. At sufficiently low pH, oleic acid solutions do not foam - just like C9 and C10 fatty acids in dilute hydrochloric acid - but the foamability of these systems markedly increases above a critical pH value.

Analogous results for a $2.3 \times 10^{-4} \text{ mol/L}$ (70 mg/L) oleate solution are shown in Figure 6-5. At this concentration, the onset of precipitation can be expected around pH 8.7.

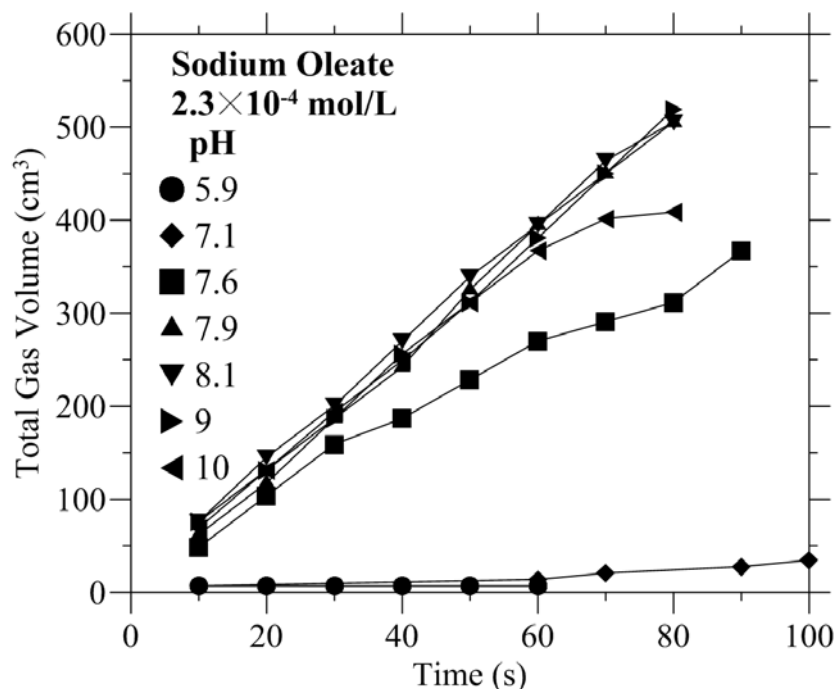


Figure 6-5. Total gas volume versus time at $J_g = 0.5\text{cm/s}$ at different pH values for 2.3×10^{-4} mol/L (70 mg/l) sodium oleate solution (pH of precipitation is 8.7)

Again, oleate solutions do not exhibit any foaming properties at lower pH, but a critical pH value exists above which the foam growth rate and gas volume reach their respective limits at the applied volumetric gas rate. The fact that higher pH enhances foamability indicates that soluble oleate species are involved in the foaming process. Advanced precipitation of oleic acid leads to complete loss of foaming capabilities. In fact the behavior of oleic acid precipitates, which form oily emulsions, is in line with the industrial application of oils as defoaming agents to prevent excessive frothing.

Although pH 7.6 and 8.1 are lower than the pH of precipitation, the concentration of soluble species are still increasing at these two pH values, which leads to a continuous increase in foamability. At a concentration of 2.3×10^{-4} mol/L at pH 8.1, 72% of the reagent is in the precipitated form and 28% is in the ionic form while at pH higher than the pH of precipitation (pH 8.7) almost all the reagent is in the soluble ionic form. Despite this difference in speciation, moving from pH 8.1 to pH 10 does not cause a measurable change in the foamability of the oleate solution. This trend coincides with the surface tension values in Figure 4-1 for 2.3×10^{-4} mol/L oleic acid. Near pH 8-9 there is not much change observed in the surface activity of the reagent, although in terms of thermodynamic calculations of speciation 78% of the reagent is in

the precipitate form at pH 8 while there is no precipitate at pH 9. So it seems that the change in the foamability behavior is not as sharp as the thermodynamic calculations dictate. It is interesting to point out that even in the case that 78% of sodium oleate is in the precipitate form, the concentration of the soluble species is still very close to CCC95.

It should still be noted that at concentrations of 6.5×10^{-5} mol/L and 2.3×10^{-4} mol/L, maximum foamability is reached at pH values near 8-9 corresponding to the lowest surface tension values (Figure 4-1).

6.1.3 Partitioning between the foam phase and bulk solution

6.1.3.1 Concentration effect

The total gas volume contained in a 200 ml system at pH 10 is presented in Figure 6-6 as a function of time for different concentrations of sodium oleate. Increasing oleate concentration did not have a significant effect on foamability at pH 10 at concentration range of 6.5×10^{-5} - 3.2×10^{-4} mol/L (20-100 mg/L). The similar foamability behavior in all cases shows that although different concentrations of oleate are available in each case, they all provide the same foaming capability at a superficial gas velocity $J_g = 0.5$ cm/s. 6.5×10^{-5} mol/L (20 mg/L) sodium oleate while solubilized at high pH gives the same foamability result as that of 3.2×10^{-4} mol/L (100 mg/L). In fact even this low concentration of sodium oleate at pH 10 could provide enough surface-active species to produce the maximum foamability at a superficial gas velocity of 0.5 cm/s. It is also important to note that all these concentrations are higher than CCC95 at pH 10. To test a concentration lower than CCC95 at pH 10, 3.2×10^{-5} mol/L (10 mg/L) sodium oleate was tested which led to a weaker foamability behavior.

At the same time, normalized TOC measurements presented in Figure 6-7 show similar uptake rates at all concentrations. Normalized data were calculated by dividing the TOC content of the samples taken from the bulk solution at a specific time by the original TOC content in the bulk solution before turning on the air. The bulk TOC concentration decreased to almost a half of its original value as a result of passing air through the system. These results show that sodium oleate is gradually removed from the solution phase and transferred to the foam phase as a result of bubbling air through the column.

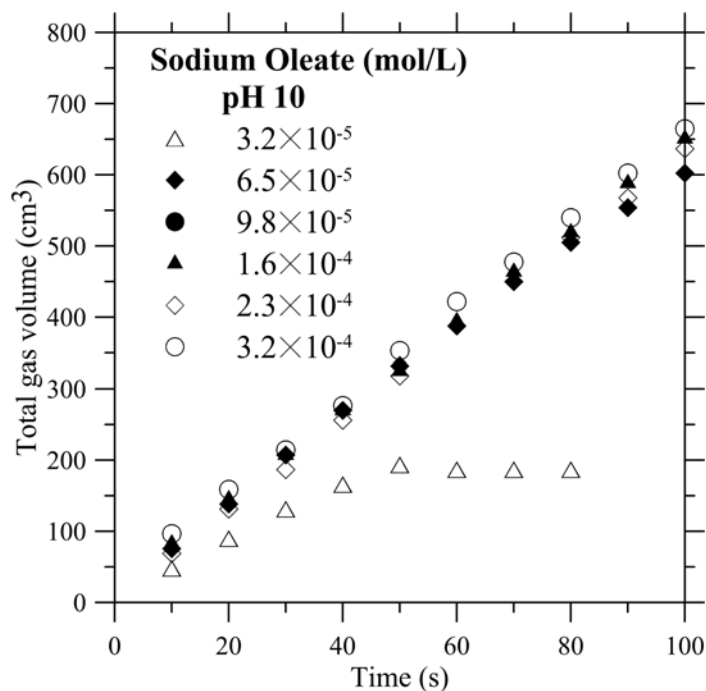


Figure 6-6. Total gas volume as a function of time at $J_g = 0.5\text{cm/s}$ and pH 10 for different concentrations of sodium oleate aqueous solution, initial volume is 200 ml

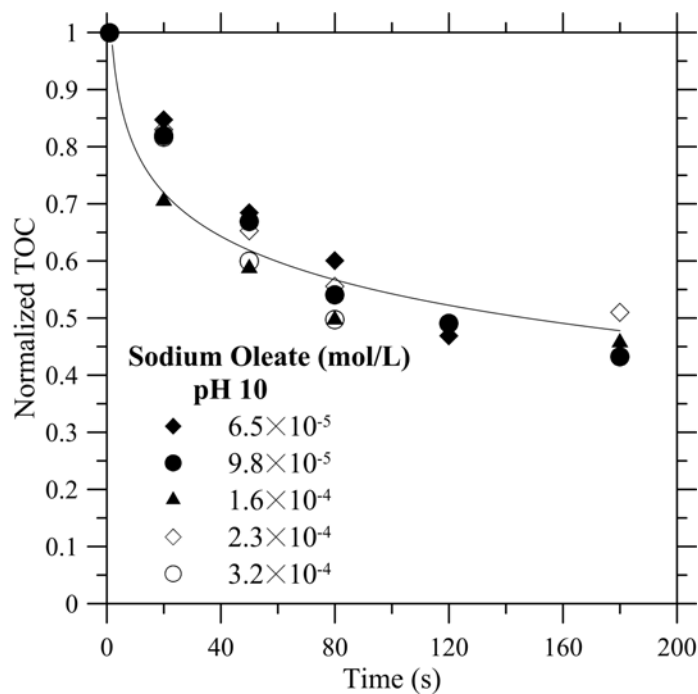


Figure 6-7. Changes in the total organic carbon content in bulk solution at $J_g = 0.5\text{cm/s}$ and pH 10 for different concentrations of sodium oleate aqueous solution

Another interesting observation was that although the initial solutions were clear at pH 10, the high concentration of surfactant, now accumulated at the relatively lower volume of

liquid in the foam compared to the bulk, caused water recovered in the foam to be very turbid. A higher concentration of fatty acid in the liquid phase of the foam most likely resulted in precipitation of colloidal fatty acid species as the solubility of the surfactant was exceeded.

6.1.3.2 *pH effect*

The same two concentrations, 6.5×10^{-5} mol/L and 2.3×10^{-4} mol/L (20 and 70 mg/L), were selected to study the effect of pH on partitioning of sodium oleate. The foamability of 200 ml of a 6.5×10^{-5} mol/L (20 mg/L) sodium oleate solution is shown in Figure 6-8 at different pH values. The simultaneous change in the surfactant concentration with time, as judged from TOC measurements, is shown in Figure 6-9.

As is demonstrated in Figure 6-9 for 6.5×10^{-5} mol/L sodium oleate, at lower pH at which foam formation is not observed, the changes in the bulk concentration of oleate are very small over the time scale of the test. This result suggests a low adsorption rate of sodium oleate at the liquid-gas interface. In the intermediate pH range of 7.7-8.7 the highest rate of decrease in concentration is observed, which indicates the highest adsorption of the surfactant on bubble surfaces. In this pH range, the foamability of sodium oleate at the tested concentration is also the highest. Finally, at pH 10 a slight decrease in the TOC depletion rate is observed.

An increase in the amount of surfactant in the foam occurs up to a certain pH just over the pH of precipitation, at which the maximum transfer occurs, after which the rate of transfer declines slightly. This is the same type of trend as was observed in equilibrium surface tension data in Figure 4-1, it is in accordance with the minimum equilibrium surface tension for sodium oleate solutions at the intermediate pH range in that figure. In other words, maximum foamability occurs when oleate solutions reach the lowest surface tension.

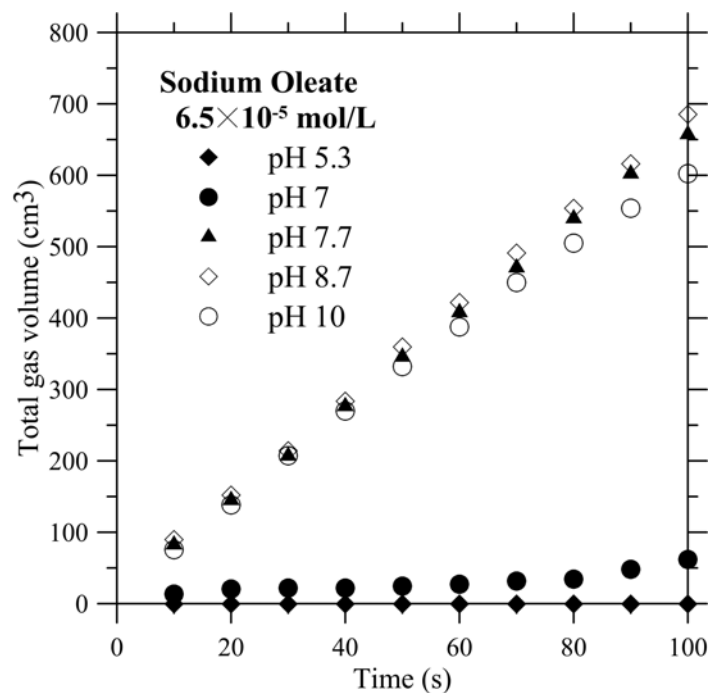


Figure 6-8. Total gas volume versus time at $J_g = 0.5 \text{ cm/s}$ and different pH values for $6.5 \times 10^{-5} \text{ mol/L}$ sodium oleate solution (this concentration is below CCC at natural pH)

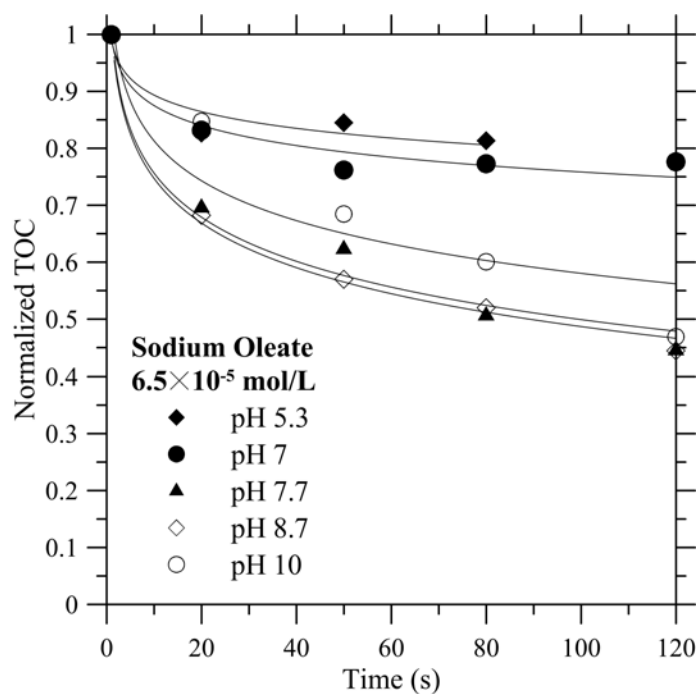


Figure 6-9. Changes in TOC in bulk solution at $J_g = 0.5 \text{ cm/s}$ at different pH values for $6.5 \times 10^{-5} \text{ mol/L}$ sodium oleate solution (pH of precipitation is 8.1)

Analogous foamability results for a 2.3×10^{-4} mol/L (70 mg/L) oleate solution are shown in Figure 6-10. A similar trend for changes in the TOC concentration is shown in Figure 6-11.

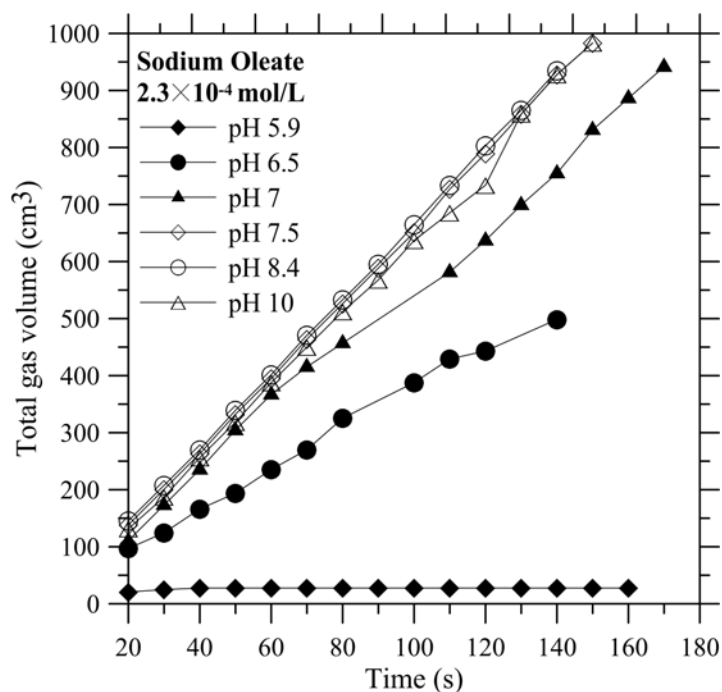


Figure 6-10. Total gas volume versus time in bulk solution at $J_g = 0.5 \text{ cm/s}$ at different pH values for 2.3×10^{-4} mol/L sodium oleate solution (pH of precipitation is 8.7)

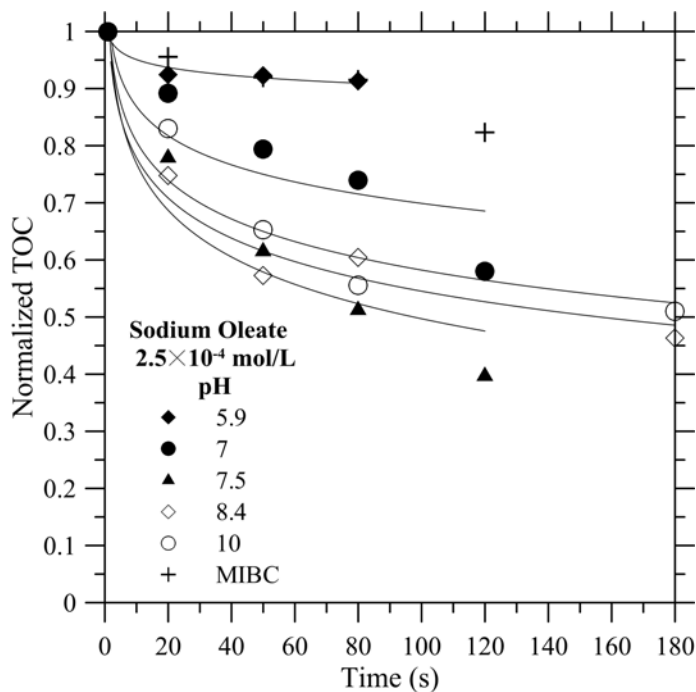


Figure 6-11. Changes of TOC in bulk solution at $J_g = 0.5 \text{ cm/s}$ at different pH values for 2.3×10^{-4} mol/L sodium oleate solution, and for 9.7×10^{-4} mol/L of MIBC

Low pH of 6 shows a very low depletion rate, pH 7.5-8.4 gives the highest rate of depletion, while there is a slight decrease in depletion rate at pH 10. The same type of experiment was repeated for 9.7×10^{-4} mol/L MIBC. The results showed very small changes in the concentration of MIBC with time, which indicates that MIBC does not transfer to the foam phase. A steady-state partition between the bulk solution and the foam phase is rather quickly established for this frother, which results from the earlier described equilibrium between foam growth and foam collapse (resulting in a steady-state foam volume).

Comparing the foaming characteristics of a long chain fatty acid to a common frother like MIBC, sodium oleate creates a foam which grows gradually till the concentration in bulk solution reaches a constant value, while for MIBC the concentration of surfactant transferred to the foam is in equilibrium with the bulk solution, seconds after the start of aeration.

Overall, it can be concluded that long chain oleate molecules exhibit a strong tendency to transfer from bulk solution to the foam phase at a sufficiently high concentration of soluble species. However at a concentration and pH of extensive precipitation, fatty acids do not transfer to the foam phase. The next section on a mixture of sodium oleate with MIBC elaborates on this behavior in more detail.

Grau and Laskowski (2006) compared two non-ionic polyglycol-type frothers: a short chain, low molecular weight frother (DF-200) with a high molecular weight frother (DF-1012). DF-200 has a molecular weight of 264.37 g/mol and the molecular weight of DF1012 is 397.95 g/mol. They briefly explained the different fractionation of these two reagents between the bulk solution and the foam phase. By using the surface tension as an indicator of the concentration of frothers in the bulk and foam phases, they observed that the liquid phase of the foam generated from an aqueous solution of DF-200 had the same surface tension as that of the bulk solution, while this trend was very different for DF-1012. Because of its surface activity, DF-1012 accumulated in the foam and its concentration in the foam quickly became higher than in the bulk solution.

Sodium oleate with a molecular weight of 304.4 g shows a very large accumulation in the foam phase at higher pH values in the presence of air. Considering the conclusions of Grau and Laskowski (2006) and the results from this thesis, it would appear that a high transfer into the foam phase is a characteristic of high molecular weight surfactants although another key

question is whether the type of electrolyte (weak or strong) plays a role in the partitioning of surfactants between the bulk solution and foam phases. This aspect will be investigated in later sections by comparing two alkyl carboxylates (weak electrolytes) with two alkyl sulfates (strong electrolytes).

Changes in the foamability of oleic acid solutions (or the dynamic behavior of the foam phase) are directly related to changes in bubble sizes in the bulk solution. For a sodium oleate solution at natural pH, foamability of sodium oleate approaches its maximum at 1.6×10^{-4} mol/L (50 mg/L), which is very close to the critical coalescence concentration (CCC) for sodium oleate at natural pH. In fact, in the case of sodium oleate when bubble coalescence is prevented in the bulk solution, no coalescence takes place in the foam either, and the foam volume and growth rate with this surfactant reach maximum values. On the other hand, even partial coalescence of air bubbles in the bulk solution (e.g., at lower pH and concentrations below the CCC) results in much lower foamability and no foam formation is observed under acidic conditions regardless of oleate concentration. The transition from coalescing to non-coalescing conditions is directly related to the dissolution of colloidal precipitates at higher pH and formation of true surfactant solutions. As long as the concentration of surface-active species is high enough to disperse bubbles, the foam growth rate is high as well.

6.1.3.3 *Mixture with MIBC*

In the cases of precipitation of oleate, the bubble size distributions show that the bubbles are relatively large. Also, foamability data under precipitation conditions show no significant foam growth – under extensive precipitation the foam does not form at all. Therefore, an argument could be made that the poor transfer of precipitates to the foam phase results from the low surface area of air bubbles available for contacts with the very small colloidal solid precipitate and from a very small volume of the generated foam. Essentially the same line of reasoning is often used for explaining the poor froth flotation of fine hydrophobic particles. In order to test the nature of precipitates in terms of their hydrophobicity and ability to attach to small bubbles, an experiment was carried out using a mixture of sodium oleate and MIBC to see if the presence of small bubbles could enhance the transfer of colloidal species to the foam. A 2.3×10^{-4} mol/L (70 mg/L) sodium oleate was mixed with a 100 mg/L MIBC solution at pH 4.5. The concentration of sodium oleate was chosen such that the solution contained a large amount of

precipitate at pH 4.5, while the concentration of MIBC was selected to be well over its CCC95 to ensure formation of as small bubbles as possible.

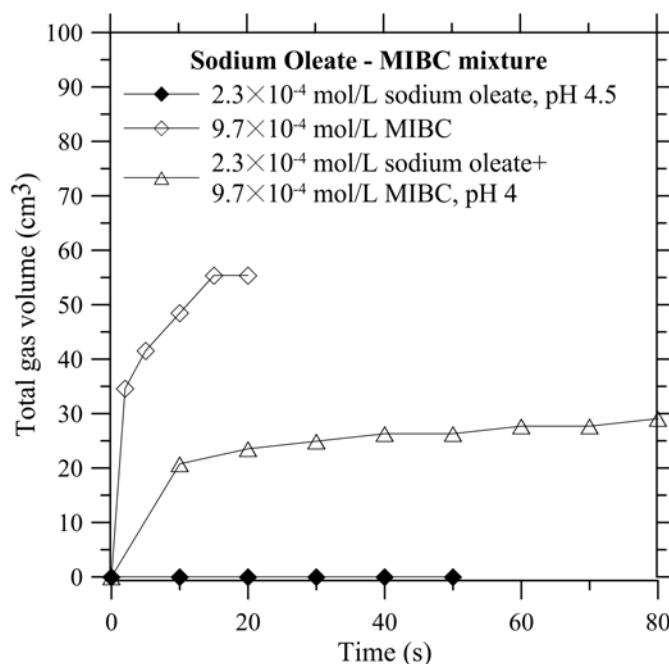


Figure 6-12. The effect of MIBC addition on the foamability of 2.3×10^{-4} mol/L sodium oleate at pH 4.5

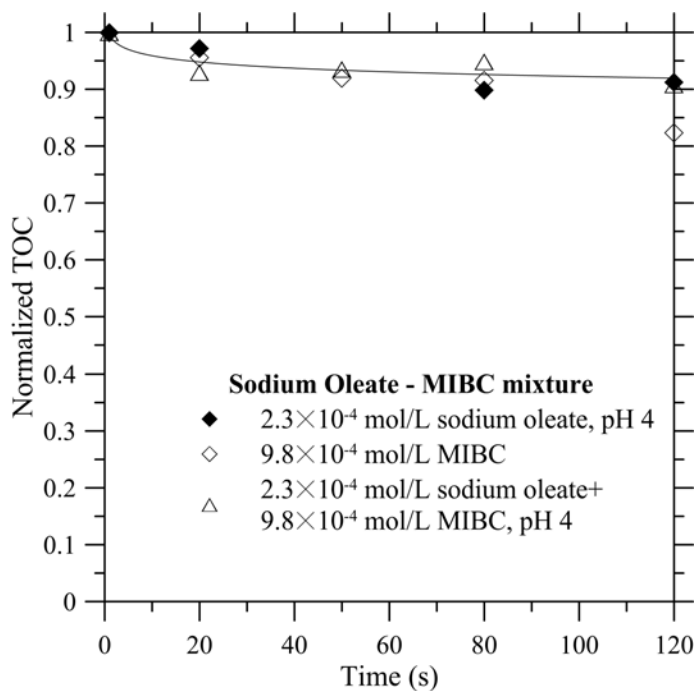


Figure 6-13. The effect of MIBC addition on surfactant transfer to the foam at 2.3×10^{-4} mol/L sodium oleate

The results in Figures 6-12 and 6-13 show that there is no evidence of any improvement in foamability or of enhanced oleate/precipitate transfer to the foam. It is quite evident that even in the presence of a large number of small non-coalescing bubbles, the precipitates do not tend to transfer to the foam phase and the bubbles do not carry colloidal precipitates to the foam. The behavior of colloidal precipitates can be explained by analogy to the main reason behind the poor flotation of very fine particles. For such small particles, the energy of their Brownian motion is comparable to the energy of bubble-particle collisions, and attachment to the bubble is equally probable as detachment even though the particles may actually be hydrophobic. At the same time, fatty acid precipitates are negatively charged under all the experimental conditions, which would also prevent adhesion and attachment of the precipitates to the negatively charged bubble surfaces through electrostatic repulsion. Overall, there is no evidence that the fatty acid precipitates adhere to air bubbles to any significant degree, but whether these precipitates are hydrophobic or not, this thesis does not quite answer that problem.

6.1.3.4 Effect of ionic strength

Semi soluble salt-type minerals such as apatite or calcite, release considerable amounts of ions into solution, which may affect the behavior of fatty acids. The effect of sodium and calcium ions on the foamability of sodium oleate solutions was thus investigated.

Figure 6-14 demonstrates the effect of 0.01 mol/L NaCl on the foamability of 6.5×10^{-5} mol/L (20 mg/L) sodium oleate solution. It seems that at natural pH, addition of NaCl enhances foamability. At higher pH, the slope of foamability curves in the presence and absence of NaCl is equal in the early stages of the test but then NaCl causes an earlier foam collapse. To investigate more on the mechanism governing this type of behavior, the surfactant concentration changes were again tracked through time in foamability tests using TOC measurements and the results are demonstrated in Figure 6-15.

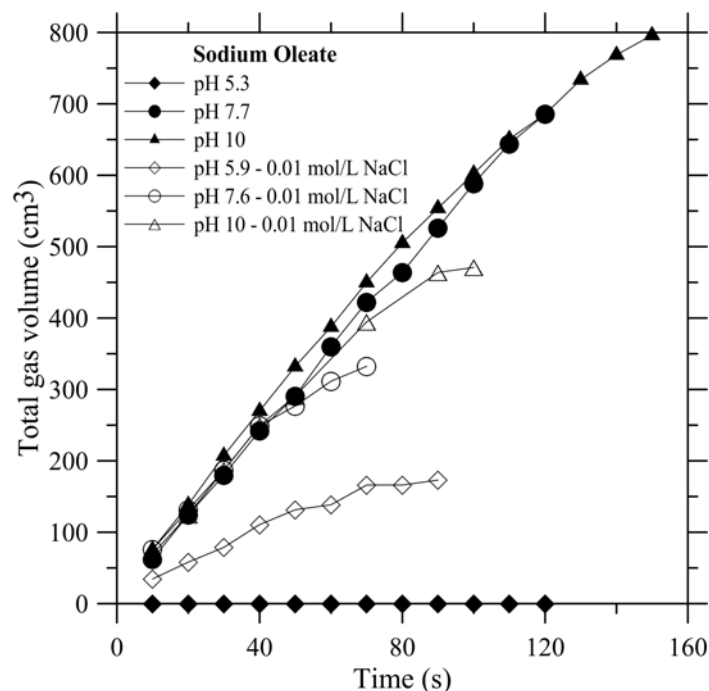


Figure 6-14. Comparison of foamability of 6.5×10^{-5} mol/L sodium oleate solution in distilled water and 0.01 mol/L NaCl at $J_g = 0.5$ cm/s

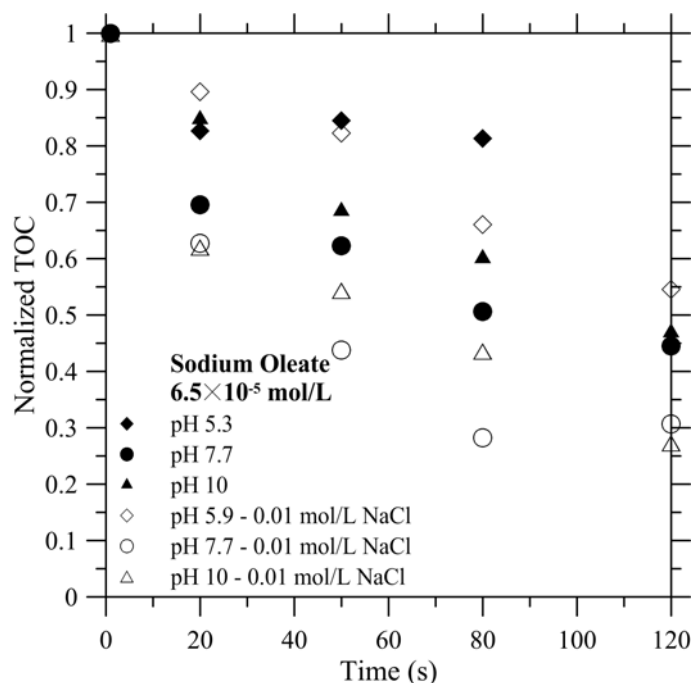


Figure 6-15. Comparison of changes in TOC of bulk solution of 6.5×10^{-5} mol/L sodium oleate in distilled water and 0.01 mol/L NaCl at $J_g = 0.5$ cm/s

The results reveal that the addition of NaCl enhances the depletion rate of the surfactant. As is shown in Figure 6-15, addition of NaCl leads to better foamability at natural pH, but a

higher depletion rate and earlier foam collapse is observed at higher pH values. The effect of NaCl can be interpreted in terms of screening of the ionic surfactant molecules by counter ions from the background electrolyte, which increases the adsorption capacity at the gas-solution interface. The same trend for addition of NaCl to 2.3×10^{-4} mol/L sodium oleate solution was observed, as is shown in Figure 6-16.

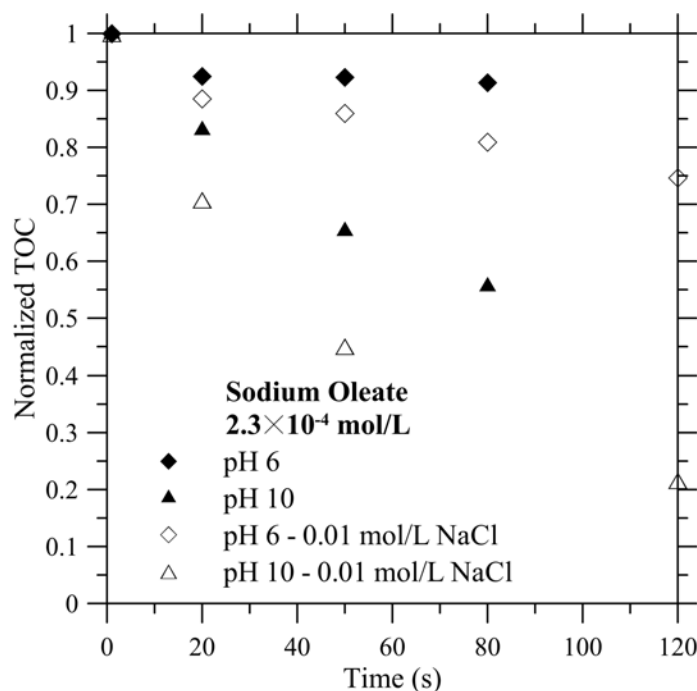


Figure 6-16. Comparison of changes in TOC in bulk solution of 2.3×10^{-4} mol/L sodium oleate in distilled water and 0.01 mol/L NaCl at $J_g = 0.5$ cm/s

These results show that a continuous transfer of oleate to the foam is required for foam stability. Low surfactant transfer rates do not enhance foamability, as seen from the results obtained at lower pH values. Too high a transfer rate initially yields maximum foamability but the resulting foam collapses quite quickly as seen in the data obtained for solutions containing sodium chloride. It therefore appears that a large volume of persistent stable foam can only be obtained at intermediate surfactant transfer rates, when only about 50% of the original amount of oleate in bulk solution gets transferred to the foam over the timescale of the foamability test. The results strongly suggest that continuous transfer of the surfactant to the foam phase leads to a steady foam growth and foam stability.

Under the same conditions that lead to enhanced formability, it should be recognized that sodium oleate also exhibits the strongest gas dispersion properties. Therefore, in addition to formation of small non-coalescing bubbles in the bulk solution, a steady surfactant transfer to the foam is also a requirement for enhanced foamability. The surfactant concentration in bulk solution should remain above the CCC95 value. This conclusion is also related to the surfactant transfer discussed earlier. At very high surfactant transfer rates, the concentration in the bulk may quickly decrease to below the CCC95 value and the gas dispersing abilities of the surfactant decline as well. It is therefore clear that foamability and gas dispersion phenomena in oleate solutions are closely related.

Addition of 400 mg/L (0.0036 mol/L) CaCl_2 salt to 2.3×10^{-4} mol/L sodium oleate solution at natural pH and pH 10 totally prevented foaming of sodium oleate at a superficial gas velocity of 0.5 cm/s. This result can be attributed to the formation of calcium oleate precipitates, which do not seem to show any foaming capabilities.

6.2 Sodium laurate

The total gas volume and simultaneous changes of TOC in bulk solution as a function of time for 6.5×10^{-5} mol/L (15 mg/L) and 2.3×10^{-4} mol/L (51 mg/L) concentration of lauric acid aqueous solution are shown in Figure 6-17 and 6-18 as a function of pH. In the case of lauric acid, foamability is much weaker than for oleic acid. A high foam growth rate is achieved at high pH at a concentration of 2.3×10^{-4} mg/L but still it does not reach the highest possible foam growth rate shown by the dashed straight line.

Although the foam growth rate, as judged from the slope of each curve, is low for sodium laurate compared to the same molar concentration of sodium oleate, it could be observed that bubble sizes in the bulk are small, which is confirmed through gas dispersion measurements for sodium laurate (Figure 5-6). The CCC95 of sodium laurate is at 7.2×10^{-5} mol/L at pH 10 (15.95 mg/L), but according to foamability measurements there is no foam forming under these conditions. At concentrations well above the CCC95, maximum foamability is still not reached. So in the case of sodium laurate, reduction of bubble sizes in the pulp does not necessarily lead to foam formation. The behavior of lauric acid is much more similar to that of short chain frothers, which do not create stable foams despite sharply decreasing bubble sizes and quickly reaching CCC95 values.

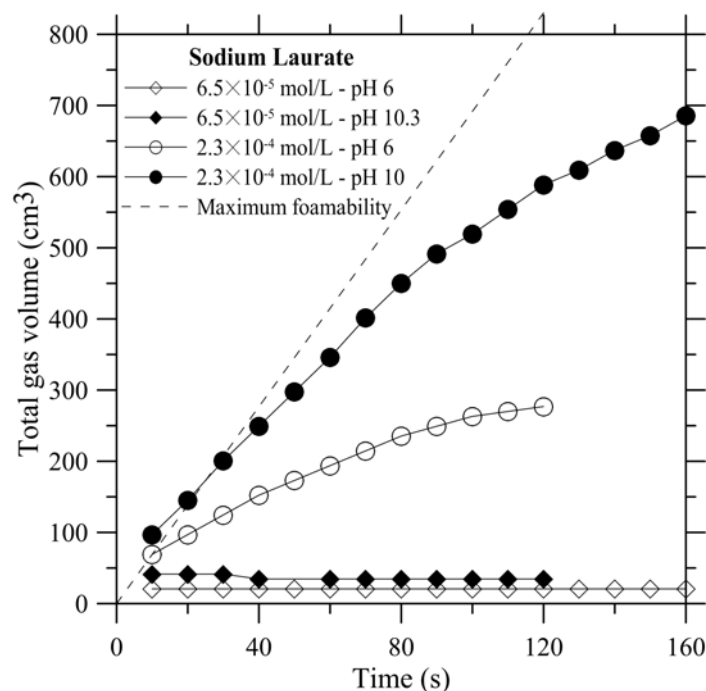


Figure 6-17. Total gas volume as a function of time at $J_g=0.5$ cm/s for different pH of 6.5×10^{-5} mol/L and 2.3×10^{-4} mol/L (15-51 mg/L) lauric acid aqueous solution

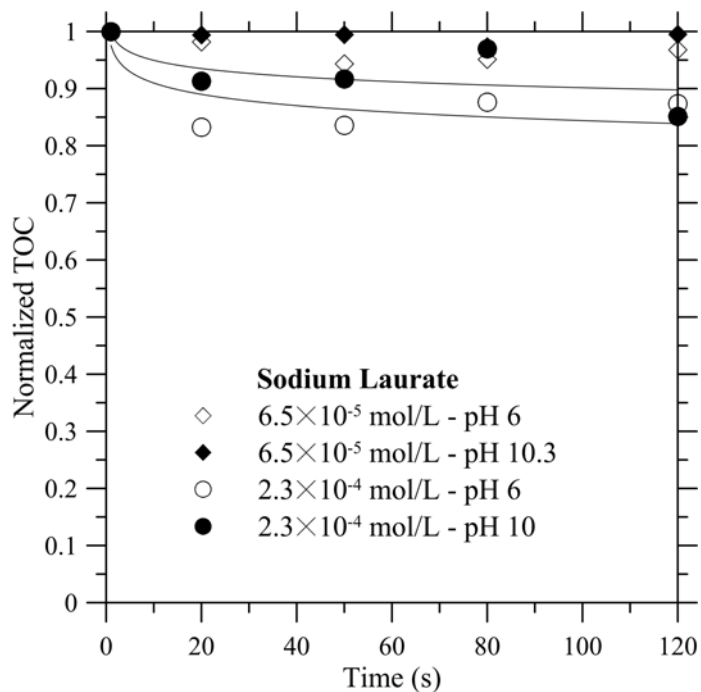


Figure 6-18. Changes of TOC in bulk solution as a function of time at $J_g=0.5$ cm/s for different pH of 6.5×10^{-5} mol/L and 2.3×10^{-4} mol/L (15-51 mg/L) lauric acid aqueous solution

In the case of sodium laurate, a portion of air supplied to the column escapes from the foam phase, so the foam growth rate and foam volume are not as high as in the case of sodium

oleate at the same surfactant concentration. In contrast to sodium oleate, laurate does not exhibit an equally high transfer from bulk solution to the foam phase.

By comparing the two weak fatty acids, a higher transfer to the foam phase in the case of oleate is most likely a result of the longer hydrocarbon chain length in the oleic acid molecule leading to higher transfer by bubbles to foam phase which leads to higher foam stability.

6.3 Sodium hexanoate

Foamability of sodium hexanoate was investigated at a concentration of 2.3×10^{-4} mol/L at two extreme acidic and alkaline pH values. Sodium hexanoate does not create a large foam volume at the tested concentration and its foamability is comparable to that of MIBC. Hexanoate reaches an equilibrium foam volume in a way very similar to MIBC. It should be mentioned that sodium hexanoate perfectly disperse gas at the same concentration tested here.

Sodium hexanoate creates more foam at low pH, which is in accordance with gas dispersion results. This is another indication that molecular nonionic species are more surface-active than the ionic species forming at alkaline pH. According to Kanicky and Shah (2002), the presence of a net charge on a surfactant polar group affects its performance in an adsorbed monolayer. If all the fatty acid molecules become ionized, repulsion between similarly charged molecules in the monolayer could result in an expansion of the monolayer at high pH, which in turn can lead to a weak and unstable film.

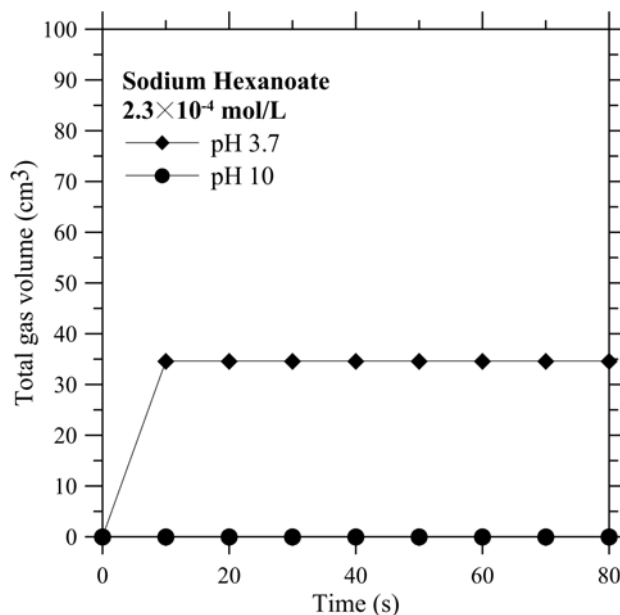


Figure 6-19. Foamability of 2.3×10^{-4} mol/L sodium hexanoate at pH 3.7 and 10

As shown in Figure 5-11, a concentration of 2.3×10^{-4} mol/L is well above the CCC95 value of MIBC, hexanoate (at pH 3.7), laurate at pH 10.4, and of oleate at pH 10.4. At this concentration, gas bubbles reach the smallest sizes possible under given hydrodynamic conditions in solutions of those surfactants. Interestingly, above the CCC95 value bubble sizes measured in solutions of those different surfactants are basically the same. However, this strong gas dispersion in bulk solutions does not translate to the same level of foamability in the same 2.3×10^{-4} mol/L solutions: MIBC and hexanoate produce foamability curves with very small equilibrium foam volumes, laurate gives much higher foam volumes, while oleate continuously generates the largest volumes of very stable foam. In other words, good gas dispersion is required to reach maximum foamability for a given surfactant, but foamability of different surfactants is a function of the hydrocarbon chain length of the surfactants. It seems that TOC transfer correlates with the surface tension of the solution. For example, there is not much TOC transfer from a high surface tension solution of a 12-carbon surfactant, while a very large transfer is observed from a low surface tension solution of an 18-carbon surfactant solution at the same pH.

6.4 Sodium octadecyl sulfate

The total gas volume and simultaneous changes of TOC in bulk solution were recorded as a function of time for 6.5×10^{-4} mol/L (25 mg/L) and 2.3×10^{-4} mol/L (85 mg/L) octadecyl sulfate (ODS) aqueous solutions at the same molar concentrations as those for sodium oleate. The trends are demonstrated at different pH values in Figures 6-20 and 6-21.

According to the results in Figure 6-20 the rate of foam growth for sodium octadecyl sulfate does not change to a great extent with pH for the two tested concentrations, which very likely results from the strong electrolyte character of the surfactant. This trend is very similar to the behavior of sodium oleate at high pH, when it is fully dissociated, and its behavior is independent of concentration in the tested concentration range.

Normalized TOC results in Figure 6-21 for both concentrations of octadecyl sulfate show that the transfer of octadecyl sulfate to the foam phase does not depend on the initial concentration over the tested concentration range.

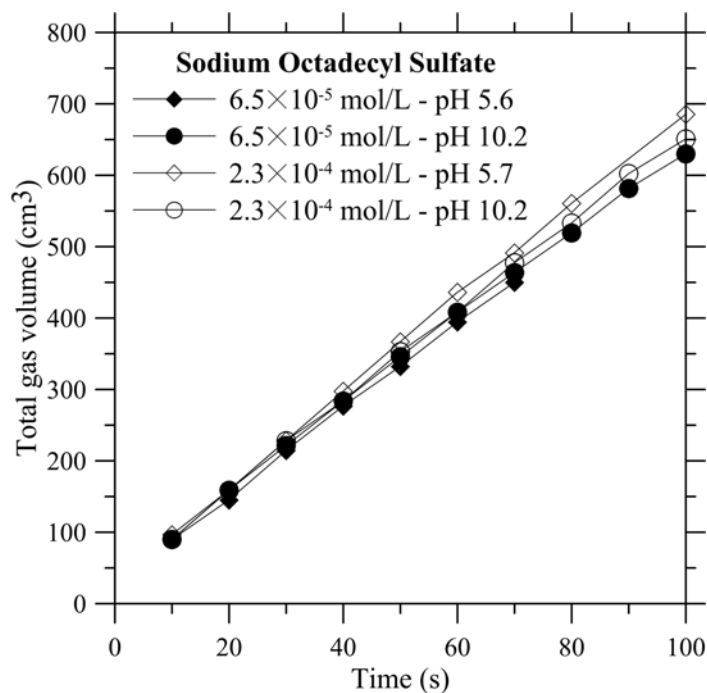


Figure 6-20. Total gas volume as a function of time at $J_g=0.5$ cm/s for different pH of 6.5×10^{-5} and 2.3×10^{-4} mol/L octadecyl sulfate aqueous solution at 50°C

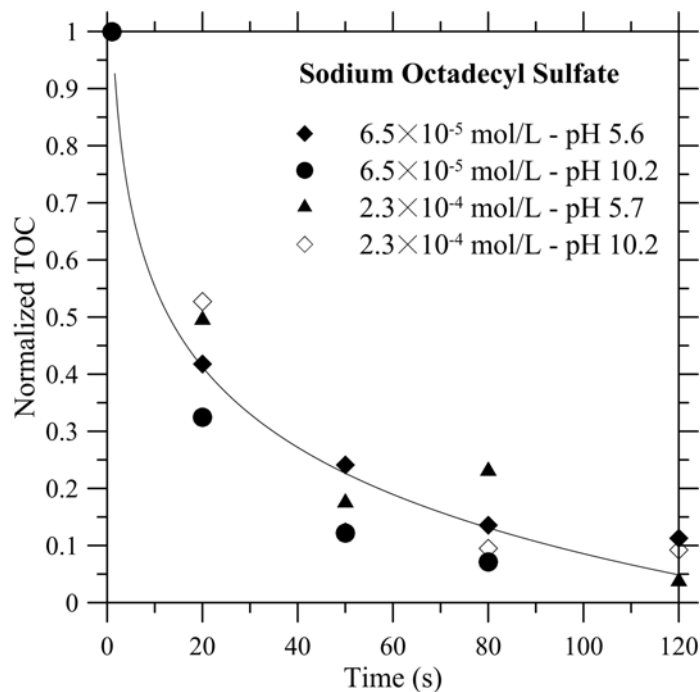


Figure 6-21. TOC changes in bulk solution as a function of time at $J_g=0.5$ cm/s for different pH of 6.5×10^{-5} and 2.3×10^{-4} mol/L octadecyl sulfate aqueous solution at 50°C

For ODS, the highest possible foamability (foam volume at a given time) was achieved for both tested concentrations. A very high transfer of long chain octadecyl sulfate takes place

between bulk solution and foam phase with over 90% of the surfactant reporting to the foam phase at the end of the test.

All the measurements for octadecyl sulfate were performed a little bit over 50°C to facilitate the dissolution of the reagent. The solubility of octadecyl sulfate at room temperature is very low with a Krafft point of 56°C (Stache, 1996). As a result, TOC measurements at room temperature gave TOC levels far below those expected from the stoichiometric composition of the surfactant. Consequently the temperature was kept at 50°C using heating bands wrapped around the column. Samples taken for TOC analysis were kept at 50°C in an incubator while being mixed, and a TOC test was performed immediately after taking the samples out of the incubator.

6.5 Sodium dodecyl sulfate

Since the solubility of sodium dodecyl sulfate (SDS) is higher than that of ODS, the foamability measurements could be done at room temperature. The total gas volume and simultaneous changes of TOC in bulk solution as a function of time for two pH values and SDS concentrations of 6.5×10^{-5} mol/L (20 mg/L) and 2.3×10^{-4} mol/L (67 mg/L) are demonstrated in Figures 6-22 and 6-23.

As the foamability tests in Figure 6-22 indicate, there is no significant effect of pH on the foamability and on the TOC results for dodecyl sulfate, just as in the case of ODS.

The TOC results in Figure 6-23 show that changes in the concentration of the samples as a function of time are not as dramatic as in the case of ODS. In the case of ODS almost all the surfactant is transferred to the foam phase, while for SDS only about 20% is transferred. In the case of SDS, a small amount transferred to the foam phase is sufficient to create large foam volume and growth rate as is demonstrated in TOC measurements.

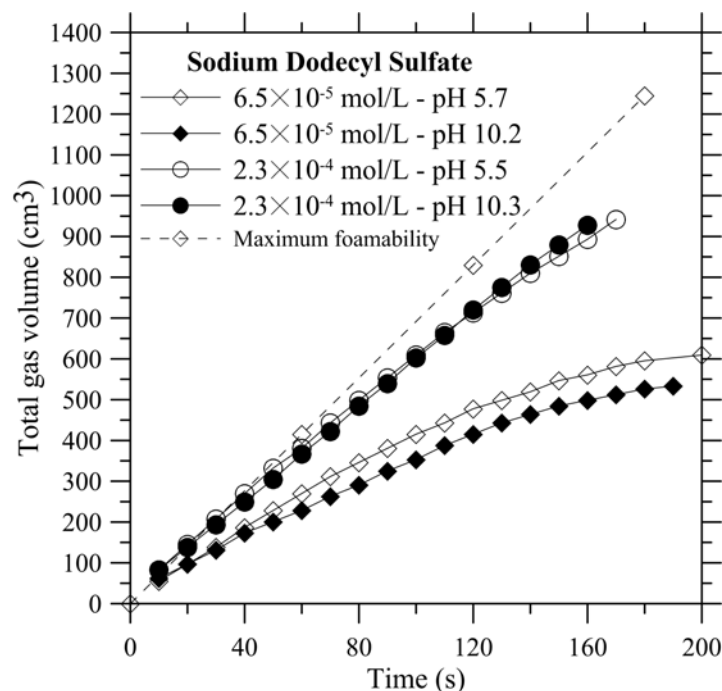


Figure 6-22. Total gas volume in bulk solution as a function of time at $J_g=0.5$ cm/s for different pH of 6.5×10^{-5} mol/L and 2.3×10^{-4} mol/L (20-67 mg/L) dodecyl sulfate solution

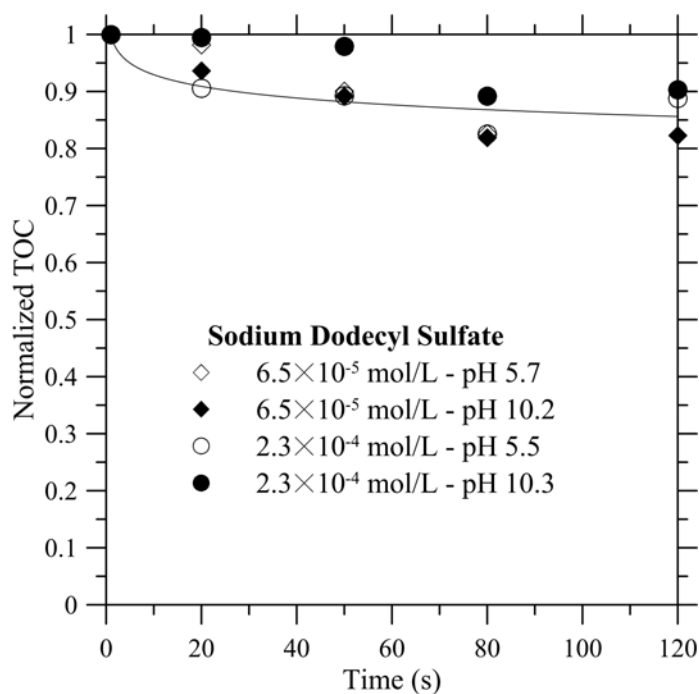


Figure 6-23. Changes of TOC in bulk solution as a function of time at $J_g=0.5$ cm/s for different pH of 6.5×10^{-5} mol/L and 2.3×10^{-4} mol/L (20-67 mg/L) dodecyl sulfate solution

The CCC95 of SDS is at 5.1×10^{-5} mol/L (14.83 mg/L) as was demonstrated in section 5.4. At a concentration of 6.5×10^{-5} mol/L (20 mg/L), although coalescence in the bulk solution is

prevented to a large extent, there is still some gas escaping from the system; consequently foamability does not reach its maximum. This behavior of C12 surfactants is qualitatively similar to the behavior of MIBC. These surfactants affect the bubble size distribution in bulk solution, but they are not capable of quickly generating large volumes of foam.

Comparing ODS and SDS as strong electrolytes, it could be concluded that the difference in these two cases is due to differences in their chain lengths. In other words, long chain surfactants indeed tend to partition into the foam phase to a much larger extent than their short chain homologues. The high foam growth rate is characteristic of long chain (C18) surfactants (high molecular weight) and this large volume of foam is usually associated with a substantial transfer of the surfactant to the foam phase. Short chain surfactants are very effective at dispersing gas into small bubbles but their foaming capabilities are relatively weak.

In case of SDS, even at concentrations leading to large foam volume, like 2.3×10^{-4} mol/L, the uptake to the foam phase is relatively small. This suggests that a large transfer of surfactant molecules to the foam phase is not necessary to achieve good foaming. SDS and ODS are strong electrolytes and both are capable of producing large volumes of foam at 2.3×10^{-4} mol/L, but their uptakes to the foam phase differ dramatically. This observation indicates that the mechanism governing foam generation in SDS is different from that of sodium oleate and octadecyl sulfate. This could be related to the difference in foam water content for these reagents.

In this context, it is important to note that the created foam appeared to contain much more water in the case of SDS compared to the other two surfactants. This visual observation was confirmed by the water content measurement, whose results are given in Table 6-1. Surfactant concentrations in water recovered with the foam are also given.

Table 6-1. Water content and foam surfactant concentration for different reagents

Surfactant	Initial surfactant concentration (mol/L)	Water recovered in foam in 60 seconds (ml)	Foam water content (%)	Surfactant concentration in water recovered with foam (mol/L)
Sodium Oleate	1.8×10^{-4}	60	15	3.2×10^{-4}
Sodium Octadecyl Sulfate	1.8×10^{-4}	45	11	5.8×10^{-4}
Sodium Dodecyl Sulfate	2.2×10^{-4}	100	25	2.3×10^{-4}

Comparing the water content in the foam generated by different reagents, at a concentration of 2.3×10^{-4} mol/L and a superficial gas velocity of 0.5 cm/s, the foam of dodecyl sulfate holds 25% of water, while the foam produced by sodium oleate contains 15% and that of octadecyl sulfate has 11% of water (Table 6-1). Since the adopted method for water content measurement required the reagent to produce a maximum achievable foamability to be comparable to other reagents, and sodium laurate did not produce maximum foamability at the tested concentrations, the water content for sodium laurate was not reported here.

It is clear that the foam produced by SDS was rather wet while the foam generated in ODS solutions was dry. The foam produced by sodium oleate had a similar water content to that of the ODS foam although it was measurably higher for oleic acid. These results basically show that the longer chain surfactants generate dry foams while shorter chain surfactants tend to produce wet foams. It is also important to note that the surfactant concentration in water recovered with the foam is much higher than the initial surfactant concentration in bulk solutions for both C18 surfactants. In contrast, the concentration of SDS in water recovered with the foam was basically equal to the initial SDS concentration in bulk solution. These results are consistent with the TOC transfer data collected during the foamability tests. In the cases of both oleic acid and octadecyl sulfate, the transfer of the reagents to the foam resulted in a rapid decrease of their concentrations in bulk solution. For SDS, however, the transfer of the surfactant to the foam was not so dramatic. All these results provide important insights into the behavior of the surfactants

during gas dispersion and foaming phenomena. For the C18 surfactants, their increased concentrations in the foam compared to the bulk strongly suggest that these long-chain surfactants are transferred to the foam by adsorption on the surfaces of air bubbles. It should be recalled that the strongest gas dispersion capabilities (i.e., smallest bubble sizes) of these surfactants were observed under conditions of low surface tension, and low surface tension is a result of surfactant adsorption at the gas-liquid interface (i.e., on bubble surfaces). In contrast to the long chain surfactants, SDS turned out to be very weakly surface active and its effect on the surface tension was minor. It can therefore be concluded that SDS is transferred to the foam by entrainment in the water film separating the bubbles, but the adsorption of SDS on the bubble surfaces is very low, as shown by the surface tension data at pH 10.

Summary and conclusions

The surface tension of fatty acid solutions is a function of pH and of the hydrocarbon chain length of the surfactant. The effect of pH is related to changes in the speciation of fatty acids in aqueous solutions. Relative amounts of dissociated (anionic, R-COO^-) and associated (acidic, RCOOH) forms, as well as the presence or absence of colloidal precipitates have the strongest influence on the surface tension data. For shorter chain (C_6 , C_{12}) surfactants, it was found that the associated acid form was significantly more surface active than the dissociated anion. Although the very low solubility of long chain oleic acid (C_{18}) made a similar comparison very difficult, the data obtained at different pH values also suggested that the surface activity of the acid is higher than the surface activity of the oleate anion. This difference in the surface activity of the anionic and associated species was attributed to the denser adsorption of the associated form at the gas-liquid interface. In the case of the dissociated carboxylate anion for shorter chain surfactants, the adsorption of these species was prevented by lateral electrostatic forces acting between the molecules adsorbed on the bubble surfaces. In the absence of electrostatic forces, the associated acid species was capable of more densely adsorbing on the bubble surfaces and thus of reducing the surface tension of aqueous solutions at low pH. As a result, and in the concentration range of interest to this research, the surface tension of laurate (C_{12}) and hexanoate (C_6) solutions at higher pH was basically equal to the surface tension of water. In the case of oleate (C_{18}) solutions, the chain length of the surfactant appeared to have a dominant contribution over speciation to the measured surface tension. Although oleic acid extensively precipitated from aqueous solutions at lower pH values, the surface tension of such colloidal dispersions was still very low. For more concentrated true solutions of oleate at higher pH values, the surface tension was only slightly higher than that of colloidal dispersions. The presence of precipitates in fatty acid solutions had important implications for the measurement of the critical micelle concentration. It was found that accurate and reliable determination of the critical micelle concentration was only possible for true solutions of the surfactants, i.e., under high pH conditions. Although it is widely recognized that the oleate-oleic acid system forms dimeric species in aqueous solutions, evidence was also presented for the presence of such complex species in more concentrated laurate-lauric acid solutions.

The gas dispersion properties of fatty acid solutions were found to be a strong function of pH. The surfactants exhibited the strongest ability to reduce bubble size under alkaline pH values corresponding to true solutions. On the other hand, the formation of colloidal precipitates under neutral and acidic pH conditions significantly reduced the gas dispersing power of the surfactants. The mechanism of gas dispersing action of fatty acids was a function of the hydrocarbon chain length of the surfactants. It was found that oleic acid, a long chain fatty acid, affected bubble sizes through two different mechanisms depending on the pH and speciation of the solution. Under conditions of extensive precipitation (low pH), oleic acid only weakly affected bubble sizes, and a small decrease in bubble sizes was observed at concentrations at which the surface tension of the solution was also substantially reduced. It was shown through theoretical calculations and through analysis of the experimental bubble size distributions that the measured bubble sizes under such conditions could accurately be predicted based solely on the corresponding surface tension value. For true solutions of oleic acid (high pH), for which the surface tension of the solution was also low, gas dispersion into smaller bubbles appeared to proceed through a combination of the surface tension effect and the surface tension gradients (the bubble break-up mechanism) generated at the bubble-solution interface. The contribution of the surface tension gradients enhanced the gas dispersing ability of oleate solutions and the resulting bubble sizes were much smaller than those measured in the presence of colloidal precipitates (low surface tension). Overall, this behavior of oleic acid is in strong contrast to the action of dedicated flotation frothers that change bubble sizes at concentrations about 100 times lower than those required to affect the surface tension.

A very similar trend was observed for lauric acid, although true solutions of lauric acid at higher pH affected bubble sizes only through mechanisms involving surface tension gradients, since the surface tension of the solution under those conditions was almost equal to the surface tension of water. In the case of lauric acid, due to its higher solubility compared to oleic acid, it was also possible to show that the associated acid species exhibited stronger gas dispersion properties than the laurate anion. As in the case of the surface tension data, this difference was attributed to a denser adsorption of the acid at the gas-liquid interface compared to the adsorption of laurate anion.

For hexanoic acid, the shortest chain fatty acid tested in this research, gas dispersion phenomena proceeded primarily through mechanisms involving surface tension gradients since,

as in the case of lauric acid, the surface tension of hexanoate solutions was not affected in the tested concentration range. Similarly to the lauric acid-laurate anion system, the associated acid species was a stronger gas dispersing species than the hexanoate anion. The behavior of hexanoic acid was very similar to the behavior of non-ionic MIBC of the same hydrocarbon chain length.

The presence of colloidal precipitates also had a very negative impact on foamability in fatty acid solutions. Since precipitation of fatty acids leads to the formation of an oily emulsion of the acid, the action of such an oily phase is consistent with the use of water-insoluble oils as defoaming agents to prevent excessive frothing.

Although the strongest foamability was observed near pH values corresponding to the lowest surface tension, when the total concentration of all soluble species reached a maximum value, the data collected at low pH, when the surface tension was also low, showed that the surface tension was not the only factor affecting the foamability results. In the case of oleic acid solutions, the conditions that favored gas dispersion in bulk solution (higher oleate concentrations and higher pH) also led to enhanced foamability. In other words, under the conditions when gas dispersion in solution proceeded only through surface tension effects - at lower pH and in the presence of precipitates - the foamability of those solutions was very poor. In contrast, gas dispersion phenomena in bulk solution involving surface tension gradients and the bubble break-up mechanism also promoted the fast formation of large volumes of foam.

Comparing all surfactant together, strong gas dispersion capability in the bulk solution translated to strongest foamability for a given surfactant. However, the absolute rate of foam formation and the volume of generated foam were found to be a strong function of the hydrocarbon chain length of the surfactant. Longer chain surfactants quickly produced large foam volumes compared to the volume of foam generated in solutions of shorter chain surfactants even though both types of surfactants reduced bubble sizes in the bulk solution to the same degree/size. Surfactant transfer and partition measurements showed that largest foam volumes and highest foam formation rates were usually associated with the highest amounts of surfactant transferred to the foam. At the same time, longer chain surfactants preferentially partitioned into the foam phase while shorter chain surfactants transferred to the foam to a much smaller degree, and it was the longer chain surfactants that gave higher foam volumes and formation rates compared to shorter chain surfactants.

At the same foam volume and foam growth rate, it was also shown that the high transfer of long chain surfactants (C18) produced dry foams, while a much lower transfer of shorter chain surfactant (C12) resulted in a wet foam. It was also demonstrated that shorter chain surfactants transferred to the foam primarily by entrainment in the water films separating the gas bubbles, while longer chain surfactants transferred to the foam mainly by adsorption on gas bubbles.

Colloidal precipitates of fatty acids were found to be unable to generate surface tension gradients and such colloidal particles did not transfer to the foam on the surfaces of air bubbles. This result also showed that the precipitates did not attach themselves to the bubble surfaces. At the same time, the role of precipitates in forming solutions of low surface tension was not clearly determined.

Overall, the main conclusions of this research can be highlighted as follows:

- Fatty acids have gas dispersion properties very similar to MIBC as a standard frother, in the absence of precipitates
- Neutral dissolved fatty acid molecules have higher surface activity than the dissociated anion due to the denser adsorption of the associated form at the gas-liquid interface
- Two mechanisms are proposed for bubble size reduction in fatty acid solutions, which are surface tension and surface tension gradient
- There is very little interaction between colloidal precipitates and bubbles, although the surface tension of colloidal dispersions is very low
- The absolute rate of foam formation and the volume of generated foam are a strong function of hydrocarbon chain length

Recommendations for future work

The following aspects arising out of this dissertation deserve to be followed up in future research work:

Experiments could be designed to define how colloidal precipitates of fatty acids interfere with coalescence prevention or contribute to coalescence. These experiments could be carried out in a small-scale test through closely analyzing pictures or videos of solutions containing precipitates of fatty acids. Gas dispersion properties of fatty acids should be studied in the presence of hydrophobic and hydrophilic solids (fine quartz). It would be interesting to determine whether each of those conditions will simulate the case of colloidal precipitates.

As was shown in this thesis, long chain fatty acids reduce bubble sizes at concentrations at which the surface tension is also reduced. Therefore, gas dispersion and foamability experiments should be carried out on solutions of model reagents with low surface tension, such as methanol, as a reagent with a very low surface tension, to define the contribution of surface tension to gas dispersion and foamability phenomena.

The effect of different sparging systems, such as porous plates versus cavitation tubes deserves additional studies. The effect of the porosity of sparger plates and of Jg on bubble size distributions could be determined.

Synergistic effects of mixed surfactant systems, such as fatty acids-frothers mixtures, on gas dispersion and foamability properties is also worth quantifying, considering that mixed surfactant systems are very common in froth flotation. Excessive and persistent frothing was reported in plants using fatty acids and frothers together, so it is interesting to understand the mechanism of interaction of these reagents.

Investigation on the effect of ionic strength at a wider concentration range deserves more detailed work. Gas dispersion studies in brine with respect to potash flotation could also be critical to proper selection of frothers.

It is also recommended to measure the dilational modulus to assess the adsorption kinetics of surfactants to complete the interfacial characterization of different species.

In terms of instrumentation for performing gas dispersion and foamability research, it would be suggested to equip the gas dispersion column with a control system and add pressure and temperature sensors to the system to be able to follow the parameters around the column more closely and continuously. For example, in the present research the steady state gas hold-up

value was recorded manually but it would be beneficial to have a controller system recording all the changes occurring in the gas hold-up values until a steady state value is reached. An automated system which could record changes in the foam growth or collapse (Bilke-Krause, and Schork 2010), bubble size distribution and water content in the foam, would be extremely useful in identifying correlations between gas dispersion in the bulk solution and foamability of the froth layer.

Bibliography

- Adamson, A. W. (1991). Surfaces, interfaces, and colloids. principles and applications. *Journal of the American Chemical Society*, 113(26), 9906-9906.
- Aktas, Z., Cilliers, J. J., & Banford, A. W. (2008). Dynamic froth stability: Particle size, airflow rate and conditioning time effects. *International Journal of Mineral Processing*, 87(1-2), 65-71.
- Ananthpadmanabhan, K. P., & Somasundaran, P. (1982). Oleate chemistry and hematite flotation. *Interfacial Phenomena in Mineral Processing: Proceedings of the Engineering Foundation Conference*. 207-227.
- Ananthpadmanabhan, K., Somasundaran, P., & Healy, T. W. (1979). Chemistry of oleate and amine solutions in relation to flotation. *Transactions of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Society of Mining Engineers of AIME*, 266, 2003-2009.
- Beneventi, D., Carre, B., & Gandini, A. (2001). Role of surfactant structure on surface and foaming properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 189(1-3), 65-73.
- Bikerman, J. J. (1953). *Foams: Theory and industrial application*. New York, United States: Reinhold Publishing Corp.
- Bilke-Krause, C., & Schork, T. (2010). Foam behavior and foam stability of aqueous surfactant solution (AN267e). Retrieved May, 2011, from <http://www.kruss.de>
- Bilke-Krause, C., & Thomson, F. (2011). Kinetic investigations into the effectiveness of surfactants (AN268e). Retrieved May, 2011, from <http://www.kruss.de>
- Castro, S., Miranda, C., Toledo, P., & Laskowski, J. S. (2013). Effect of frothers on bubble coalescence and foaming in electrolyte solutions and seawater. *International Journal of Mineral Processing*, 124, 8-14. doi:10.1016/j.minpro.2013.07.002

- Chamberlain, J., & Rulison, C. (2004). Considerations before making non-equilibrium surface tension measurements (TN307). Retrieved May, 2011, from www.Kruss.de
- Cho, Y. S., & Laskowski, J. S. (2002). Bubble coalescence and its effect on dynamic foam stability. *Canadian Journal of Chemical Engineering*, 80(2), 299-305.
- Cho, Y., & Laskowski, J. (2002). Effect of flotation frothers on bubble size and foam stability. *International Journal of Mineral Processing*, 64(2-3), 69-80. doi:10.1016/S0301-7516(01)00064-3
- Comley, B., Harris, P., Bradshaw, D., & Harris, M. (2002). Frother characterization using dynamic surface tension measurements. *International Journal of Mineral Processing*, 64(2-3), 81-100. doi:10.1016/S0301-7516(01)00065-5
- Czarnecki, J., Malysa, K., & Pomianowski, A. (1982). Dynamic frothability index. *Journal of Colloid and Interface Science*, 86(2), 570-572. doi:10.1016/0021-9797(82)90101-1
- Dai, Q., & Laskowski, J. S. (1991b). The krafft point of sodium laurate. *Unpublished Results*.
- Davies, J. T., & Rideal, E. K. (1961). *Interfacial phenomena*. New York: Academic Press.
- Derjaguin, V. (1989). *Theory of stability of colloids and thin films*. New York: Plenum press.
- Dominguez, A., Fernandez, A., Gonzalez, N., & Iglesias, E. (1997). Determination of critical micelle concentration of some surfactants by three techniques. *Journal of Chemical Education*, 74(10), 1227-1227.
- Dukhin, S. S., Miller, R., & Loglio, G. (1998). Physico-chemical hydrodynamics of rising bubbles. In D. Mubius, & R. Miller (Eds.), *Studies in interfacial science, drops and bubbles in interfacial research* (pp. 367-432) Elsevier Science.
- Fa, K. Q., Tao, J. A., Nalaskowski, J., & Miller, J. D. (2003). Interaction forces between a calcium dioleate sphere and calcite/fluorite surfaces and their significance in flotation. *Langmuir*, 19(25), 10523-10530. doi:10.1021/la035335j

- Finch, J. A., & Smith, G. W. (1972). Dynamic surface tension of alkaline dodecylamine acetate solutions in oxide flotation. *Transactions of the Institution of Mining and Metallurgy, Section C: Mineral Processing and Extractive Metallurgy*, 81(793), c213-c218.
- Finch, J. A., Nasset, J. E., & Acuna, C. (2008). Role of frother on bubble production and behavior in flotation. *Minerals Engineering*, 21(12-14), 949-957.
doi:10.1016/j.mineng.2008.04.006
- Fuerstenau, D. W., & Bunge, R. C. (2006). The complex behavior of fatty acids in fluorite flotation. *XXXII Mineral Processing Congress*, Istanbul.
- Fuerstenau, M. C. (1982). Chemistry of flotation in solution. In R.P. King (Ed.), *Principals of flotation* (pp. 1-16). Johannesburg: South African Institute of Mining and Metallurgy.
- Fuerstenau, M. C., Miller, J. D., & Kuhn, M. C. (1985). *Chemistry of flotation*. New York: Society of Mining Engineering.
- Fuerstenau, M. C., & Elgilanni, D. A. (1966). Calcium activation of sulfonate and oleate flotation of quartz. *AIME Transactions*, 235, 405-413.
- Gomez, C. O., & Finch, J. A. (2007). Gas dispersion measurements in flotation cells. *International Journal of Mineral Processing*, 84(1-4), 51-58.
- Gorain, B. K., Franzidis, J. P., & Manlapig, E. V. (1997). Studies on impeller type, impeller speed and air flow rate in an industrial scale flotation cell. part 4: Effect of bubble surface area flux on flotation performance. *Minerals Engineering*, 10(4), 367-379.
doi:10.1016/S0892-6875(97)00014-9
- Grau, R. A., & Laskowski, J. S. (2006). Role of frothers in bubble generation and coalescence in a mechanical flotation cell. *Canadian Journal of Chemical Engineering*, 84(2), 170-182.
- Harkins, W. D. (1952). *The physical chemistry of surface films*. New York: Reinhold.

- Harris, P. (1982). Frothing phenomena and frothers. In R. P. King (Ed.), *Principles of flotation* (Monograph Series No.3 ed., pp. 237-250) African IMM.
- Healy, T. W., & Fuerstenau, D. W. (2007). The isoelectric point/point-of zero-charge of interfaces formed by aqueous solutions and nonpolar solids, liquids, and gases. *Journal of Colloid and Interface Science*, 309(1), 183-188. doi:10.1016/j.jcis.2007.01.048
- Hernandez-Aguilar, J., Rao, S. R., & Finch, J. A. (2005). Testing the k-sb relationship at the microscale. *Minerals Engineering*, 18(6), 591-598. doi:10.1016/j.mineng.2004.10.003
- Hernandez-Aguilar, J., & Finch, J. A. (2005). Validation of bubble sizes obtained with incoherent imaging on a sloped viewing window. *Chemical Engineering Science*, 60(12), 3323-3336. doi:10.1016/j.ces.2004.12.022
- Hunter, R. J. (1993). *Introduction to modern colloid science*. New York: Oxford university press.
- Kanicky, J. R., Poniatowski, A. F., Mehta, N. R., & Shah, D. O. (2000). Cooperativity among molecules at interfaces in relation to various technological processes: Effect of chain length on the pKa of fatty acid salt solutions. *Langmuir*, 16(1), 172-177. doi:10.1021/la990719o
- Kanicky, J., & Shah, D. (2002). Effect of degree, type, and position of unsaturation on the pK(a) of long-chain fatty acids. *Journal of Colloid and Interface Science*, 256(1), 201-207. doi:10.1006/jcis.2001.8009
- Kracht, W., & Finch, J. A. (2009). Bubble break-up and the role of frother and salt. *International Journal of Mineral Processing*, 92(3-4), 153-161. doi:10.1016/j.minpro.2009.03.011
- Laskowski, J. (1999). Weak electrolyte collectors. In B. K. Parekh, & J. D. Miller (Eds.), *Advances in flotation technology* (pp. 59). Littleton: SME Inc.
- Laskowski, J. S. (1993). Electrokinetic measurements in aqueous solutions of weak electrolyte type surfactants. *Journal of Colloid and Interface Science*, 159(2), 349-353. doi:10.1006/jcis.1993.1333

- Laskowski, J. S., Pawlik, M., & Ansari, A. (2007). Effect of brine concentration on the krafft point of long chain primary amines. *Canadian Metallurgical Quarterly*, 46(3), 295-300.
- Laskowski, J. S., Yordan, J. L., & Yoon, R. H. (1989). Electrokinetic potential of microbubbles generated in aqueous solutions of weak electrolyte type surfactants. *Langmuir*, 5(2), 373-376.
- Laskowski, J., & Nyamekye, G. (1994). Colloid chemistry of weak electrolyte collectors : The effect of conditioning on flotation with fatty acids. *International Journal of Mineral Processing*, 40(3-4), 245-256. doi:10.1016/0301-7516(94)90046-9
- Leja, J. (1982). *Surface chemistry of froth flotation*. New York: Plenum press.
- Levich, V. G. (1962). *Physicochemical hydrodynamics* (2nd ed.). Englewood Cliffs, N.J.: Prentice - Hall.
- Lunkenheimer, K., & Kretzschmar, G. (1975). Study of the elasticity of soluble adsorption films by the pulsed bubble method. I. effective surface elasticity of sodium alkane sulfonates. *Zeitschrift Fuer Physikalische Chemie (Leipzig)*, 256(4), 593-605.
- Malysa, K., Miller, R., & Lunkenheimer, K. (1991). Relationship between foam stability and surface elasticity forces: Fatty acid solutions. *Colloids and Surfaces*, 53(1-2), 47. doi:10.1016/0166-6622(91)80035-M
- Malysa, K. (1992). Wet foams. formation properties and mechanism of stability. *Advances in Colloid and Interface Science*, 40, 37-83.
- Marangoni, C. (1897). Density measurements with two areometers. *Nuovo Cimento*, 6(4), 407.
- Matijevic, E., & Pethica, B. A. (1958). The properties of ionized monolayers. 2. the thermodynamics of the ionic double layer of sodium dodecyl sulphate. *Transactions of the Faraday Society*, 54(9), 1390-1399. doi:10.1039/tf9585401390

- Miller, C. A., & Neogi, P. (1985). *Interfacial phenomena :Equilibrium and dynamic effects* M. Dekker.
- Moroi, Y., Sugii, R., & Matuura, R. (1984). Examination of micelle formation by phase rule. *Journal of Colloid and Interface Science*, 98(1), 184-191.
- Morrison, R. T., & Boyd, R. N. (1994). *Organic chemistry* (6th edition ed.) Prentice Hall.
- Moyo, P., Gomez, C. O., & Finch, J. A. (2007). Characterizing frothers using water-carrying rate. *Canadian Metallurgical Quarterly*, 46(3), 215-220.
- Mukerjee, P., & Mysel, K. (1971). *Critical micelle concentration of aqueous surfactant solutions*. (No. NSRDS-NBS 36). Washington, D.C.: Office of Standard Reference Data, National Bureau of Standards.
- Nesset, J. E., Finch, J. A., & Gomez, C. O. (2007). Operating variables affecting the bubble size in forced-air mechanical flotation machines. *Publications of the Australasian Institute of Mining and Metallurgy*, 1/2007(Ninth Mill Operators' Conference, 2007), 55-65.
- Nesset, J. E., Hernandez-Aguilar, J., Acuna, C., Gomez, C. O., & Finch, J. A. (2006). Some gas dispersion characteristics of mechanical flotation machines. *Minerals Engineering*, 19, 807-815.
- Novales, B., Riaublanc, A., Navailles, L., Houssou, B. H., Gaillard, C., Nallet, F., & Douliez, J. (2010). Self-assembly and foaming properties of fatty acid-lysine aqueous dispersions. *Langmuir*, 26(8), 5329-5334. doi:10.1021/la9034613
- Parkinson, L., & Ralston, J. (2011). Dynamic aspects of small bubble and hydrophilic solid encounters. *Advances in Colloid and Interface Science*, 168(1-2), 198-209. doi:10.1016/j.cis.2011.08.002
- Peck, A. S., & Wadsworth, M. E. (1964). Infrared study of depression effect of fluoride, sulfate, and chloride on chemisorption of oleate on fluorite and barite. *7th International Mineral Processing Congress*, 259-267.

- Peters, J., & Heller, W. (1970). Mechanical and surface coagulation - 2. *Journal of Colloid and Interface Science*, 33(4), 578-585.
- Polkin, S. I., & Najfonow, T. V. (1964). Concerning mechanism of collector and regulator interaction in flotation of silicate and oxide minerals. *7th International Mineral Processing Congress*, 307-318.
- Prud'homme, R. K., & Khan, S. A. (1995). *Foams: Theory, measurements, and applications*. New York: Marcel Dekker.
- Pugh, R., & Stenius, P. (1985). Solution chemistry studies and flotation behavior of apatite, calcite and fluorite minerals with sodium oleate collector. *International Journal of Mineral Processing*, 15(3), 193-218. doi:10.1016/0301-7516(85)90035-3
- Pugh, R. J. (1996). Foaming, foam films, antifoaming and defoaming. *Advances in Colloid and Interface Science*, 64, 67-142. doi:10.1016/0001-8686(95)00280-4
- Ralston, A., & Hoerr, C. (1942). The solubilities of the normal saturated fatty acids. *Journal of Organic Chemistry*, 7(6), 546-555. doi:10.1021/jo01200a013
- Rosano, H. L., Breindel, K., Schulman, J. H., & Eydt, A. J. (1966). Mechanism of ionic exchange with carrier molecules through non-aqueous liquid membranes. *Journal of Colloid and Interface Science*, 22(1), 58-67.
doi:[http://dx.doi.org.ezproxy.library.ubc.ca/10.1016/0021-9797\(66\)90067-1](http://dx.doi.org.ezproxy.library.ubc.ca/10.1016/0021-9797(66)90067-1)
- Rosen, M. J. (2004). *Surfactants and interfacial phenomena* (3rd edition ed.) Wiley-Interscience.
- Rubinstein, J. B. (1995). *Column flotation: Processes, designs, and practices*. Yverdon, Switzerland ; Langhorne, Pa.: Gordon and Breach Science Publishers.
- Sharma, M. K., Shah, D. O., & Brigham, W. E. (1984). Correlation of chain length compatibility and surface properties of mixed foaming agents with fluid displacement efficiency and effective air mobility in porous media. *Industrial & Engineering Chemistry, Fundamentals*, 23(2), 213-220.

- Shimadzu Corporation Analytical & Measuring Instruments Division. *Total organic carbon analyzer (TOC-VCPH/CPN) user manual (for TOC-control V ver.2)*, Kyoto, Japan.
- Shinoda, K., & Becher, P. (1978). *Principles of solution and solubility*. New York: Marcel Dekker.
- Shinoda, K. (1963). *Colloidal surfactants: Some physicochemical properties*. New York: Academic Press.
- Somasundaran, P., & Krishnakumar, S. (1997). Adsorption of surfactants and polymers at the solid-liquid interface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 123-124, 491-513. doi:10.1016/S0927-7757(96)03829-0
- Stache, H. (1996). *Anionic surfactants: Organic chemistry*. New York: Marcel Dekker.
- Sweet, C., van Hoogstraten, J., Harris, M., & Laskowski, J. S. (1997). The effect of frothers on bubble size and frothability of aqueous solutions. *Finch, J.A., Rao, S.R., Holubec, I. (Eds.), Processing of Complex Ores, 2nd UBC-McGill Symposium Series on Fundamental in Mineral Processing*. 235-246.
- Theander, K., & Pugh, R. J. (2001). The influence of pH and temperature on the equilibrium and dynamic surface tension of aqueous solutions of sodium oleate. *Journal of Colloid and Interface Science*, 239(1), 209-216. doi:10.1006/jcis.2000.7543
- Wantke, K., Malysa, K., & Lunkenheimer, K. (1994). Relation between dynamic foam stability and surface elasticity. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 82(2), 183-191. doi:10.1016/0927-7757(93)02614-K
- Ward, A. F. H., & Tordai, L. (1946). Time-dependence of boundary tensions of solutions .1. the role of diffusion in time-effects. *Journal of Chemical Physics*, 14(7), 453-461. doi:10.1063/1.1724167
- Yoon, R., & Yordan, J. (1986). Zeta-potential measurements on microbubbles generated using various surfactants. *Journal of Colloid and Interface Science*, 113(2), 430-438. doi:10.1016/0021-9797(86)90178-5

- Zhang, W., Nasset, J. E., Rao, R., & Finch, J. A. (2012). Characterizing frothers through critical coalescence concentration (CCC95)-hydrophile-lipophile balance (HLB) relationship. *Minerals*, 2(3), 208-227.
- Zhang, W., Kolahdoozan, M., Nasset, J. E., & Finch, J. A. (2009). Use of frother with sampling-for-imaging bubble sizing technique. *Minerals Engineering*, 22(5), 513-515.
- Zhang, W., Nasset, J. E., & Finch, J. A. (2010). Water recovery and bubble surface area flux in flotation. , 49(4) 353-362.
- Zimmels, Y., & Lin, I. J. (1974). Stepwise association properties of some surfactant aqueous solutions. *Colloid and Polymer Science*, 252(7-8), 594-612.

Appendices

Appendix 1: Dynamic surface tension

- Maximum bubble pressure (MBP)

Dynamic surface tension measurement was initially performed through the maximum bubble pressure method since the technique seemed to mimic well the conditions of bubble formation in a surfactant solution. By making small changes in the surface ages of bubbles through the mass flow controller of the instrument, surface tension was recorded for a range of bubble surface ages. Airflow adjustments were done through an 8-mL/min flow meter to get the lowest flow possible and measure surface tension at longer surface ages. According to Figure A1-1 for 3×10^{-3} mol/L (900 mg/L) oleic acid at pH 10 in a background electrolyte of 0.1 mol/L NaCl, it takes a few seconds for the surface tension to reach a steady state value. At concentrations in the range most relevant to this research, 6.5×10^{-5} mol/L (20 mg/L) and 2.3×10^{-4} mol/L (70 mg/L) at pH 10, and in the absence of a background electrolyte, the surface tension measured through the maximum bubble pressure method does not differ from the surface tension of water over the tested time scale, which is due to the low adsorption rate of these species specially at low concentrations and in the absence of a background electrolyte.

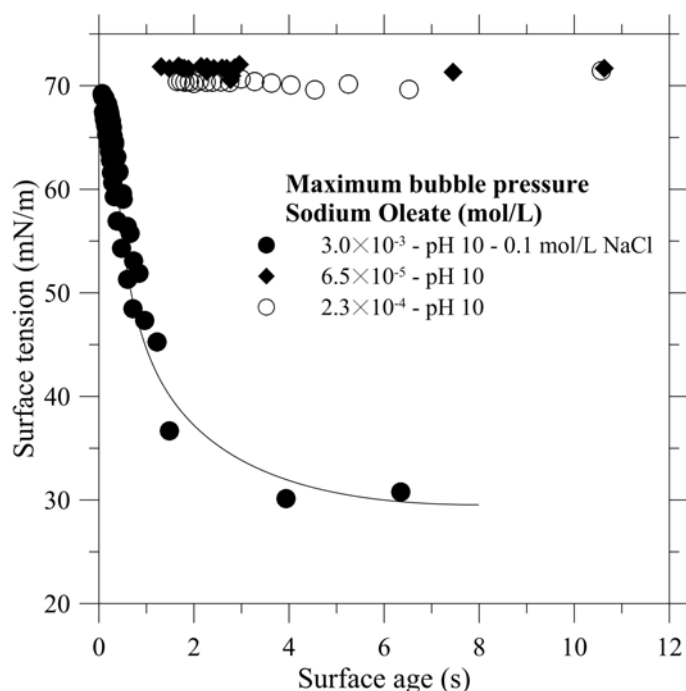


Figure A1- 1. Dynamic surface tension of 6.5×10^{-5} and 2.3×10^{-4} mol/L sodium oleate at pH 10 in addition to 3×10^{-3} mol/L oleic acid in a background electrolyte of 0.1 mol/L NaCl as a function of bubble surface age measured by maximum bubble pressure method at 23°C

- Pendant drop method for sodium oleate and laurate

In order to be able to observe the dynamic effects within the concentration range of this study, the surface tension was measured through the pendant drop method by forming a droplet of the solution at the needle tip and measuring surface tension changes as a function of time. The measurements were initially made at the natural pH of those solutions. As is demonstrated in Figure A1-2, low oleate concentrations require a very long time to reach a steady state surface tension value. At the same time, oleate concentrations of at least 1.6×10^{-4} mol/L (50 mg/L) approach steady state conditions relatively quickly.

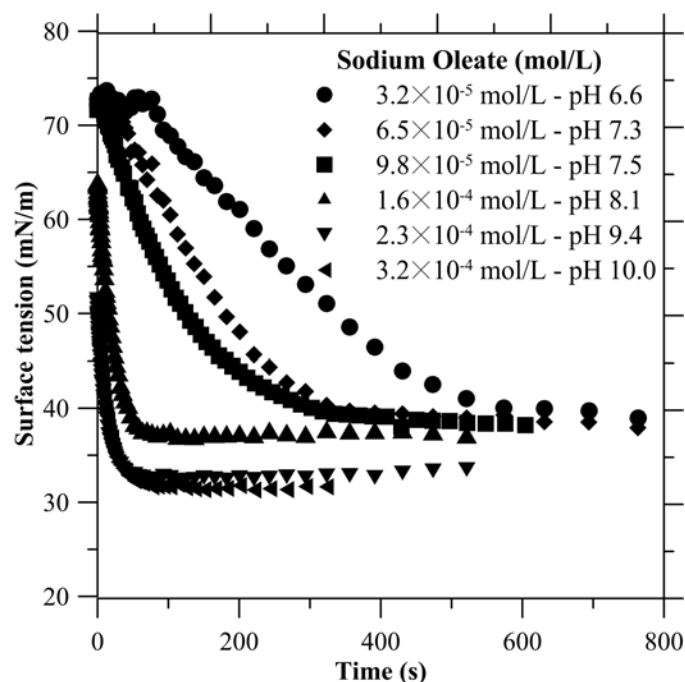


Figure A1- 2. Dynamic surface tension of sodium oleate as a function of concentration at natural pH measured by pendant drop method

The concentration of soluble species increases at higher concentration and pH, which leads to fast adsorption, while at lower pH the presence of precipitates causes delay in adsorption at the interface. Interestingly, the final steady-state surface tension values do not seem to differ much for the different concentrations. These results indicate that the transport to and adsorption of sodium oleate at the gas-liquid interface are much faster at higher oleate concentration, which is in accordance with the Gibbs adsorption equation (equation 2-24), and there is basically no difference between the data at 2.3×10^{-4} mol/L (70 mg/L) and 3.2×10^{-4} mol/L (100 mg/L) of oleate.

Below a concentration of 1.6×10^{-4} mol/L (50 mg/L), the natural pH values of the solutions are much lower than the pH of precipitation, while for concentrations higher than 1.6×10^{-4} mol/L the natural pH values are higher than corresponding pH of precipitation. As a result, those solutions with lower oleate concentrations contained colloidal precipitates while solutions with higher concentrations are closer to the true solution state.

The surface tension data shown in Figure A1-3 demonstrate the dynamic behavior of sodium oleate as a function of pH at a concentration of 10^{-3} mol/L (300 mg/L). The equilibrium surface tension measured at the droplet surface is achieved at longer time scales for lower pH

values. Higher pH values up to pH 9 and 10 result in faster adsorption at the bubble surface, which consequently allows the system to faster reach a steady-state surface tension value.

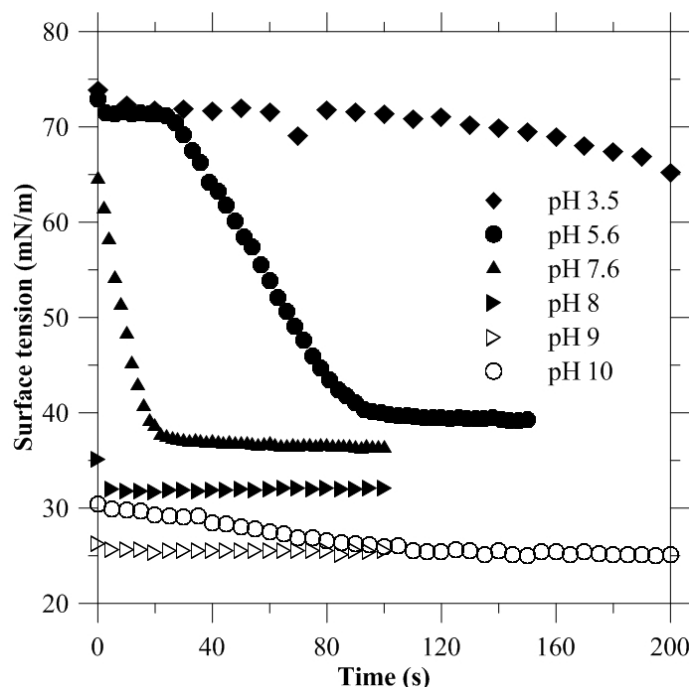


Figure A1-3. Dynamic surface tension of 10^{-3} mol/L oleic acid at different pH values measured by pendant drop method, pH of precipitation is 9.3

The surface tension data shown in the following figure demonstrate the dynamic behavior of sodium oleate at 2.3×10^{-4} mol/L sodium oleate as a function of pH. Steady-state conditions are reached much faster at higher pH, and a lower adsorption rate can be observed at lower pH. Overall, the rate of adsorption is lower at this concentration compared to a concentration of 10^{-3} mol/L. Similarly to the 2.3×10^{-4} mol/L data in Figure 4-1, the final steady-state surface tension values approach 30-40 mN/m.

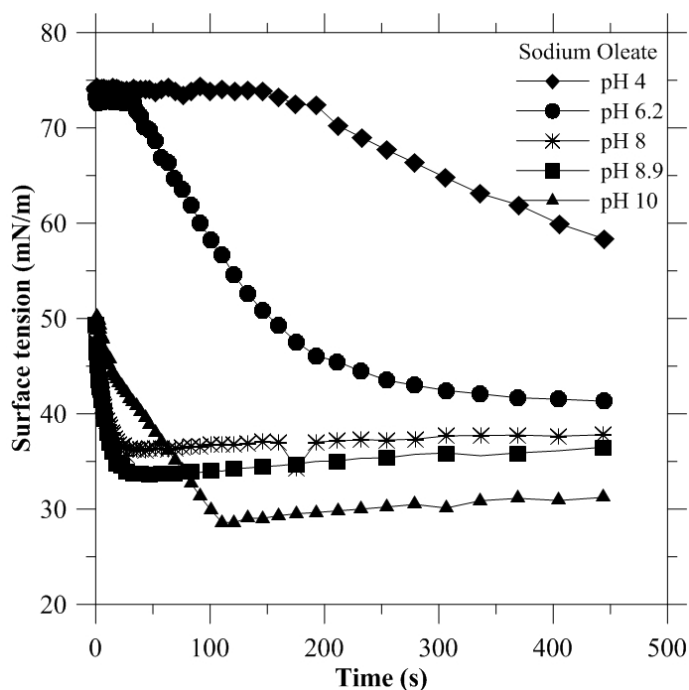


Figure A1- 4. Dynamic surface tension of 2.3×10^{-4} mol/L sodium oleate at different pH values measured by pendant drop method

The surface tension data shown in the following figure demonstrate the dynamic behavior of 6.5×10^{-5} and 2.3×10^{-4} mol/L solutions of sodium laurate at pH 4 and 9. In contrast to the results for sodium oleate, the final steady state values differ by about 30 mN/m, and no indications of laurate adsorption can be found at higher pH. These results are consistent with the equilibrium surface tension data from Figure 4-3 that showed that at a concentration of 2.3×10^{-4} mol/L at high pH the surface tension of laurate solutions was basically equal to that of water. As in the case of equilibrium surface tension data, the undissociated lauric acid species appears to be more surface-active and adsorbs faster than the dissociated laurate anion.

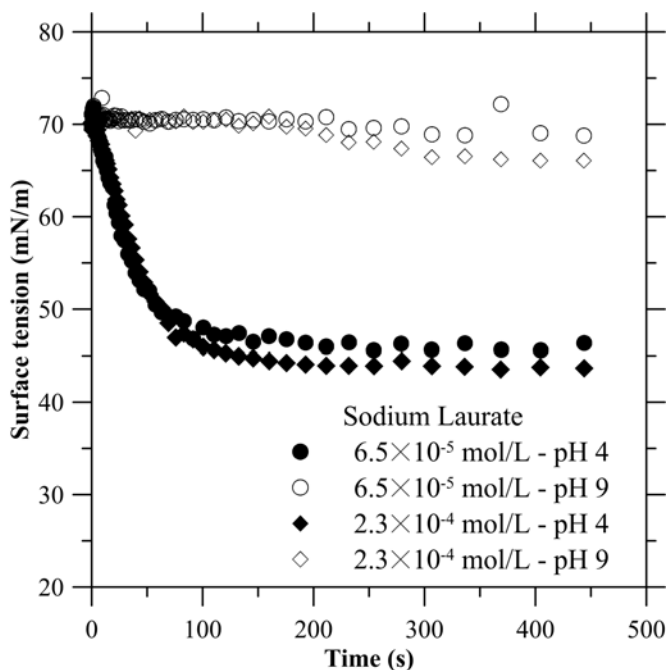


Figure A1- 5. Dynamic surface tension of 6.5×10^{-5} and 2.3×10^{-4} mol/L sodium laurate at pH 4 and 9 measured by pendant drop method, pH values of precipitation at the tested concentrations are 5.3 and 5.9

The significant trends in the dynamic surface tension data are:

- 1) For oleic acid, adsorption is faster at higher surfactant concentrations and at higher pH. Adsorption is slower at lower pH and in the presence of precipitates.
- 2) For lauric acid, the adsorption rate is very slow at high pH and it is much higher at low pH, the effect of concentration at a given pH is insignificant. Perhaps another conclusion is that even if precipitate forms at pH 4 in laurate solutions, adsorption is still fast which also seems to show that precipitates do not interfere with the adsorption of undissociated acid.
- 3) If the timescales of adsorption are compared under high adsorption conditions (or at low surface tension), at a concentration of 2.3×10^{-4} mol/L, the adsorption of oleate anion (at pH 8-9) is much faster than adsorption of undissociated lauric acid at pH 4. It takes about 25 seconds for oleate to reach equilibrium, but it takes about 100 seconds for lauric acid to reach steady state.

Appendix 2: Gas hold-up measurements

According to Figure A2-1, gas hold up keeps increasing with increasing concentration of sodium oleate, and exhibits higher values at pH 10 than at natural pH, which correlates with the bubble size data. The maximum gas hold-up value reached for the tested concentrations is around 9% at 3.2×10^{-4} mol/L (100 mg/L). The gas hold up data did not change much at a background electrolyte of 0.01 mol/L NaCl at pH 10.4.

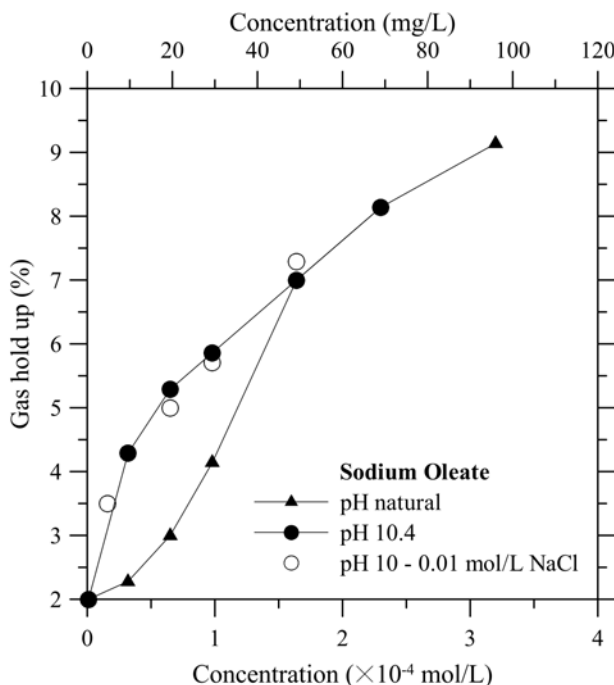


Figure A2- 1. Gas hold up of sodium oleate solutions at natural pH (6.7-10.5) and pH 10.4

Although bubble sizes start to stabilize above a certain concentration, gas hold up keeps increasing. This could be explained through differences in bubble size distributions in that concentration range; at higher concentrations, a larger fraction of finer bubbles are produced, as is demonstrated in Figure 5-3 for pH 10.4, which leads to an increase in gas hold up. Therefore apart from the mean bubble size, analyzing bubble size distributions is a useful tool to further investigate the differences between two gas dispersion systems. Gas hold up as a function of pH for sodium oleate is demonstrated in Figure A2-2.

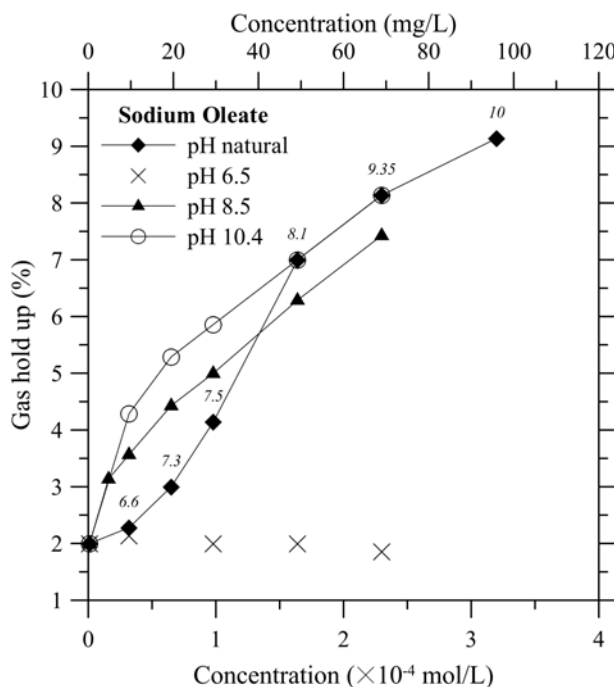


Figure A2- 2. Gas hold up of sodium oleate at pH 6.5, natural pH, pH 8.5 and pH 10 (natural pH values are labeled on the corresponding data points)

Large bubble sizes at pH 6.5 do not allow the bubbles to reside for a long time in solution and the bubbles quickly pass through measuring column. As a result, the gas hold-up at pH 6.5 is rather low. Although no clear differences in mean bubble sizes at pH 8.5 and 10.5 were observed, the gas hold up is slightly higher at pH 10.5 compared to pH 8.5.

The corresponding gas hold-up results for lauric acid are demonstrated in Figure A2-3. In an acidic environment, at a low concentration (1.2×10^{-5} mol/L) when there is no precipitate and also when the concentration of precipitates is low, gas hold-up increases, but when the concentration of precipitates increases, gas hold up decreases. However, under alkaline conditions, in the absence of precipitates, the gas hold up significantly increases with surfactant concentration.

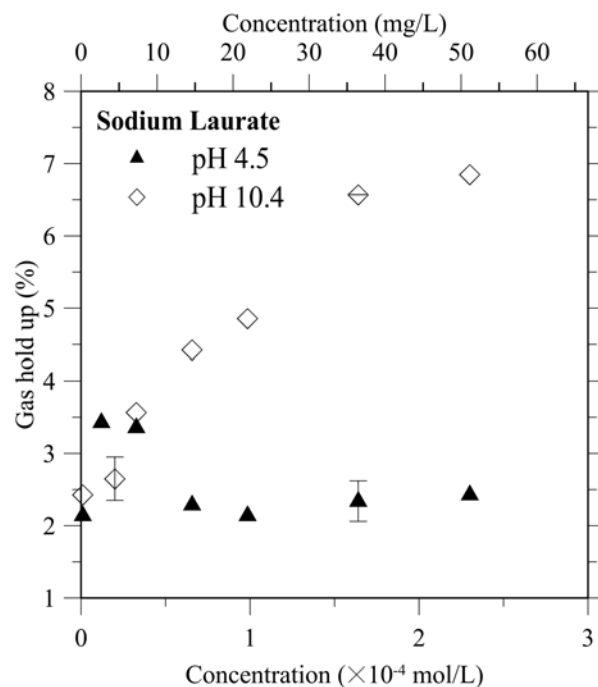


Figure A2- 3. Gas hold-up of sodium Laurate at pH 4.5 and 10.4

Gas hold up for solutions of SDS at pH 4.5 and pH 10 is demonstrated in Figure A2-4. A maximum of 1% difference in gas hold up values is observed for natural pH and pH 10.

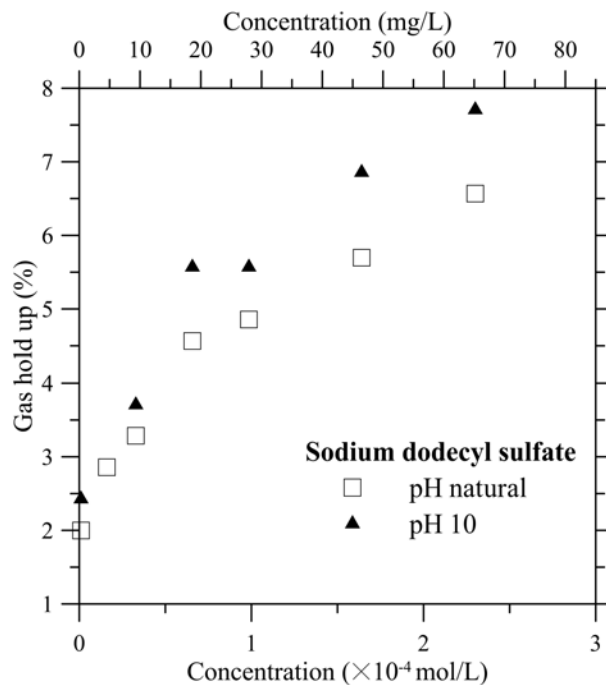


Figure A2- 4. Gas hold-up of sodium dodecyl sulfate at natural pH (4.1-4.7) and pH 10

Gas hold-up for sodium oleate, laurate and sodium dodecyl sulfate is compared at pH 10.4 in the following figure. Sodium laurate shows smaller gas hold-up values compared to the other two reagents.

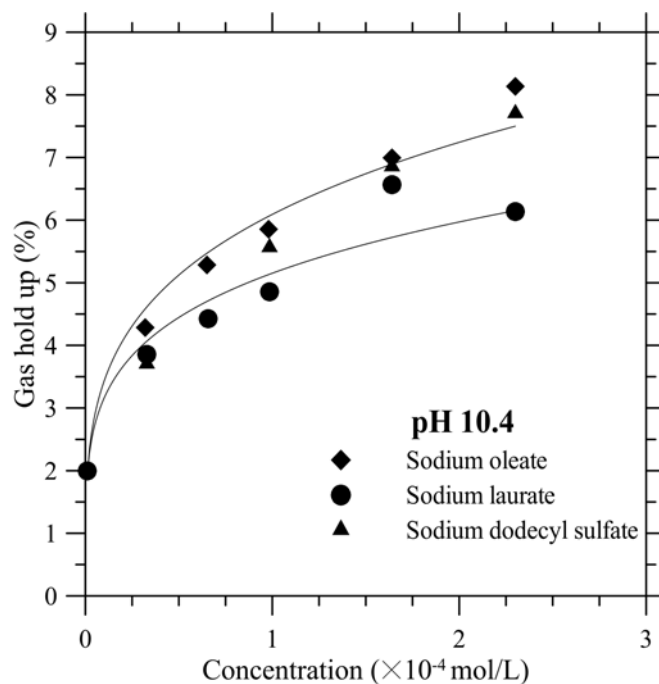


Figure A2- 5. Gas hold up of sodium oleate, dodecyl sulfate and laurate at pH 10.4

Appendix 3: Mixture of sodium oleate and MIBC

In order to identify whether adding a frother in addition to sodium oleate has any synergistic effect on gas dispersion properties, two combinations of equal concentrations of MIBC and sodium oleate were tested and compared to the effect of individual reagents.

Mixtures of 8.2×10^{-6} mol/L (2.5 mg/L) sodium oleate and 2.5×10^{-5} mol/L (2.5 mg/L) MIBC (equals to a total concentration 5mg/L) as well as 1.6×10^{-5} mol/L (5 mg/L) of sodium oleate and 4.9×10^{-5} mol/L (5 mg/L) MIBC (equals to a total concentration of 10 mg/L) were tested for gas dispersion properties at pH 10.4 to investigate if there were any synergistic effects of using these two reagents together. At a concentration of 2.5 mg/L, each of these reagents produces an average bubble size of over 2.5 mm while a combination of these two surfactants generates a bubble size of 1.83 mm. At 5 mg/L, each of these reagents gives a bubble size of over 2 mm, while a 1:1 combination of these two surfactants generates a bubble size of 1.79 mm. It appears that a mixture of MIBC and oleate exhibits stronger gas dispersion capabilities than the two surfactants alone. According to the author's knowledge there is no systematic data in literature on the effect of frother-collector combination on gas dispersion properties.

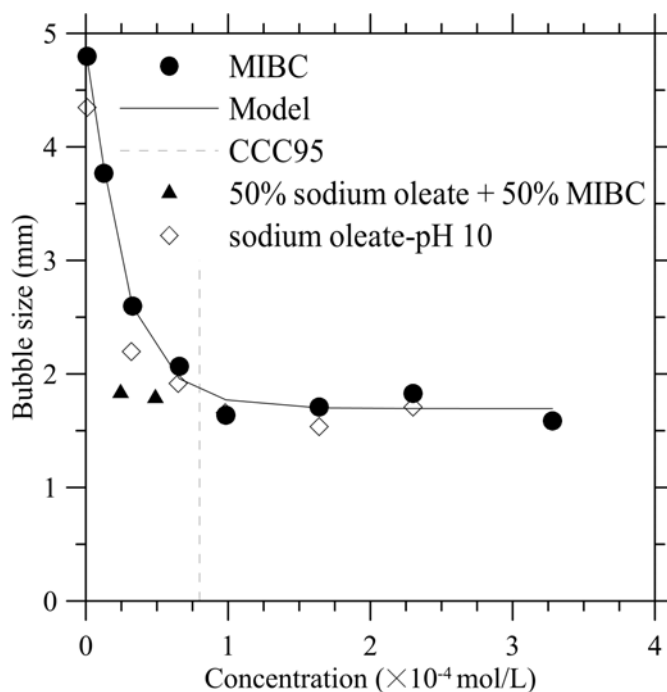


Figure A3- 1. Average bubble size for MIBC and combinations of two concentrations of sodium oleate and MIBC at pH 10 (based on MIBC concentration)

Appendix 4: Gas dispersion measurement (in McGill set up)

The impact of sodium oleate addition on the Sauter mean diameter is illustrated in Figure A4-1, with an example of the size distribution evolution in Figure A4-2. These measurements were performed at the McGill column laboratory.

The average bubble size trend matches with the size distribution evolution, which shows the initial bi-modality followed by convergence to a narrow mono-modal distribution. The critical coalescence concentration for oleic acid at natural pH can be estimated at ca. 1.6×10^{-4} mol/L (50 mg/L) and approximately the same value can be observed for tall oil. At pH 10, the CCC of sodium oleate decreases to about 9.9×10^{-5} mol/L (30 mg/L). The evolution of the bubble size distribution in the presence of sodium oleate is very similar to that exhibited by common frothers. These changes can be explained by bubble coalescence at low concentrations producing both larger and smaller bubbles, but as the CCC is approached and exceeded, bubble coalescence is prevented, the average bubble size decreases, and the bubble size distribution gradually becomes narrower and mono-modal.

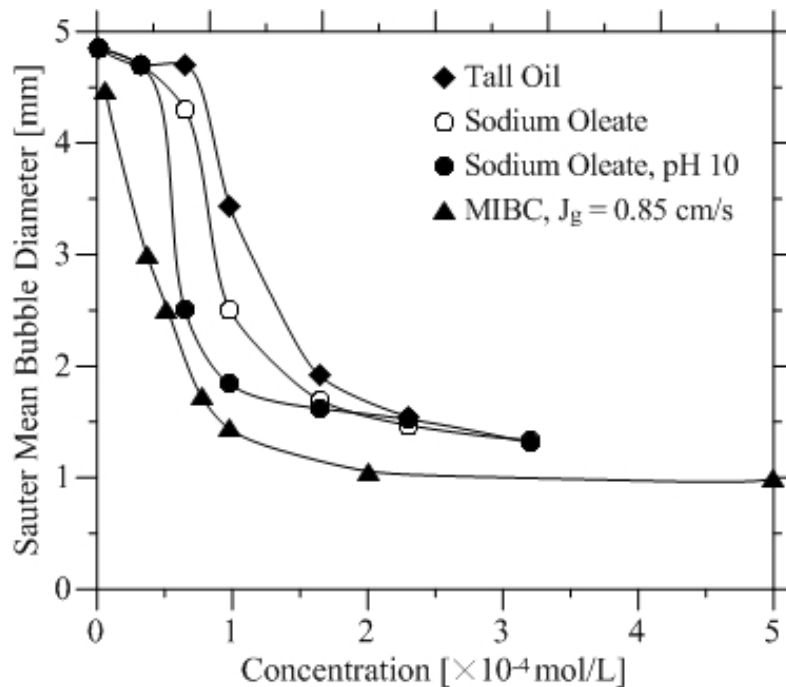


Figure A4- 1. Effect of sodium oleate and tall oil concentration on bubble mean diameter at $J_g=0.5$ cm/s, the MIBC data were taken from Azgomi et al 2007

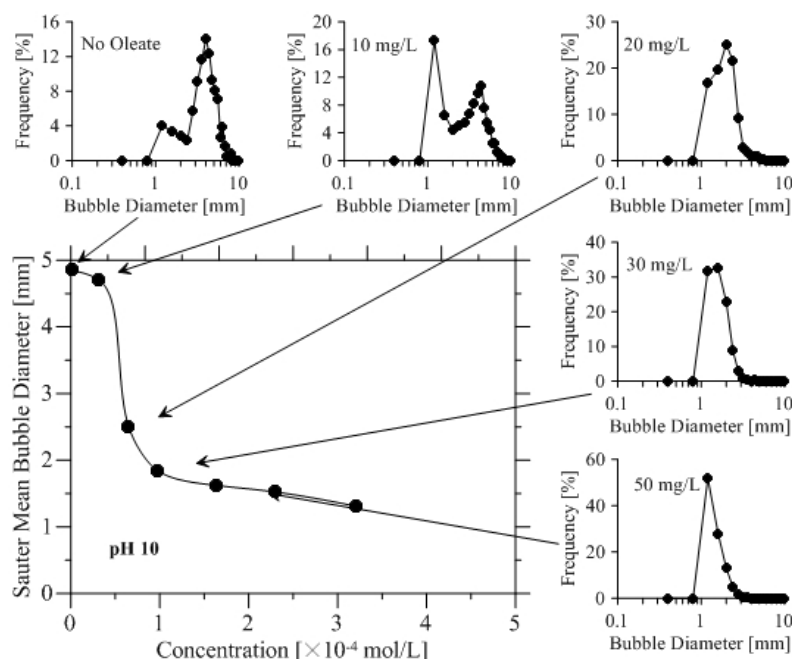


Figure A4- 2. Changes in the bubble size distribution as a function of oleate concentration at pH 10 (This type of data presentation was obtained from Finch et al, 2008)

CCC is very close to the CMC value measured in this study, which is in the range of 10^{-4} to 3×10^{-4} M (30-90 mg/L).

A set of bubble size data for methyl-isobutyl carbinol, MIBC, (Azgomi et al, 2007) is included in Figure A4-1 for comparison. These MIBC results were obtained using the same methodology. As MIBC is considered to be a rather weak frother, it is quite clear that the frothing power of sodium oleate is even lower.

The results for tall oil are qualitatively similar to those obtained for sodium oleate. Natural pH in the case of tall oil solutions ranged from 7 to 8.73. Although it is difficult to define a pH value for the onset of precipitation for this mixture of various organic acids, it was clearly seen that these solutions were turbid, which indicated that a substantial amount of tall oil or of some of its components was precipitated from solution. It is apparent from Figure A4-1 that the CCC value for tall oil is similar to that for sodium oleate. It is therefore reasonable to conclude that tall oil can be characterized by a frothing power comparable to that of sodium oleate.

The corresponding gas hold-up data are presented in Figure A4-3 for tall oil and sodium oleate. At low concentrations, the effect of the surfactants is insignificant but at higher

concentrations the gas hold-up values increase more sharply. This overall trend also follows the changes in the bubble size data shown in Figure A4-1.

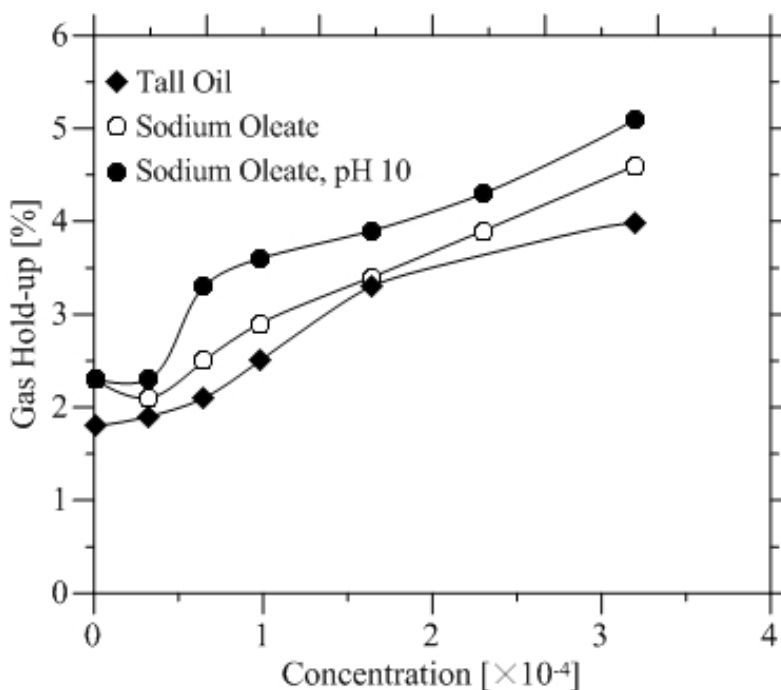


Figure A4- 3. Effect of collector concentration on gas hold-up

As gas bubbles become smaller and the surface area flux of gas bubbles increases, their rising velocities decrease and more gas is retained within the bulk solution over a given period of time. By residing in the bulk solution for a longer period of time, these bubbles are more likely to collide and attach to fine mineral particles. On this basis, sodium oleate is a stronger frother at pH 10 than at natural pH. Tall oil is not as effective. However, it should be noted that gas hold-up does not reach a plateau value for any of the reagents and tends to continuously increase with concentration. This result was reported for several typical frothers and the reasons for this gradual increase at higher surfactant concentrations, or when the average bubble size does not significantly change, are not entirely clear (Azgomi et al, 2007). The Author's approach is that although the average bubble sizes do not differ much at higher concentration, since the fraction of small bubbles increases, the gas hold up values keep increasing.

Appendix 5: Foamability and gas dispersion set ups



Figure A5-1. UBC foamability set up

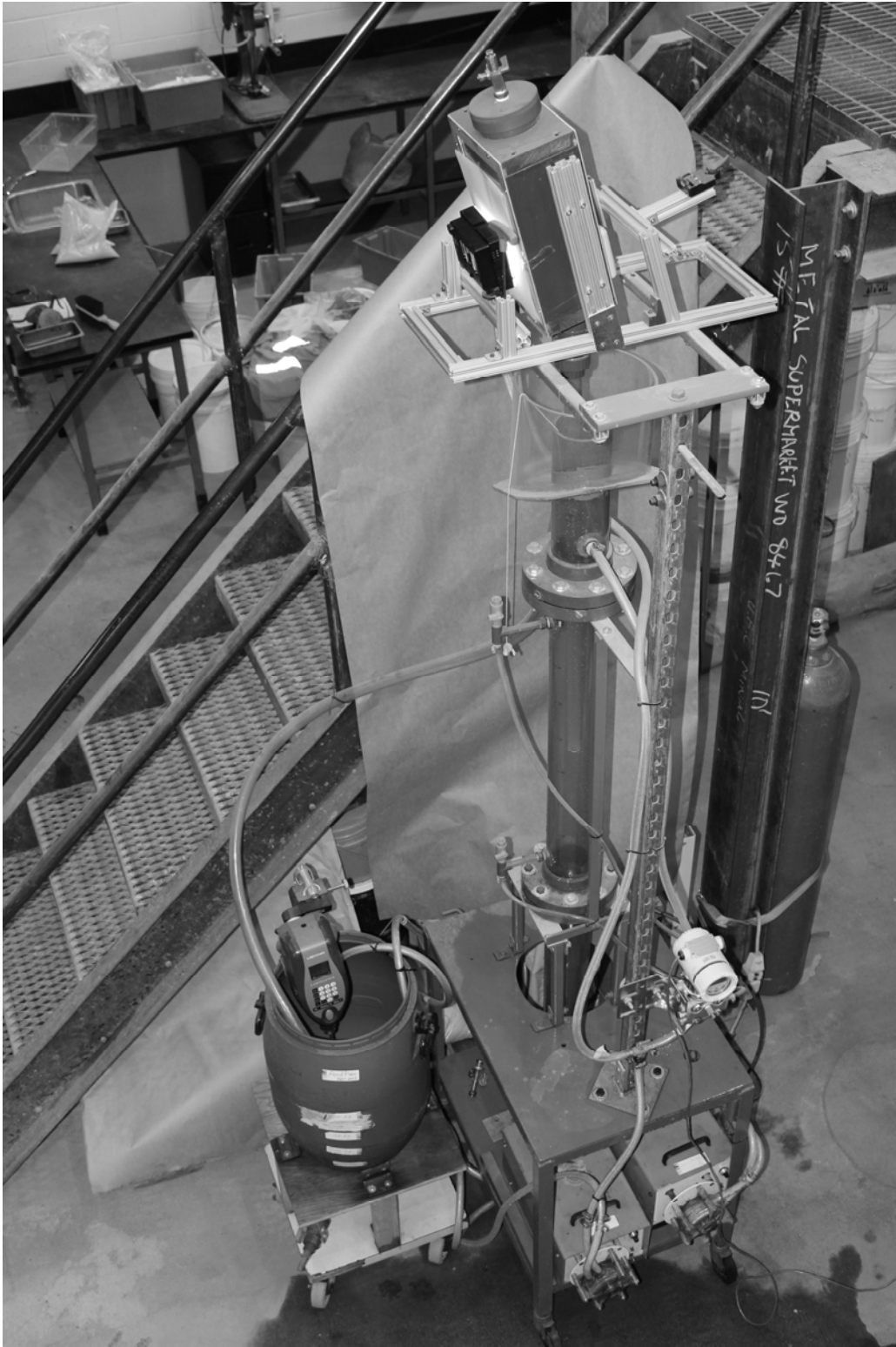


Figure A5-2. UBC gas dispersion set up