

Dynamics of Thin Surfactant Films

BY

SOUMYADIP SETT

B.P.E., Jadavpur University, Kolkata, India, 2011

THESIS

Submitted as a partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Mechanical Engineering
in the Graduate College of the
University of Illinois at Chicago, 2016

Chicago, Illinois

Defense Committee

Alexander L. Yarin,	Chair and Advisor
W.J. Minkowycz,	Mechanical and Industrial Engineering
Kenneth Brezensky,	Mechanical and Industrial Engineering
Kumar Natesaiyer,	United States Gypsum Corporation
Suman Sinha-Ray,	Mechanical and Industrial Engineering.

I dedicate this thesis to my mother Smt. Mita Sett and my father Sri Sukanta Kumar Sett,
without whose love and support it would never have been accomplished.

ACKNOWLEDGEMENTS

First and foremost I want to thank my advisor, Professor Alexander L. Yarin for being a tremendous mentor. I would like to thank him for encouraging my research and for allowing me to grow as a research scientist. It has indeed been an honor to be his Ph.D. student. I am grateful for his contributions of time, ideas, and funding to make my Ph.D. experience productive and simulating. The joy and enthusiasm he has for research and teaching was contagious and motivational for me, even during the toughest times in pursuit of Ph.D. I am thankful to him for sharing the wonderful historical anecdotes of great scientists, inspiring me to leave a mark in the field of science. Professor Yarin has been supportive and has always given me the freedom to pursue various projects without objection. Without his consistent help and support, this dissertation would not have been possible.

I would like to thank my thesis committee members for their suggestions, support and assistance, which helped me in achieving my goals. A very special thanks to my parents for their never ending support and encouragement without which this journey would never even have started. Words cannot express how grateful I am to my parents for all their sacrifices that they have made on my behalf. I would like to take this opportunity to thank my cousin, Dr. Joydeep Mukherjee for being my mentor in life and shaping my thoughts and aspirations. He was, and remains my best role model for a scientist, mentor and teacher. I would also like to thank Prof. Amitava Dutta and Prof. Ranjan Ganguly from Jadavpur University for their help and guidance. They inculcated my interest in research during my undergraduate years and have been there for me whenever needed.

I will forever be thankful to all my lab mates whose help and support in all stages of this journey have been instrumental in completion of my Ph.D. I am grateful to my seniors and co-authors of my publications, Dr. Suman Sinha Ray, Dr. Rakesh Prasad Sahu, Dr. David Pelot, and Dr. MinWook Lee for their help and guidance in my work. In addition, I would also like to thank the undergraduate students Martin Weith, Shalin Patel, Maninder Singh and Kais Kavar, who helped me immensely in the experimental work. I wish to express my sincere thanks to David Mecha and Eric Schmidt from the Scientific Instrument Shop for their significant contributions in making my experiments successful.

S.S.

Some parts of this thesis have been published in peer-reviewed journals. Sections 2.1 and 3.1, as well as Chapter 4, were published in *Langmuir* of the American Chemical Society (Sett, S., Sinha-Ray, S., & Yarin, A. L. (2013). Gravitational Drainage of Foam Films. *Langmuir*, 29(16), 4934-4947). Sections 2.2, 3.2, and Chapter 5 were published in *Langmuir* of the American Chemical Society (Sett, S., Sahu, R. P., Sinha-Ray, S., & Yarin, A. L. (2014a). Superspreaders Versus “Cousin” Non-Superspreaders: Disjoining Pressure in Gravitational Film Drainage. *Langmuir*, 30(10), 2619-2631). Sections 2.3, 3.3, and Chapter 7 were published in *Langmuir* of the American Chemical Society (Sett, S., Sahu, R. P., Pelot, D. D., & Yarin, A. L. (2014b). Enhanced Foamability of Sodium Dodecyl Sulfate Surfactant Mixed with Superspreader Trisiloxane-(poly) ethoxylate. *Langmuir*, 30(49), 14765-14775). Sections 2.4, 3.5 and Chapter 9 were published in *Advances in Colloid and Interface Science* of Elsevier (Sett, S., Karakashev, S. I., Smoukov, S. K., & Yarin, A. L. (2015). Ion-specific effects in foams. *Advances in Colloid and Interface Science*, 225, 98-113). Sections 2.5, 3.6 and Chapter 10 were published in *Electrochimica Acta* of Elsevier (Sett, S., Sahu, R. P., Sinha-Ray, S., & Yarin, A. L. (2016). Experimental Investigation of Eletrokinetic Stabilization of Gravitational Drainage of Ionic Surfactants Films. *Electrochimica Acta*, 187, 693-703). Permission letters given by the publisher are in the Appendix.

CONTRIBUTION OF AUTHORS

The work on gravitational drainage of foam films in Section 2.1, Section 3.1, and Chapter 4 represents a published manuscript [Sett et al. (2013)] for which I am the primary author, conducted all the experiments and analyzed the experimental results. Dr. Sinha-Ray contributed in the design of the experimental setup and assisted in developing the theory. The work on superspreaders vs “cousin” non-superspreaders in Section 2.2, Section 3.2, and Chapter 5 represents a published manuscript [Sett et al. (2014a)] for which I am the primary author and did all the experiments. Dr. Sahu contributed in analyzing the results and Dr. Sinha-Ray assisted in developing the theory. The work on enhanced foamability of SDS with superspreader trisiloxane surfactant in Section 2.3, Section 3.3, and Chapter 7 represents a published manuscript [Sett et al. (2014b)] for which I am the primary author and did all the experiments. Dr. Pelot contributed in the design of the experimental setup and Dr. Sahu assisted in analyzing the results. The work on ion specific effects in foams in Section 2.4, Section 3.5, and Chapter 9 represents a published manuscript [Sett et al. (2015)] for which I am the primary author. I did all the experiments on planar vertical film drainage and gravity settler column. Dr. Karakashev and Dr. Smoukov contributed in developing the theory for prediction of the critical salt concentration and also in the literature survey of the works related to effect of ions in foams. The work on electrokinetic stabilization of ionic surfactant films in Section 2.5, Section 3.6, and Chapter 10 represents a published manuscript [Sett et al. (2016)] for which I am the primary author and did all the experiments. Dr. Sahu contributed in the design of the experimental setup and Dr. Sinha-Ray assisted in developing the theory. In all published works my advisor, Dr. Yarin, supervised the experimental and theoretical work and contributed to the writing of the manuscript. Chapter 6 is an

unpublished experiments related to foam drainage in gravity settler using superspreaders and soaps used by United States Gypsum Corporation. Chapter 8 is an unpublished work related to increasing fluidity of gypsum-foam slurry production of dry wallboards conducted for United States Gypsum Corporation.

TABLE OF CONTENTS

<u>CHAPTER</u>	<u>PAGE</u>
1. INTRODUCTION	1
1.1 History of soap film	1
1.2 Foam	2
1.3 Thesis objectives	2
2. BACKGROUND AND LITERATURE SURVEY	4
2.1 Gravitational drainage of thin films	4
2.2 Superspreaders and their aggregates	6
2.3 Drainage of foam	8
2.4 Ion specific effects – Hofmeister series	10
2.5 Electrokinetic effect in thin surfactant films	15
2.5.1 Electrokinetic effect	15
2.5.2 Micellization of surfactants	15
3. RESEARCH OUTLINE	17
3.1 Gravitational drainage of foam films	17
3.2 Drainage of planar vertical “superspreader” films	18
3.3 Enhanced foamability of superspreader trisiloxane surfactants and their mixture with ordinary surfactants	19
3.4 Fluidity enhancement of gypsum-foam slurry	20
3.5 Ion specific effects in foams	20
3.6 Electrokinetic stabilization of ionic surfactant films	21
4. GRAVITATIONAL DRAINAGE OF FOAM FILMS	22
4.1 Introduction	22
4.2 Experimental materials and methods	22
4.2.1 Materials	22
4.2.2 Solution preparation	23
4.2.3 Experimental setup	23
4.2.4 Experimental method	27
4.3 Theoretical	33
4.3.1 Drainage of plane soap film	33
4.3.2 Drainage of spherical soap bubble	41
4.4 Results and discussion	45
4.4.1 Drainage of plane soap film	45
4.4.2 Drainage of spherical soap bubble	56
4.4.3 Comparison with data from literature	60
4.5 Conclusions	63

TABLE OF CONTENTS (continued)

<u>CHAPTER</u>	<u>PAGE</u>
5. SUPERSPREADERS VERSUS “COUSIN” NON-SUPERSPREADERS: DISJOINING PRESSURE IN GRAVITATIONAL FILM DRAINAGE	65
5.1 Introduction	65
5.2 Experimental	66
5.2.1 Materials	66
5.2.2 Solution preparation	67
5.2.3 Experimental setup and method	67
5.3 Experimental results	68
5.4 Theoretical	84
5.4.1 Effect of disjoining pressure on drainage rate	84
5.5 Discussion: experiments versus theory	89
5.6 Conclusions	102
6. FOAMABILITY ENHANCEMENT USING TRISILOXANE SURFACTANTS	104
6.1 Introduction	104
6.2 Experimental materials and methods	104
6.2.1 Materials	104
6.2.2 Experimental method	105
6.3 Results and discussion	108
6.4 Conclusions	114
7. DRAINAGE OF SODIUM DODECYL SULFATE SURFACTANT MIXED WITH SUPERSREADER TRISILOXANE-(POLY)ETHOXYLATE	115
7.1 Introduction	115
7.2 Experimental	116
7.2.1 Materials	116
7.2.2 Solution preparation	116
7.2.3 Surface tension measurement	119
7.2.4 Drainage of plane films	120
7.2.5 Gravity settler	121
7.3 Results and discussion	122
7.3.1 Drainage of plane films	122
7.3.2 Foam drainage in gravity settler	138
7.4 Conclusions	150

TABLE OF CONTENTS (continued)

<u>CHAPTER</u>		<u>PAGE</u>
8.	FLUIDITY ENHANCEMENT OF GYPSUM-FOAM SLURRY WITH THE ADDITION OF SUPERSPREADER	152
8.1	Introduction	152
8.2	Experimental	152
8.2.1	Materials	152
8.2.2	Experimental procedure	152
8.2.2.1	Addition of superspreader to foam water while keeping the foam volume fixed and reducing the initial amount of water in gypsum	153
8.2.2.2	Addition of superspreader to gypsum water	156
8.2.2.3	Addition of superspreader to foam water while keeping initial amount of water in gypsum slurry fixed, and reducing foam water in gypsum slurry by reducing foam density	157
8.3	Results and discussion	160
8.3.1	Addition of superspreader to foam water while keeping volume of foam fixed and reducing the initial amount of water in gypsum slurry	160
8.3.2	Addition of superspreader to gypsum water	169
8.3.3	Addition of superspreader to foam water while keeping the initial amount of water in gypsum slurry fixed, and reducing foam water in gypsum slurry by reducing foam density	173
8.4	Conclusions	180
9.	ION-SPECIFIC EFFECTS IN FOAMS	182
9.1	Introduction	182
9.2	Experimental	182
9.2.1	Materials	182
9.2.2	Solution preparation	183
9.2.3	Experimental setups and methods	183
9.2.3.1	Vertical foam film	183
9.2.3.2	Foam column experiments	185
9.2.3.3	Surface tension measurements	186
9.3	Results and discussion	186
9.3.1	Thin film experiments and analysis	186
9.3.2	Foam experiments and analysis	196
9.4	Conclusions	201
10.	EXPERIMENTAL INVESTIGATION OF ELECTROKINETIC STABILIZATION OF GRAVITATIONAL DRAINAGE OF IONIC SURFACTANTS FILMS	202
10.1	Introduction	202
10.2	Experimental section	203
10.2.1	Experimental setup	203

TABLE OF CONTENTS (continued)

<u>CHAPTER</u>		<u>PAGE</u>
	10.2.2 Preparation of solutions	205
	10.3 Results and discussion	206
	10.4 Discussion of the experimental results	216
	10.5 Conclusions	225
11.	CONCLUSION	232
12.	CITED LITERATURE	234
13.	APPENDIX	249
14.	CURRICULUM VITAE	257

LIST OF TABLES

<u>TABLE</u>	<u>PAGE</u>
4.1 Plane DTAB solution films	47
4.2 Plane SDS solution films	49
4.3 Plane films of the non-ionic C ₈ E ₄ solutions	54
4.4 Plane films of the non-ionic Pluronic P-123 solutions	55
4.5 Spherical bubbles of Pantene Shampoo solution and DTAB solutions	59
4.6 Comparison of surface elasticity ε measured for different concentrations of cationic DTAB solutions with data in literature	61
4.7 Comparison of surface elasticity ε measured for different concentrations of the anionic SDS solutions with data in literature	61
4.8 Comparison of surface elasticity ε measured for different concentrations of the non-ionic C ₈ E ₄ solutions with data in literature	62
4.9 Comparison of surface elasticity ε measured for different concentrations of the non-ionic Pluronic P-123 solutions with data in literature	62
5.1 Superspreader SILWET L-77 solution films	90
5.2 Scaling exponents for the disjoining pressure of the superspreader SILWET L-77 solutions found using the slope of the scaling laws	93
5.3 Superspreader BREAK-THRU S 278 solution films	94
5.4 Scaling exponents for the disjoining pressure of the superspreader BREAK-THRU S 278 solutions found using the slope of the scaling laws	97
5.5 Non-superspreader SILWET L-7607 solution films	100
5.6 Non-superspreader BREAK-THRU S 233 solution films	101
7.1 Concentration of SILWET L-77 in 4 mM, 8 mM, and 12 mM SDS aqueous solutions for mixing ratios of SDS to SILWET L-77 1:0.5, 1:1, 1:2, 1:5, and 1:10..	118
7.2 Plane SDS-alone solution films	124
7.3 Superspreader SILWET L-77 alone solution films	128

LIST OF TABLES (continued)

<u>TABLE</u>	<u>PAGE</u>
7.4 SDS and superspreader SILWET L-77 mixture solution films	131
7.5 Liquid drainage from the SDS-alone and the superspreader SILWET L-77-alone foams	141
7.6 Drainage of liquid from the SDS/SILWET L-77 mixture foams	145
8.1 Composition and concentration of different materials at different WSR	155
8.2 Labeling of different samples used for the gypsum-foam slurry tests where the total volume of foam added was kept constant	156
8.3 Labelling of different samples used for the gypsum slurry tests without addition of foam	157
8.4 Composition and concentration of different materials at different WSR	159
8.5 Labeling of different samples used for the gypsum-foam slurry tests where the initial water added to gypsum slurry was kept constant	159
8.6 Percentage increase in strength of gypsum-foam cubes for samples containing 0.1% superspreader in foam water	166
9.1 The lifetime of the foam lamellas in the presence of 0.5 mM SDS and of added salt	191
9.2 Added salt and corresponding lifetimes of the foam lammelaes for the cases of LiCl and NaCl	194
10.1 Micellar properties	215

LIST OF FIGURES

<u>FIGURE</u>	<u>PAGE</u>
4.1 (a) Schematic of the experimental setup with drainage from plane films. (b) Image of the experimental setup	24
4.2 (a) Schematic of the experimental setup with drainage of spherical soap bubble. (b) Image of the experimental setup	25
4.3 Drainage of D10.0 plane film	28
4.4 (a) The image of an empty wire frame. (b) Color image of the frame with a film. (c) The film image with the wire frame	29
4.5 Thickness of planar film measured using the intensities of red, green and blue light, I_r , I_g and I_b , respectively, filtered digitally.	31
4.6 Drainage of D10.0 spherical bubble.	32
4.7 Sketch of vertical plane soap film on a frame	34
4.8 Sketch of spherical soap film. R denotes the bubble radius	41
4.9 Drainage of DTAB solution films	46
4.10 Drainage of SDS solution films	48
4.11 Drainage of $C_{8}E_4$ solution films	53
4.12 Drainage of Pluronic P-123 solution films	55
4.13 Drainage at the top of a spherical bubble of Pantene Shampoo solution...	57
4.14 Drainage at the top of spherical bubbles of DTAB solutions	57
5.1 Schematic of the experimental setup	68
5.2 Surface tension measured using the Wilhelmy plate technique	69
5.3 Aggregate size distribution for 0.5 %v/v solutions of: (a) SILWET L-77, (b) SILWET L-7607, (c) BREAK-THRU S 278, and (d) BREAK-THRU S 233.....	70
5.4 Drainage of the plane films of the superspreader SILWET L-77 solutions	73
5.5 Drainage of the superspreader SILWET L-77-1.0 film	75

LIST OF FIGURES (continued)

<u>FIGURE</u>	<u>PAGE</u>
5.6 Drainage of the superspreader BREAK-THRU S 278 solution films	77
5.7 Drainage of the non-superspreader SILWET L-7607 solution films	79
5.8 Drainage of the non-superspreader BREAK-THRU S 233 solution films	81
5.9 Drainage of (a) the superspreader Silwet L-77, and (b) its “cousin” non-superspreader Silwet L-7607. Drainage of the superspreader (c) BREAK-THRU S 278, and (d) its “cousin” non-superspreader BREAK-THRU S 233	83
5.10 Sketch of a plane vertical surfactant film on a wire frame	85
5.11 The dependences of M and p_{disj} on the film thickness h for the superspreader SILWET L-77 solutions	91
5.12 Disjoining pressure versus the film thickness for SILWET L-77 solutions of different concentration	92
5.13 The dependences of M and p_{disj} on the film thickness h for the superspreader BREAK-THRU S 278 solutions	95
5.14 Disjoining pressure versus the film thickness for BREAK-THRU S 278 solutions of different concentration	96
5.15 Sketch of fluffy surfaces of the film formed by long hanging superspreader bilayers	98
6.1 Filling gravity settler using the funnel-hose system. The system is raised with the foam height so that the foam exiting the hose is at the top of the foam column	106
6.2 Sketch of the experimental setup	106
6.3 Images taken during drainage of 0.5 %v/v SILWET L-77 with 0.5 %v/v USG stable soap foam	108
6.4 Dimensionless volume of liquid drained as function of time from foam generated	110
6.5 Volume of liquid drained as function of time from foam generated	112
6.6 Foamability of trisiloxane surfactants at different concentrations	113

LIST OF FIGURES (continued)

<u>FIGURE</u>	<u>PAGE</u>
7.1 Surface tension measured using the Wilhelmy plate technique for mixed solutions	119
7.2 (a) Schematic of the experimental setup for drainage of plane vertical films. (b) Filling gravity settler using flexible funnel – hose system, and (c) Drained liquid from the foam recorded using a CCD camera	120
7.3 Drainage of the SDS-alone solution films	123
7.4 Drainage of the superspreader SILWET L-77-alone solution films	126
7.5 Disjoining pressure of the SILWET L-77-alone solution films	127
7.6 Drainage of (a) S2.0, (b) L0.1, and (c) SL12-0.5 plane film	130
7.7 Drainage of the plane thin films of SDS/SILWET L-77 mixed solutions	133
7.8 Disjoining pressure of the SDS/ SILWET L-77 mixed solutions	137
7.9 Drainage of plane films of S4.0 (line and data 1: SDS alone), L1.0 (line and data 2: SILWET L-77-alone), and SL4-1.0 (line and data 3: SDS/SILWET L-77 mixture)	138
7.10 Volume of liquid drained for the first 1500 s from the films of (a) the SDS-alone, and (b) superspreader SILWET L-77-alone solutions	139
7.11 Drainage curves for different concentrations of (a) the SDS-alone solutions, and (b) SILWET L-77-alone-solutions	140
7.12 Foamability of (a) the SDS-alone, and (b) the SILWET L-77-alone solutions. The symbols represent the experimental data, which are spanned by curves for convenience	142
7.13 (a) Volume of liquid drained for the first 1500 s, and (b) drainage curves for the 4 mM SDS/SILWET L-77 mixture solutions	143
7.14 (a) Volume of liquid drained for the first 1500 s, and (b) drainage curves for the 8 mM SDS/SILWET L-77 mixture solutions	146
7.15 (a) Volume of liquid drained for the first 1500 s, and (b) drainage curves for the 12 mM SDS/SILWET L-77 mixture solutions	147
7.16 Foamability of the SDS/SILWET L-77 mixture solutions	148

LIST OF FIGURES (continued)

<u>FIGURE</u>	<u>PAGE</u>
8.1 Slump tests of gypsum-foam slurry for the samples with and without superspreader in foam water	160
8.2 Gain in WSR on addition of 0.1 % superspreader to foam water to obtain the same slump diameter	162
8.3 Temperature curves during setting of the gypsum-foam slurry for samples (a) without and (b) with 0.1% superspreader SILWET L-77 in foam water	164
8.4 Crushing test results for samples without and with 0.1% superspreader SILWET L-77	165
8.5 Dry densities of samples.....	167
8.6 Normalized strength test results	168
8.7 Slump tests of gypsum slurry samples with increasing concentration of superspreader SILWET L-77	170
8.8 Temperature curves during setting of the gypsum slurry for samples with increasing concentration of superspreader SILWET L-77	171
8.9 TRS curves for different trials of gypsum slurries	171
8.10 Crushing test results for samples with increasing concentration of SILWET L-77 in gypsum water	172
8.11 Dry densities of samples with increasing concentration of superspreader in gypsum water	171
8.12 Slump tests of gypsum-foam slurry for the samples with and without superspreader in foam water	174
8.13 Gain in WSR on addition of 0.1 % superspreader to foam water to obtain same slump diameter	175
8.14 Temperature curves during setting of the gypsum-foam slurry for samples (a) without and (b) with 0.1% superspreader SILWET L-77 in foam water	177
8.15 Crushing test results for samples without and with 0.1% superspreader SILWET L-77	178
8.16 Dry densities of samples with and without superspreader in foam water	179

LIST OF FIGURES (continued)

<u>FIGURE</u>	<u>PAGE</u>
8.17 Normalized strength test results	180
9.1 (Left) Schematic of the experimental setup. (Right) Images of the time evolution of a vertical foam film	184
9.2 Drainage of plane films of SDS – salt solutions: (a) 11 mM LiCl, (b) 11 mM NaCl, and (c) 11 mM KCl	185
9.3 Drainage of plane films of SDS – salt solutions	187
9.4 The dependence of the lifetime of the foam lamella on the concentration of the added salt in the presence of 0.5 mM SDS	188
9.5 The lifetime of the foam lamella versus the specific energy of counter-ion adsorption for films stabilized	189
9.6 Surface tension isotherms of 0.5 mM SDS + added salts. The relative experimental error is ± 0.2 mN/m	192
9.7 Adsorption of DS ⁻ ions on the air/water interface of 0.5 mM SDS as a function of the concentration of added salt (MCl, M=Li, Na, K)	193
9.8 Velocity of film drainage versus surface tension of air/water interface for the three particular cases – 0.5 mM SDS + LiCl, 0.5 mM SDS + NaCl, and 0.5 mM SDS + KCl	195
9.9 (A) Volume of liquid drained for the first 2000 s and (B) drainage curves for 0.5 mM SDS + 10 mM KCl, 25mM KCl, 35 mM KCl and 45 mM KCl	197
9.10 (A) Volume of liquid drained for the first 3500 s and (B) drainage curves for 0.5 mM SDS + 500 mM LiCl, 700 mM LiCl, 900 mM LiCl and 1100 mM LiCl... ..	199
9.11 (A) Volume of liquid drained for the first 3500 s and (B) drainage curves for 0.5 mM SDS + 90 mM NaCl, 200 mM NaCl, 300 mM NaCl and 400 mM NaCl... ..	200
10.1 (a) Schematic of the experimental setup. (b) The photograph of the film-supporting frame with the interferometric pattern seen on the film	205
10.2 Film thickness near the top versus time for the 0.5 mM non-ionic surfactant C ₈ E ₄	206

LIST OF FIGURES (continued)

<u>FIGURE</u>	<u>PAGE</u>
10.3 Film thickness near the top versus time for the 16 mM anionic SDS films. Line 1-no voltage applied, 2-top electrode is cathode at voltage of 40 V, 3-top electrode is anode at voltage of 40 V	208
10.4 Film thickness near the top versus time for the for the 30 mM cationic DTAB films. Line 1-no voltage applied ($\tau = 42$ s), 2-top electrode is cathode at voltage of 40 V ($\tau = 56$ s), 3-top electrode is anode at voltage 40 V ($\tau = 85$ s)	209
10.5 Measured electric current versus time for plane films of (a) 6 mM, (b) 10 mM, and (c) 16 mM SDS solutions	210
10.6 Specific conductance versus time t for (a) 6 mM, (b) 10 mM, and (c) 16 mM SDS solution films	212
10.7 Specific conductance for different concentrations of SDS when the top electrode was cathode (Case I)	214
10.8 (a) Sketch of the experiments with gravity settler. (b) Volume of liquid drained. (c) Drainage curves	224
10.A1 The imposed electric field structure	231

SUMMARY

The goal of this work is to elucidate drainage of thin surfactant films. The interplay between gravitational and concentrational Marangoni forces principally drives drainage of the solution from such thin films. Other forces and effects, such as the disjoining pressure, ionic effects and electric forces can be introduced depending on the type of surfactant, addition of salts or the application of the electric potential. They can play a significant role in the drainage process of such thin films. Different surfactant solutions can then be understood in terms of their physical parameters like the characteristic time of drainage, the overall surface elasticity and the disjoining pressure within their thin films. Foam stability of surfactant solutions depends on drainage of liquid between the lamellae connecting two gas bubbles and an insight into planar film drainage would help in understanding the physical phenomena in foam. The foamability and foam stability of different surfactant solutions can thus be predicted from the physical parameter values determined from planar film drainage.

Several fundamental questions are associated with dynamics of such thin surfactant films. The fundamental question that arises is how the gravitational and concentrational Marangoni forces affect the thinning down of such films in time. The role of concentration and nature of surfactant in the drainage characteristics is also of significant importance. How does surface elasticity and the disjoining pressure affect gravitational drainage? How will the characteristics of planar film drainage correspond to drainage of foams? Does salt addition to such surfactant solutions enhance or stabilize drainage? How would drainage be affected due to the application of an external electric field? This work answers all the questions raised above both experimentally and theoretically.

The first part of this thesis describes the development of a novel straightforward experiment using microinterferometry to measure the time evolution of planar film thickness in gravitational drainage of different surfactant solutions. A corresponding theory is developed accounting for the surface elasticity and relating it to the characteristic drainage time, which can be determined experimentally. The measured values of the surface elasticity for different surfactant solutions are compared to the available data from literature and found in agreement with them. This establishes the tool developed in this thesis as an adequate tool for measuring the surface elasticity.

In the following chapter of this thesis, trisiloxane surfactants known as superspreaders are studied as the foam-forming materials. The superspreader films, though not being in contact with any nonwetable surface (where superspreaders are presumably active), have distinctly different drainage characteristics as compared to the ordinary surfactants. They show complicated interferometric color patterns and remarkable stabilization of the latter stages of drainage, causing them to last much longer than those of their counterpart “cousin” non-superspreaders or the ordinary surfactant. This dramatic stabilization is rationalized to result from the high disjoining pressure generated by large bilayer aggregates of the superspreader “hanging” from the film surfaces. The disjoining pressure in such films was found from the measurement of the experiments conducted in the present work.

The next section of this thesis deals with reducing water intake for manufacturing of wallboards, which uses the injection of stable superspreader foams into gypsum slurries. In other words enhancing fluidity of gypsum-foam slurry is facilitated by superspreader presence. Wallboard manufacturing is a multi-billion-dollar industry and gypsum wallboard is one of the most preferred indoor construction product. Over the years, the drive has been in

producing lighter wallboards, with the voids inside providing the excellent thermal and acoustic properties. For this purpose, the gypsum stucco (along with other additives) is initially mixed with water followed by foam injection. The porous light wallboards are created with pores resulting from the injected foam. The entire mixing process occurs in less than a minute, since reaction of gypsum with water is a fast process and leads to gradual drying of the entire slurry. Thus the foam characteristics, its stability, bubble size and drainage are a primary concern in manufacturing of wallboards. This section of the thesis involves experiments with a stable superspreader foam being added to gypsum slurry, while maintaining both the foam and dry wallboard characteristics same as before. This results in lesser water requirement for manufacturing wallboards, thereby saving significant costs in water and energy consumption.

In the subsequent section of this thesis the effect of the addition of ionic salts on the drainage characteristics of foam is elucidated. The addition of ionic salts initially stabilizes the surfactant films up to a critical concentration, beyond which they act as defoaming agents. In this work the critical salt concentration predicted by calculating the critical surfactant adsorption level is compared with the present experimental results.

To explore whether the electrokinetic effects on the gravitational drainage of thin planar surfactant films are significant, the experimental setup initially designed was modified to introduce electrodes on the top and bottom parts of the film. Contrary to general expectations and inaccurate data and claims in the literature that only a single polarity would lead to film stabilization, whereas flipping polarity would lead to destabilization, we observed for the first time film stabilization in both cases. A theoretical explanation of these results is proposed.

In the final part of this thesis, in addition to measuring the time-dependant film thickness, the electric current through the film is also measured and the electric conductivity is calculated. The experimental results revealed novel physical phenomena never explored before in drainage of thin surfactant films.

CHAPTER 1

INTRODUCTION

Soap bubbles and soap films have fascinated mankind for centuries. As Boys (1958) in his interesting and lucid treatise on soap bubbles puts it, everyone has occasionally blown a soap bubble and admired its brilliant colors and perfect shape. Collection of such several hundred bubbles leads to formation of foam, which is primarily dispersion of gas in liquid. The formation of foams, bubbles and thin lamellae films are associated with surfactants [Mysels (1959)], molecules which are amphiphilic in nature containing hydrophilic and hydrophobic parts.

1.1 History of soap films

One of the earliest treatises on soap films can be dated back to Plateau (1873). Ever since, numerous studies have been conducted on the behavior of foams and individual films, the latter being primarily to investigate factors affecting the collective behavior of many such films in a foam [Mysels (1959)]. The color changes in such thin surfactant or soap films were studied extensively by Newton (1704) who also recognized the existence of black films, or Newton's black ring as we know them today. In fact, the observation of the interference colors of such thin films led to the initial understanding of the wave properties of light [Mysels (1959); Jenkins and White (1957)]. Drainage of films from a variety of solutions was studied by Miles et al. (1950), distinguishing between fast draining films of low surface viscosity and slow draining ones of higher surface viscosity [Mysels (1959)]. The beautiful interferometric colors during the early stages of such thin films drainage gradually reveals areas of black films [Lawrence (1929) and Mysels (1959)]. Over the last few decades, soap films, their drainage and the physical forces

responsible for it have been extensively studied and documented [Boys (1958); Mysels (1959) and Isenberg (1992)].

1.2 Foam

A foam is a two phase system having gas entrapped within a liquid [Weaire and Hutzler (2001)]. The lifetime and stability of foam depend on stabilizing the thin liquid lamellar films against rupture. Foams are in a metastable state, implying that after the formation of foam, different physical phenomena like liquid drainage, bubble coalescence (foam coarsening or the Ostwald ripening), and bubble evolution lead to a gradual disappearance of the foam.

Liquid foams are present practically everywhere in everyday life: in soaps, cleaning agents, shaving products, and beverages [Weaire and Hutzler (2001)]. They also have applications in a wide variety of industries. Foams are an essential part in fire-fighting. Foam filtration is used for separation of impurities in chemical engineering. Enhanced oil recovery is another industry where foam finds wide applications. Different solution mixtures can be separated using foam fractionation. Food foams, used in everyday life, are usually made in kitchen by beating or whipping. Foams are also an important component of the indoor construction materials. They are used for manufacturing dry wallboards for making them light and thermally insulating.

1.3 Thesis objectives

Though soap films and foam have been studied extensively over the last 50 years, the basic physical mechanisms governing the drainage of thin lamellar films that in turn govern the stability of foam are still not properly understood. Different surfactant solutions are used for their

foamability and stability in the industry without an in-depth knowledge of the dynamics of foam drainage. The research aims of this work are to understand drainage of thin liquid surfactant films, the forces that play a role, and how addition of salts and other forces like those related to the electrokinetic phenomena can stabilize or destabilize such thin films. The results are then used to evaluate film stability and to correlate it to foamability and foam stability. Chapter 4 aims at elucidating interfacial properties like surface elasticity of surfactant films from measurements of time-dependent film thickness. The effect of disjoining pressure on the stability of foam films is investigated in chapter 5. Chapters 6 and 7 study the effects of individual and mixed surfactants on foam. The enhancement in fluidity of gypsum slurries for the manufacturing of wallboards involving foam is investigated in chapter 8. Finally, the effects of addition of salts and of the electrokinetic phenomena on planar foam films are studied in chapters 9 and 10, respectively. Conclusions are drawn in chapter 11.

CHAPTER 2

BACKGROUND AND LITERATURE SURVEY

2.1 Gravitational drainage of thin films

(This section has been previously published in Sett et al. (2013)).

Liquid drainage from foam films is a complex, intriguing and practically important phenomenon. It is associated with the interplay of viscous flow of solvent, diffusion and convection of surfactant molecules, their adsorption and desorption at the film interfaces and the associated changes in the surface tension, as well as the appearance of the concentration-dependent surface tension gradients leading to the Marangoni effect equivalent to the surface elasticity. In addition, surface viscosity of thick (e.g. protein-stabilized) interfaces can also be of importance. Moreover, when the draining films become sufficiently thin (about and below 100 nm), the disjoining pressure becomes important and its steric, electric and van der Waals components affect the film thinning and contribute either to its deceleration (stabilization) or localized acceleration (destabilization). Such a plethora of physical phenomena entangled with the solvent drainage driven by different fluid mechanical mechanisms (capillary pressure, gravity, wave propagation) kept foam films in focus for at least 60 years. Different physical aspects of the prior foam drainage research are covered in several monographs, collective works and review articles [Sheludko (1967); Derjaguin et al. (1987); Derjaguin (1989); Levich (1962); Israelachvili (1992); Edwards et al. (1991); Langevin and Sonin (1994); Valkovska et al. (2002); Weaire and Hutzler (1999); Morrison and Ross (2002); Miller and Liggieri (2009); Exerowa and Kruglyakov (1998); Nguyen and Schulze (2004)], whereas the applied aspects of foam

stabilization by surfactants, proteins and nanoparticles are exposed in a number of review articles [Murray and Ettelaie (2004); Hunter et al. (2008) and Dickinson (2010)].

Capillary-driven drainage of horizontal circular films trapped in the Scheludko cell was one of the main tool in studying surface elasticity of foams [Langevin and Sonin (1994); Exerowa and Kruglyakov (1998); Karakashev et al. (2005); Karakashev et al. (2007); Karakashev et al. (2008a); Karakashev et al. (2008b); Karakashev and Nguyen (2009); Karakashev and Ivanova (2010a); Karakashev et al. (2010b); and Karakashev et al. (2011)]. The micro-interferometry, assisted with CCD camera recording and digital filtering allowed for elucidation of the capillary drainage of parallel-surface and wavy films down to the black films of thicknesses of the order of 30 nm [Karakashev et al. (2005); Karakashev et al. (2007); Karakashev et al. (2008b); Karakashev and Nguyen (2009); and Karakashev and Ivanova (2010a)]. Not only fully freely-suspended films with two free surfaces were studied [Karakashev et al. (2005); Karakashev et al. (2007); Karakashev et al. (2008b); Karakashev and Nguyen (2009); and Karakashev and Ivanova (2010a)], but also capillary drainage of films with one free surface supported on a glass slide was explored [Karakashev et al. (2011)]. These results were used to evaluate the validity ranges of the existing theories of capillary-driven film drainage including the effects of the different components of the disjoining pressure [Karakashev et al. (2008a) and Karakashev et al. (2010b)]. An important result of the capillary drainage experiments in the Scheludko cell was the elucidation of the surface elasticity characterizing the strength of the surfactant-concentration-driven Marangoni effect. The role of the dissolved air bubbles on the film rupture was also elucidated.

Gravity-driven drainage of spherical bubbles located at the free surface of a liquid pool was studied experimentally and theoretically for polymer melts where a long life of a bubble is

associated with very high viscosity, rather than with the presence of surfactants in distinction from the soap film/bubbles [Debregeas et al. (1998)].

Surprisingly, gravity-driven drainage attracted much less attention than the capillarity-driven one. Formation of a “young” soap film withdrawn on a vertically-oriented wire frame was addressed as a phenomenon in which a film is still connected to the pool and supported against gravity by the osmotic pressure, while convection driven by gravity was neglected de Gennes (2001). Drainage of foam in a gravity settler is associated with gravity-driven viscous flow of water along the Plateau borders [Koehler et al. (2000)]. This type of foam drainage was recently revisited in the framework of the consolidation theory which includes viscous resistance to the gravity-driven flow and the overall medium elasticity associated with air in the bubbles but does not incorporate the film surface elasticity (the Marangoni effect) Jun et al. (2012). In addition, flowing foams in porous media reveal plethora of physical mechanisms responsible for foam rupture, such as coarsening due to air diffusion through the liquid lamella from smaller to larger bubbles, various instability mechanisms, etc. [Kornev et al. (1999)] but also expose the importance of the concentration-driven Marangoni effect [Bazilevsky and Rozhkov (2012)].

2.2 Superspreaders and their aggregates

(This section has been previously published in Sett et al. (2014a)).

The aqueous solutions of trisiloxane-(poly)ethoxylate surfactants are widely applied as agricultural adjuvants, solid modifiers, and cleaners. Such surfactants are commonly denoted as $M(D'E_nOMe)M$, with $M-D'-M$ being the trisiloxane hydrophobe, E_n - the ethylene oxide, Me - the methyl group, and O – oxygen [Venzmer (2011)]. Water drops with added superspreaders easily spread on hydrophobic surfaces such as polyethylene (PE) or polypropylene (PP). The

superspreading ability of trisiloxane-(poly)ethoxylate surfactants is determined by the length of the (poly)ethylene oxide group. Two drastically different “cousin” types of trisiloxane-(poly)ethoxylate surfactants with $n=7.5$ (which is the superspreader known under the product name SILWET L-77; ref 1) and $n=16$ (which is the non-superspreader, denoted as $M(D'E_n)M$ under the product name SILWET L-7607, [Walderhaug and Knudsen (2008)]) are distinguished. The superspreader BREAK-THRU S 278 has a similar nominal structure as that of SILWET L-77 [Venzmer (2013)]. Its “cousin” non-superspreader BREAK-THRU S 233 has an OH-terminated polyether group containing both ethylene oxide and propylene oxide [Venzmer (2013)]. The length of the poly(ethylene oxide) increases, thereby indicating a larger hydrophilic head group for the non-superspreaders SILWET L-7607 and BREAK-THRU S 233 than that of the superspreaders SILWET L-77 and BREAK-THRU S 278, respectively.

The physico-chemical origins of the superspreading on hydrophobic surfaces are debated [Venzmer (2011); Walderhaug and Knudsen (2008); Venzmer (2013)]. Formation of bilayer structures was assumed for superspreaders and argued to be the reason of the superspreading effect on hydrophobic surfaces [Venzmer (2011)]. On the other hand, the “cousin” non-superspreaders presumably do not form large-scale bilayer structures above cmc but rather ordinary micelles [Venzmer (2011)]. Superspreading is frequently related to the assumed propensity of superspreaders to settle onto hydrophobic substrates close to the moving contact line, which presumably leads to an increase in surface tension there, the increased concentration-gradient-related Marangoni effect, and an enhanced spreading [Karapetsas et al. (2011) and Maldarelli (2011)].

2.3 Drainage of foam

(This section has been previously published in Sett et al. (2014b)).

Foam is a large conglomerate of gas bubbles, separated from each other by thin liquid lamellae. It has wide applications in chemical, pharmaceutical, construction, textile and food industries and in the enhanced oil recovery [Kornev et al. (1999); Koehler et al. (2000); and Prud'homme (1996)]. Foam is a material, which is sustained in a quasi- equilibrium state, which can deteriorate or vanish in time due to a number of physical processes, among which are liquid drainage, the Ostwald ripening and bubble coalescence being primary [Exerowa and Kruglyakov (1998)]. Gravitational drainage of water from foam occurs along the Plateau borders of the lamellae [Koehler et al. (2000) and Jun et al. (2012)]. Various surfactants, both ionic and non-ionic are employed to stabilize foams, and different techniques are used to measure the liquid content in foam during drainage [Germick et al. (1994); Ramani et al. (1993); and Magrabi et al. (2001)]. However, due to complexity of the drainage process it is hard to reach any general conclusion regarding the link between foamability, which is the volume of foam generated from a certain initial volume of surfactant solution and the overall foam stability, which is the time the structure of the generated foam lasts before the entire entrapped air is lost .

The thin film drainage is a useful tool in characterizing thin surfactant solutions and it has been extensively employed for more than 50 years [Sheludko (1967); Derjaguin et al. (1987); Derjaguin (1989); Israelachvili (1992); Langevin and Sonin (1994); Miller and Liggieri (2009)]. This technique reveals the effects of surfactant type, concentration, additives, temperature and other variables on foam stability under the conditions close to many important applications, and thus attracted significant attention in the past [Mysels et al. (1959); Mysels et al. (1961); Mysels and Cox (1962)]. In the framework of the thin film drainage technique an in-depth information

on the effect of each of the above-mentioned parameters can be elucidated, which is an uneasy task for the methods using the gravity settler techniques [Jun et al. (2012)]. The concentration-related Marangoni effect, which is responsible for the surface elasticity [Langevin and Sonin (1994); Stubenrauch and Miller (2004)] and the effects related to the internal energy of surfactant generating disjoining pressure [Bergeron (1997) and Santini et al. (2007)] were measured and characterized using the thin film drainage technique. Gravitational drainage technique was introduced for the first time to measure surface elasticity of the ordinary surfactants (ionic and nonionic surfactants, which form micelles) [Sett et al. (2013)] and the disjoining pressure of superspreaders (nonionic surfactants, which form bilayers) [Sett et al. (2014a) in plane films using micro-interferometric technique. In the following work Saulnier et al. (2014), this technique was adopted to study film stabilization by some other ordinary surfactants, and a correlation between the foam stability and foamability of surfactant solutions. However, no correlation was established between thin film stability and foamability for the system studied [Saulnier et al. (2014)].

Foam drainage using a mixture of surfactants has also been studied [Carey and Stubenrauch (2010); Zhao and Zou (2013); Carey and Stubenrauch (2013); and Theander and Pugh (2003)]. The aqueous foams generated from a mixture of non-ionic and ionic surfactants revealed foamability similar to those of the individual surfactants [Carey and Stubenrauch (2010); Carey and Stubenrauch (2013)]. Notably, the foam stability of the mixture of surfactants was higher than those for the either one of the individual surfactants.

2.4 Ion specific effects – Hofmeister series

(This section has been previously published in Sett et al. (2015).

Since the middle of the 19th century, specific effects of salts on the physicochemical properties of solvents, solutes, dispersed systems and biological cells have been widely studied. Arrhenius and Kreichgauer [Kunz et al. (2004a)] reported that different inorganic salts affect the inner friction of their aqueous solutions. On the contrary, Poiseuille (1844) reported that some salts increase the inner friction of their aqueous solutions, while others decrease the latter, although these effects appeared to be difficult to distinguish. Ostwald (1886) reported that lowering the vapor pressure of water by the same concentration of different salts was almost the same. However later he established that the vapor pressure does depend weakly on the type of the added salt. Similarly, Raoult (1888) reported almost identical lowering of freezing point of water caused by addition of different salts and found small differences that depend on the type of salt. Moreover, he reported that the molecular diffusion of the inorganic salts against water depends on both the inner friction of their aqueous solutions and their water absorbance. He established differences in the molecular diffusion of different salt molecules in water under identical conditions, but the results remained doubtful due to the complexity of the experiments conducted at that time.. Hugo de Vries [Pringsheim et al. (1858)] determined the behavior of live plant cells in different salt solutions. He reported that the protoplasm of the cell peels away from the cell wall, leaving gaps between the cell wall and the membrane (plasmolysis) at certain specific concentration of each salt. Sometime later, Hamburger (1886) confirmed similar effects of salt concentration seen on red blood cells. Hence, the first instances of salt specific effects were thus mentioned, though it appeared that the effects were pronounced only on living cells. The most significant and important contribution in this field was made by Hofmeister [Kunz et

al. (2004a)]. He and his team [Lewith (1887); Hofmeister (1888a); Hofmeister (1888b); Limbeck (1888); Hofmeister (1890); Hofmeister (1891); and Munzer (1898)] published a whole series of seven papers entitled “About the science of the effect of salts”. They established that the blood proteins precipitate at specific concentrations of added salts, with some salts being stronger precipitators than other ones. The precipitation of the proteins were caused by both, the cations and the anions of the salt, though the contribution by the anions were stronger. With the development of experimental methods and techniques, these were confirmed recently by means of small angle X-ray scattering (SAXS) on interacting protein molecules [Finet et al. (2004)]. Moreover, it was found that the salt ions affect the properties of the protein molecules in a specific way [Bostrom et al. (2004)]. The findings of Hofmeister and his team were used for building of a series of anions and cations ordered according to their precipitation ability:

Cations: $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{NH}_4^+ < \text{NMe}_4^+$

Anions: $\text{ClO}_4^- < \text{BF}_4^- < \text{NO}_3^- < \text{Br}^- < \text{Cl}^- < \text{OH}^- < \text{F}^- < \text{CH}_3\text{COO}^-$

The above-mentioned series is known as the Hofmeister series [Leontidis (2002); Bauduin et al. (2004); Kunz et al. (2004b); Kunz (2010); and Ivanov et al. (2011)]. Hofmeister established the same effects of the added salts on the stability of aqueous suspension of isinglass, colloidal ferric oxide, and sodium oleate [Hofmeister (1888b)] . With these findings as the backbone, a whole new interdisciplinary field of research was thus established. To name a few such contributions, it was recently found that the ions effect the catalytic activities of some enzymes in specific ways [Bauduin et al. (2004)], thus being important in medicine, pharmacy and bio-physics.

While Hofmeister was establishing the Hofmeister series, almost at the same time Setschenow established independently [Setschenow (1889)] that the organic solutes in water

precipitate (salt out) at certain concentration of added sodium chloride. He arrived at an empirical equation predicting the solubility of many non-electrolyte organic substances at different concentrations of sodium chloride. He introduced the “Setschenow’s empirical constants”, which are specific for individual organic substance. It was established much later [Gorgenyi et al. (2006)] that both the anions and the cations of the salt have specific contributions to the values of “Setschenow’s constants”.

A few years after Hofmeister,, Heydweiller (1910) found that the addition of salt increases the surface tension of the air/water interface in surfactant free solutions. Moreover, he established that the relative effect of the ions on the surface tension of the air/water interface is in close accordance with the Hofmeister series, thus concluding that the two phenomenas are related. His discovery was followed by significant contributions by Langmuir (1917), Wagner (1924), Onsager and Samaras (1934), Jones and Ray (1935); (1937); (1941a); (1941b); (1942) and many other renowned scientists since the 1930s to the present [Dole (1938); Dole and Swartout (1940); Randles (1957); Jarvis and Scheiman (1968); Bhuiyan et al. (1991); Weissenborn and Pugh (1996); Bostrom et al. (2001); Jungwirth and Tobias (2001); Markin and Volkov; Bostrom et al. (2005); Dos Santos and Levin (2011); Slavchov and Novev (2012); Markovich et al. (2014); Karakashev et al. (2001); Ennis et al. (1995); Kjellander (1995); and Sakai (1988)]. Their studies revealed complicated interactions between the ions of the salt and the air/water (oil/water) interface resulting in the formation of spatially separated cation-depleted and anion-depleted layers at the very inter-phase boundary, thus increasing its surface tension. The parameters of these layers and the corresponding increase of the surface tension depend on the types of ions in the salt. Considerable efforts have been put into developing the statistical

mechanical models for describing the behavior of strong electrolytes in close proximity to the interface boundary.

The Poisson–Boltzmann (PB) theory treats the ions in close proximity of charge interfaces in the classical way. It is good for predicting the behavior of univalent ions which are not too close to the interface for low electrolyte concentrations. Unfortunately, this theory breaks down at the very surface at higher surface charge densities. Consequently, further development with fewer approximations of the PB equation is needed to describe a more realistic picture. More importantly, this theory does not account for any differences between the different counterions, while experiments reveal clear differences in interactions at either biological or non-biological surfaces. The “counterion effect” is directly related to the Hofmeister series for cations or anions [Koelsch et al. (2007)].

Bhuiyan et al. (1991) described the ions from the diffusive part of the double layer as hydrated spheres in the limits of the primitive model of aqueous solutions of electrolytes, while the surface was modelled like idealized dielectric discontinuity. Furthermore, Ennis et al. (1995) introduced the pair correlation function in a form identical to the Debye–Hückel theory and renormalized the charges of the ions in form of “dressed ions” instead of the bare ion charges. According to these works, the “ion free layer” model appears to be crude. Instead, it is more probable that the ion concentration profile from the fluid interface is more complex and can even go through several abrupt oscillations before the bulk ion concentration is reached. The increment of the surface tension has been related to the hydration radius [Weissenborn and Pugh (1996)]. In this respect, it is important to mention the experimental work of Sakai (1988), who reported the variation in the relative concentration of ions as a function of the relative distance

from the bubble surface. He measured the concentration profile of Mg^{2+} ions from aqueous solution of MgCl_2 as a function of the distance from the bubble surface. The experimental results showed that at the relative distance of 0.2 (the distance for the bulk concentration is taken to be 1) from the interface, the concentration of Mg^{2+} is at least two times higher than the concentration in the bulk solution. At shorter distances, the concentration of Mg^{2+} is at least three times higher. This general picture of the concentration profiles of the ions in close proximity to the surface of the bubble was challenged in the last decade and was awarded as the highlight of the year by Science [Tobias and Hemminger (2008)] some years ago. Moreover, it was established that a strong salt-specific effect modifies the dynamic interaction between such bubbles. In this sense, it was found out that some salts impedes the coalescence of bubbles in surfactant free solutions above certain specific concentration for each salt, while others do not have any such effect [Marrucci and Nicodemo (1967); Prince and Blanch (1990); Craig et al. (1993a); Craig et al. (1993b); Pashley and Craig (1997); Karakashev et al. (2008c)]. The physical reason for these effects are still obscure, despite several attempts for explaining the phenomena [Prince and Blanch (1990); Marrucci (1969); Weissenborn and Pugh (1995a); Weissenborn and Pugh (1995b); Marcelja (2006)]. Moreover, the mean activities, the osmotic coefficients [Pitzer (1973); Pitzer and Mayorga (1973); Pitzer and Mayorga (1974); Pitzer and Kim (1974)] and the solubility of salts [Kunz et al. (2004)] in their surfactant free solutions appeared to be salt-specific as well.

2.5 Electrokinetic effect in thin surfactant films

2.5.1 Electrokinetic effect

Electrokinetic phenomena have recently been in focus as an attractive means of transport in nanochannels and nanopores [Yossifon and Chang (2008); Chang and Yeo (2010); Chang et al. (2012)]. In these and several other works [Squires and Bazant (2004); Squires and Quake (2005)] electroosmosis was demonstrated as an effective driving mechanism in flows in nanochannels and nanopores with solid walls. Liquid electrolytes are polarized near solid walls with the embedded or induced charges and the electroosmotic flows arise in such polarized near-wall layers when they are subjected to an imposed electric field strength component parallel to the wall. An intriguing opportunity is opened by subjecting vertical films of cationic solutions to the electric field in the vertical direction, which revealed the electroosmotic flows directed against gravity and resulting in the film thickening, which was attributed to an electrical analog of the Landau-Levich-Derjaguin withdrawal by a moving solid surface [Bonhomme et al. (2013)].

2.5.2 Micellization of surfactants

(This section has been previously published in Sett et al. (2016)).

Extensive studies were conducted on Sodium Dodecyl Sulfate (SDS) and other dodecyl sulfate micellization using small-angle neutron scattering [Hayter and Penfold (1983); Berr et al. (1986); Quina et al. (1995); and Bezzobotnov et al. (1988)], time-resolved fluorescence quenching [Croonen et al. (1983)], stopped-flow experiments [Baumgardt et al. (1982)], small-angle light scattering [Young et al. (1978) and Xia et al. (1992)], dynamic light scattering [Brown et al. (1992); Schurtenberger et al. (1983); Dorshow et al. (1983); Cates and Candau

(1990)], spectroscopy methods [Dominguez et al. (1997)], conductivity measurements [Dominguez et al. (1997) and Jones (1967)], and surface tension measurements [Jones (1967)]. These works revealed the micelles structure [Hayter and Penfold (1983); Young et al. (1978)], the effect of different counter-ions on the Stern layer structure [Berr et al. (1986)], elucidated growth of micelles and inter-micellar interactions with increasing SDS concentration [Quina et al. (1995); Bezzobotnov et al. (1988); Croonen et al. (1983); Schurtenberger et al. (1983); Dorshow et al. (1983); Cates and Candau (1990)], as well as interactions of SDS micelles with polymers [Xia et al. (1992); Brown et al. (1992); and Jones (1967)]. Similar works were also conducted on Dodecyltrimethylammonium Bromide (DTAB) micellization [Bergstrom and Pedersen (1967); Bahri et al. (2006); and Kale et al. (1980)].

CHAPTER 3

RESEARCH OUTLINE

3.1 Gravitational drainage of foam films

(This section has previously been published in Sett et al. (2013)).

Drainage of surfactant films can be gravity-driven or capillarity-driven. Capillarity-driven drainage has attracted significant attention over the years. Surprisingly, only a few works addressed gravity-driven drainage. This work aims at explaining the gravity driven drainage mechanism from surfactant films.

The aim of the present work is to study, both experimentally and theoretically, plane vertical soap films and hemi-spherical bubbles. The experiments were designed to measure thicknesses of such surfactant films using micro-interferometry kindred to those used in experiments in the Scheludko cell. Depending on the charge of the hydrophilic head and hydrophobic tail, surfactants can be cationic, anionic, or non-ionic. In this work, all three types of surfactants were used, namely cationic Dodecyltrimethylammonium Bromide (DTAB), anionic Sodium Dodecyl Sulfate (SDS), anionic Pantene shampoo which primarily contains sodium lauryl sulfate, non-ionic Tetraethylene Glycol Monooctyl Ether (C_8E_4) and non-ionic Pluronic (P-123). They were used at different concentrations, both below and above their respective critical micelle concentration (cmc). A theory is to be developed to explain the drainage mechanism and a new method was developed to measure the surface elasticity of the surfactant films. The measured surface elasticity should be compared with the experimental results on the above mentioned surfactants. The approach and results are novel, since to the best of our knowledge, none of the previous works dealt with such approach to measurements of

surface elasticity from film thickness variation. It should be emphasized that such technique in elucidating thin surfactant films is of significant importance for understanding foamability and foam stability of liquid foams which have applications in food processing, indoor construction materials, and in pharmaceuticals.

3.2 Drainage of planar vertical “superspreader” films

(This section has previously been published in Sett et al. (2014a)).

Superspreaders are a special type of trisiloxane surfactants which facilitate water spreading even on hydrophobic surfaces. Extensive research has been conducted to understand the mechanism of such spreading on solid surfaces. The present work deals with planar films of such superspreaders in aqueous solutions having no contact with any solid hydrophobic surface. Gravitational drainage of vertical films supported on a wire frame of two superspreaders SILWET L-77 and BREAK-THRU S 278 and their respective “cousin” non-superspreaders SILWET L-7607 and BREAK-THRU S 233 were studied. The superspreader films showed drastic differences with their counterpart “cousin” non-superspreaders. The superspreader films showed complicated dynamic “turbulent”-like interferometric patterns in distinction from the ordered color bands of the “cousin” non-superspreaders which were similar to those of the ordinary surfactants. Nevertheless, the superspreader films stabilized themselves at the thickness about 35 nm and revealed an order of magnitude longer life time before bursting compared to that of the “cousin” non-superspreaders. The self-stabilization of the superspreader films is attributed to significant disjoining pressure probably related to long superspreader bilayers hanging from the free surfaces. The scaling law for the disjoining pressure was found as $p_{\text{disj}}(h) \sim h^{-m}$ (with $m \approx 9-11$) for the sufficiently concentrated superspreader solutions, and as

$p_{\text{disj}}(h) \sim h^{-s}$ (with $s \approx 6$) for more dilute solutions (in both cases concentrations were above cmc). The non-superspreaders do not possess any significant disjoining pressure even in the films with thicknesses in the 35-100 nm range. The results show that gravitational drainage of vertical films is a useful simple tool for measuring disjoining pressure of such surfactant films.

3.3 Enhanced foamability of superspreader trisiloxane surfactants and their mixture with ordinary surfactants

(This section has previously been published in Sett et al. (2014b)).

Gravitational drainage from thin vertical films of superspreader surfactants reveal drastic stabilization in the later stages of drainage due to the high disjoining pressure generated by the large bilayer aggregates. The aim of the present work is to elucidate the effect of the superspreaders in free drainage of foam in a settler column. Also, gravitational drainage in a settler column is used to study the behavior of foams based on two-surfactant mixtures. Namely, solutions of the anionic Sodium Dodecyl Sulfate (SDS) and non-ionic superspreader SILWET L-77, and their mixtures at different mixing ratios are studied. It is found, for the first time to the best of our knowledge, that solutions having a longer lifetime in the vertical film drainage process also possess a higher foamability. Thus, we can correlate vertical planar film drainage to foam column drainage. An additional and unexpected unique result is that when using a mixed surfactant system, the foamability can be much greater than the foamabilities of the individual components.

3.4 Fluidity enhancement of gypsum-foam slurry

Wallboard manufacturing is a multi-billion-dollar industry involving complicated steps of manufacturing. The gypsum stucco along with other additives is initially mixed with water followed by injection of foam, which is then sandwiched between two papers leading to the final product. The water content added to gypsum stucco is more than doubled than that required for the equilibrium hydration of calcium sulfate in gypsum. This is because the entire slurry needs to flow through all the processes in the plant, get sandwiched between two layers of paper, before the excessive water can be evaporated and the finished dry wallboard can be formed. A large consumption of energy in the plant is thus required for drying the excessive water at the end of the process. The wallboard manufacturing industry is always interested in reduction of water and energy consumption, thereby reducing cost, while maintaining the same strength, density, and porosity of the finished wallboard. In the present work, more stable foam generated from superspreader solutions is injected into the gypsum slurry. Due to higher foamability of the superspreader solutions, same volume of foam can be generated from significantly lesser volume of solution, thereby reducing the total water required for wallboard manufacturing. The rate of reaction and fluidity of the gypsum slurries and the strength of the produced dry wallboard are tested and ensured that they remain unchanged.

3.5 Ion specific effects in foams

(This section has previously been published in Sett et al. (2015)).

In the present work, different concentrations of inorganic salts (LiCl, NaCl, and KCl) are added to a fixed concentration of SDS surfactant solution and gravitational drainage of planar vertical films and free drainage in settler column are experimentally studied. An unexpectedly

strong ion-specific effect of the counter-ions on the stability and the rate of drainage of the foam films as a function of the concentration of the specific salt are found. It is observed experimentally that the counter-ions stabilize the foam films up to a critical concentration, beyond which they destabilize them. The ordering of the destabilization is in the same order as the Hofmeister series, while the stabilization order is in the reverse order. Though the critical concentration is different for different salts, calculating the critical surfactant adsorption level allows one to predict the critical concentration of any salt. In this work, such theoretical prediction of the critical concentration of the salts is compared with our experimental results.

3.6 Electrokinetic stabilization of ionic surfactant films

(This section has previously been published in Sett et al. (2016)).

In the present work, gravitational drainage of vertical films of ionic surfactants supported on a frame with the upper and lower parts being electrodes is studied. The electric field introduces three additional physical phenomena: (i) the surface charge redistribution, which eventually changes surface elasticity, (ii) the electroosmotic flow in the diffuse layer, and (iii) pressure build-up near the electrode toward which the electroosmotic flow is directed. It is shown that stabilization of the films is possible either due to the traction imposed by the electroosmotic flow directed upward (against gravity), or due to the pressure build-up near the lower end of the frame, in cases where the electroosmotic flow is directed downward (in the gravity direction) and enters a dead end at the lower electrode.

CHAPTER 4

GRAVITATIONAL DRAINAGE OF FOAM FILMS

This chapter has been previously published in Sett et al. (2013).

Reprinted with permission from [Sett, S., Sinha-Ray, S., & Yarin, A. L. (2013). Gravitational drainage of foam films. *Langmuir*, 29(16), 4934-4947]. Copyright 2013 American Chemical Society.

4.1 Introduction

This work aims at the gravity-driven drainage of vertical films of surfactant solutions withdrawn on a frame from a pool, as well as at spherical bubbles located at the pool surface, with the special attention paid to the surface elasticity and its measurement. The next section describes the materials and the experimental setup, followed by a section on the theoretical aspects. This is followed by results and discussion and finally conclusions are drawn.

4.2 Experimental materials and methods

4.2.1 Materials

The following surfactants were used: Dodecyltrimethylammonium Bromide, DTAB, with molecular weight $M_w = 308.34$ Da - a cationic surfactant; Sodium Dodecyl Sulfate (SDS) with molecular weight $M_w = 288.38$ Da - an anionic surfactant (both obtained from Sigma Aldrich); Pantene shampoo which primarily consists of sodium lauryl sulfate; Tetraethylene glycol mono-octyl ether (C_8E_4) with molecular weight $M_w = 306.44$ Da - a non-ionic surfactant

(obtained from Sigma Aldrich). In addition, a non-ionic surfactant, Pluronic P-123 with molecular weight $M_w = 5750$ Da, obtained from BASF Corporation was used.

4.2.2 Solution preparation

DTAB, a cationic surfactant, SDS, an anionic surfactant, and C_8E_4 , a non-ionic surfactant were used to prepare solutions as follows. Using DTAB, 3.5 mM, 5 mM, 10 mM, 12 mM, 15 mM, 18 mM, and 20 mM aqueous solutions were prepared and denoted D3.5, D5.0, D10.0, D12.0, D15.0, D18.0, and D20.0, respectively. Using SDS, 2 mM, 4 mM, 6 mM, 8 mM, and 10 mM aqueous solutions were prepared and denoted SD2.0, SD4.0, SD6.0, SD8.0, and SD10.0, respectively. Using C_8E_4 , 0.1 mM, 0.5 mM, 1 mM, 7.5 mM and 10 mM aqueous solutions were prepared and denoted C0.1, C0.5, C1.0, C7.5 and C10.0, respectively. The surfactant concentrations used for preparing the solutions were both below and above the critical micelle concentration, which is 15 mM for DTAB [Sonin et al. (1994)], 8 mM for SDS [Berg et al. (2005) and Mysels (1986)] and 7.5 mM for C_8E_4 [Karakashev et al. (2010b)]. For non-ionic surfactant Pluronic P-123, a 1 mM aqueous solution was initially prepared and then diluted to 0.5 mM, 0.1 mM and 0.052 mM and denoted as P0.5, P0.1 and P0.052, respectively. The critical micelle concentration of Pluronic P-123 is 0.052 mM at 25°C [Alexandridis et al. (1994)]. Pantene soap solution was prepared by adding 5.0 ml of Pantene shampoo to 100 ml of deionized water. This solution was named PS5.0 and used only to form spherical soap bubbles.

4.2.3 Experimental setup

The schematic of the experimental setup in which drainage from plane foam films was studied is shown in Fig. 4.1. The light source used was Rayovac 145 lumen white light. The light

was kept at the focal length of a plano convex lens ($f = 12.5$ cm) which produced parallel beam of light. To obtain a uniform parallel white light, Lumiquest diffuser was used.

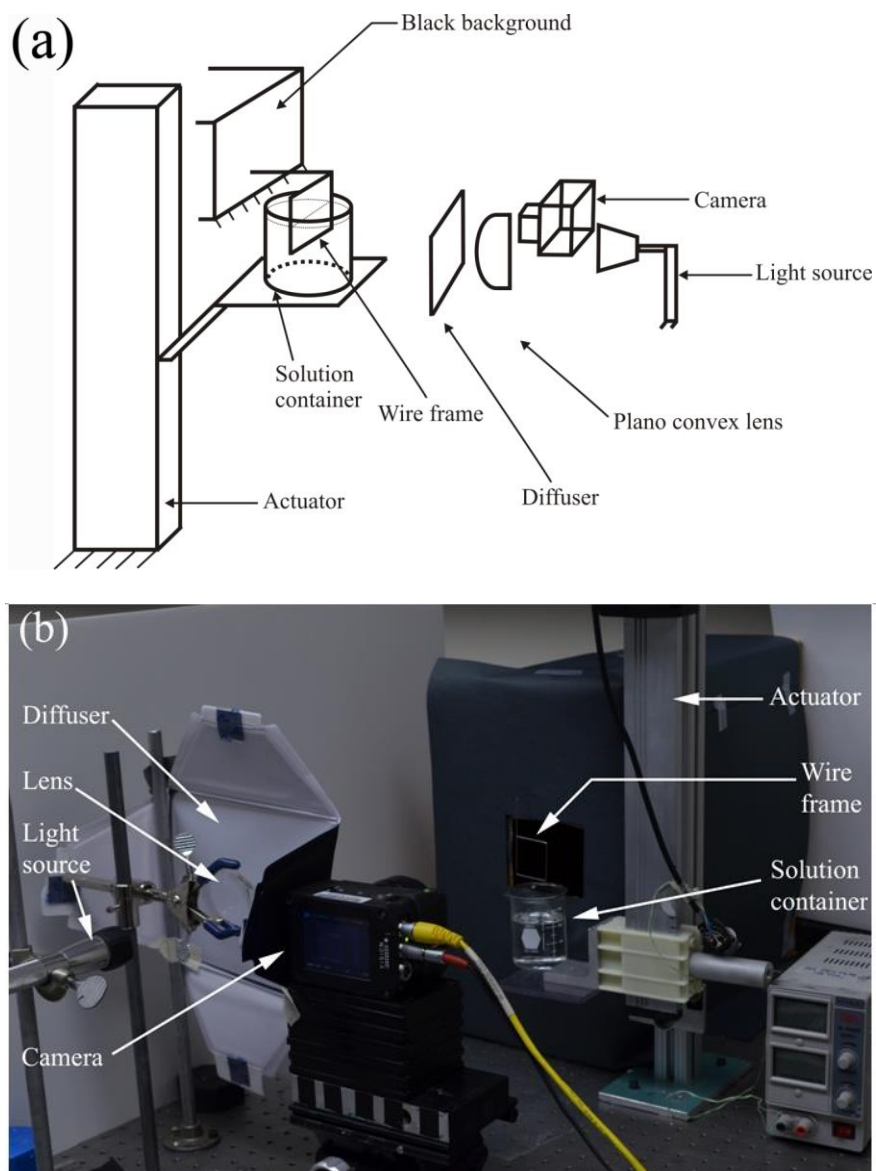


Figure 4.1. (a) Schematic of the experimental setup with drainage from plane films. (b) Image of the experimental setup.

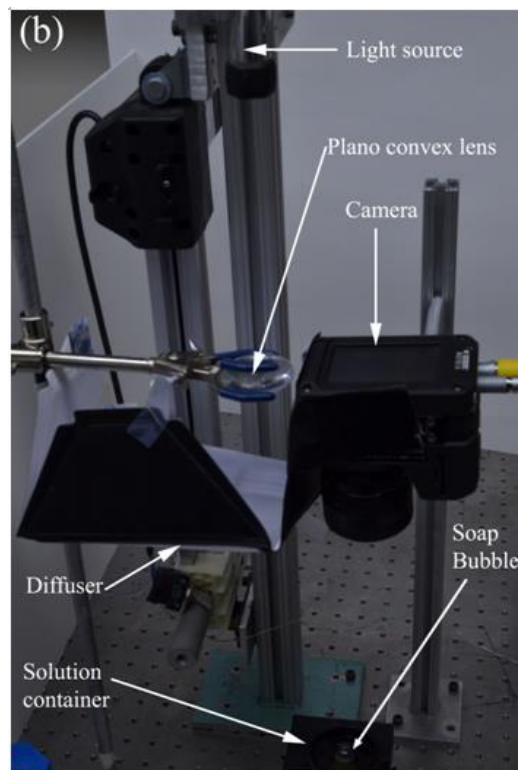
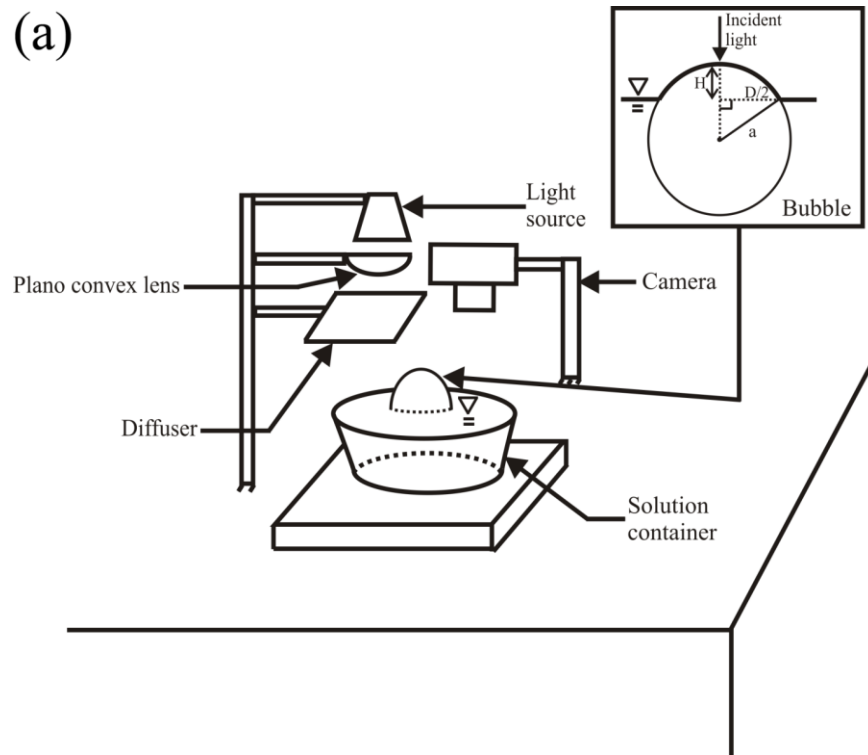


Figure 4.2. (a) Schematic of the experimental setup with drainage of spherical soap bubble. (b)

Image of the experimental setup.

A thin aluminum wire ($4\text{ cm} \times 4\text{ cm} \times 0.087\text{ cm}$) was used to withdraw and support plane soap films. The frame was fixed on a vertical black surface as shown in Fig. 4.1 in such a way that it could be dipped into solutions in the container. The solutions were placed in a 100 ml beaker supported on a flange attached to a linear actuator. The beaker was initially raised to dip the frame completely into the solution in the container and then lowered using the linear actuator connected to a stand. The speed of the actuator was controlled with a 12V dc supply. The frame with a film on it was fully withdrawn from the container and did not have any direct contact with the solution bulk throughout the entire experiment. The background of the frame was completely black to prevent any unwanted reflections from the surroundings. The film on the frame was photographed using a CCD camera (Phantom Miro 4), and the data stored in the computer. Once the beaker was lowered, the camera was triggered. The withdrawal velocities of the frame were in the range 0.67-2.17 cm/s. The initial film thicknesses in this range practically did not change with withdrawal velocity. For example, for D10.0 films the initial film thickness at the top h_0 varied in the range 4006-4043 nm and at the bottom the initial thickness h_{bi} was in the range 4360-4389 nm. Therefore, the gravitational drainage time practically did not depend on the withdrawal velocity.

The schematic of the experimental setup with drainage from spherical bubbles is shown in Fig. 4.2. The light source, the plano convex lens and diffuser were the same as those used for the plane film. A small container having the base diameter of 4.5 cm and a height of 3 cm was used. The solution was filled to the brim of the container. The container was completely black in color to reduce any unwanted reflections from its walls. A 5 cm^3 syringe was cut to make its length equal to the container height and fixed to its bottom at the center. A single 1 cm^3 bubble released at the liquid surface in the container at the center of the “fence” created by the cut 5 cm^3 syringe

stayed at the same location during the entire observation time. The bubble was photographed using a CCD camera (Phantom Miro 4), and the data stored in the computer.

4.2.4 Experimental method

Using color images with white light sources are preferable than using monochromatic light [Afanasyev et al. (2011)]. A monochromatic light source produces alternate bands of dark and bright fringes. However, when using white light as in the present case, black bands appear only when the film thickness is small compared to the shortest visible wavelength. So, the black film provides a good reference point in determining the order of the color bands in the film as discussed below.

All films were mobile rather than rigid following terminology of Mysels (1968), and correspondingly the duration of the drainage process was on the scale of 100 s (cf. Fig. 4.3). In plane films the film thickness at the top was measured right below the top wire and 2 cm from the left wire, which is halfway across the frame. So the side wires did not have any effect on the film thickness. The film thickness was practically homogeneous horizontally across the wire frame. This is corroborated by the fact that the interference color bands were uniformly colored horizontally at any location along the x-axis at any time (Figs. 4.3a-4.3e). The different interference color bands in these figures show that the film thickness varies in the vertical direction but is uniform in the horizontal direction.

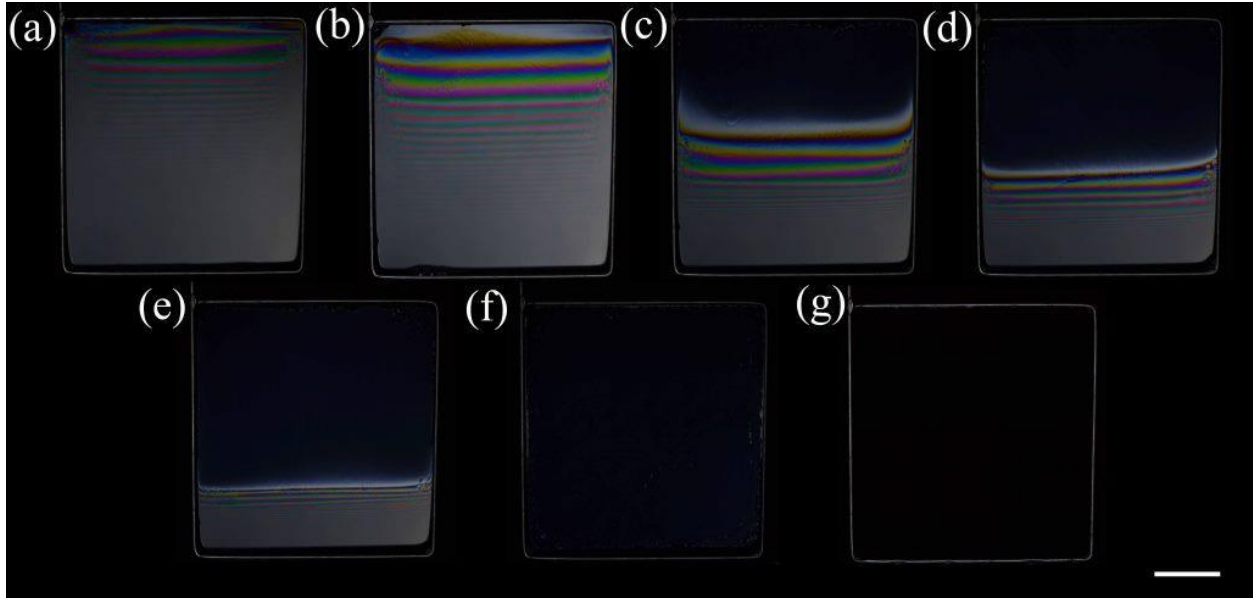


Figure 4.3. Drainage of D10.0 plane film. Interference pattern at (a) $t = 25$ s, (b) $t = 50$ s, (c) $t = 60$ s, (d) $t = 70$ s, and (e) $t = 80$ s. The formation of the black film can be seen at the top at (b) $t = 50$ s. After that the lower boundary of the black film is advancing downward until the entire film becomes black at (f) $t = 90$ s. The film explodes at (g) $t = 98$ s. The scale bar is 1 cm.

The background image (with no film) shown in Fig. 4.4a was subtracted from the film image shown in Fig. 4.4b using MATLAB 2011a. Then, each resulting color image (Fig. 4.4c) was analyzed using MATLAB 2011a. Each pixel in such color image was mapped as a vector of three intensity components, i.e. $I(x, y) = \{I_r(x, y), I_g(x, y), I_b(x, y)\}$, where I_r , I_g and I_b refer to the red, green and blue light components, respectively, with the wavelengths $\lambda = 650$ nm for red, $\lambda = 500$ nm for green and $\lambda = 450$ nm for blue light. In other words, the digital light filtering [Karakashev et al. (2007)] was applied to the images produced by a single light source and three different monochromatic light wavelengths corresponding to the red, green and blue light were used independently in comparison.

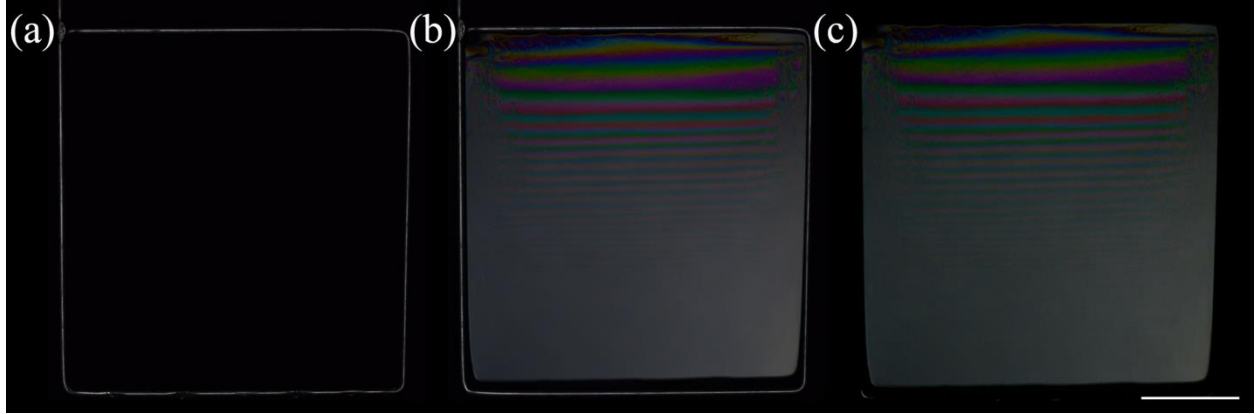


Figure 4.4. (a) The image of an empty wire frame against the black background. (b) Color image of the frame with a film against the black background. (c) The film image with the wire frame and background subtracted. The scale bar is 1 cm.

For each wavelength of the red, green and blue light, the local film thickness h was calculated using the following interferometric formula [Karakashev et al. (2005); Karakashev et al. (2007); Karakashev et al. (2008a); Karakashev and Nguyen (2009) and Karakashev et al. (2008b)] corresponding to either $I=I_r, I_g$ or I_b .

$$h = \frac{\lambda_i}{2\pi n} \left[m\pi \pm \arcsin \sqrt{\frac{\Delta_i(1+r^2)^2}{(1-r^2)^2 + 4r^2\Delta_i}} \right] \quad (4.1)$$

where $\Delta_i = (I_i - I_{\min,i}) / (I_{\max,i} - I_{\min,i})$; I_i is the instantaneous intensity corresponding to the wavelength λ_i (i stands for either red, green, or blue light), and $I_{\min,i}$ and $I_{\max,i}$ are the minimum and maximum intensities, respectively, which were found using image analysis software developed on the platform of MATLAB R-2011a. In addition, r is the Fresnel's reflection coefficient given by $r = (n-1)/(n+1)$ for the normal incident light, with n being the refractive index of the film liquid (water), m is the order of interference, $m=0,1,2,\dots$. The refractive index for soap water in air films was taken as $n=1.333$.

When a film bursts near the top wire, the light intensity from that area is minimal, i.e. $\Delta_i = 0$. On the other hand, the film thickness is also zero, which means that according to Eq. (4.1) one should assign $m=0$ to the top part of the film at the moment of bursting. Tracing the recorded light intensity at the film top back in time from the moment of bursting, one has to increase m by 1 and change the plus sign by the minus sign each time $\arcsin \sqrt{\Delta_i(1+r^2)^2 / [(1-r^2)^2 + 4r^2\Delta]}$ becomes equal to $\pi/2$ after increasing from 0 (when the plus sign was used). This allows one to establish the values of m at the film top at any time. Then, for any instantaneous intensity pattern, the value of m is increased by 1 in moving from the film top when the value of the arcsine becomes zero.

It was found that for the film thicknesses above 30 nm the results obtained using different wavelengths corroborated each other and were identical, as is seen in Fig. 4.5. The figure shows that the accuracy of the film thickness measurements is about ± 7 nm, and fully reliable and self-consistent data can be acquired for the film thicknesses above 30 nm. It is emphasized that to obtain accurate results, a background image was subtracted from each image containing soap film using MATLAB 2011a. For planar films, the axis of the camera was always normal to the tangent plane of the film, making the incidence angle $\theta = 0^\circ$ (cf. Fig. 4.1). The film thickness was measured for the entire lifetime of planar films all over their lengths.

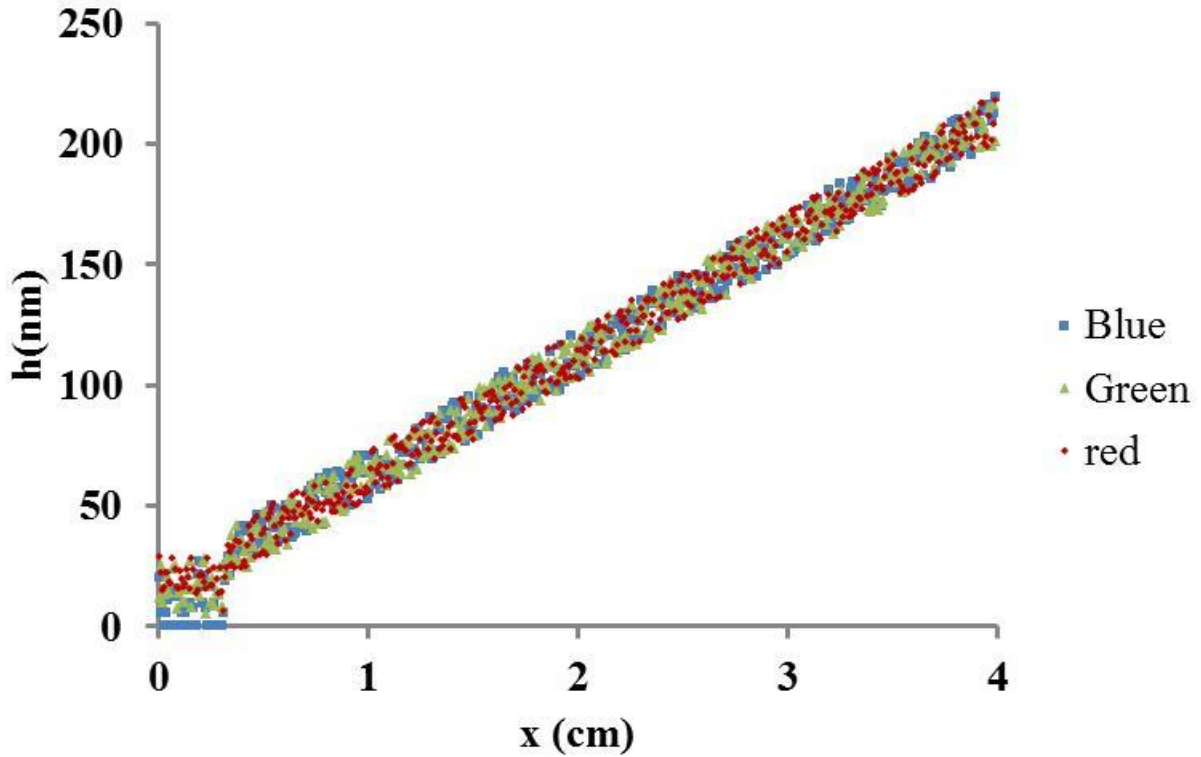


Figure 4.5. Thickness of planar film measured using the intensities of red, green and blue light, I_r , I_g and I_b , respectively, filtered digitally. DTAB solution D10.0 film at $t = 70$ s; $x = 0$ corresponds to the topmost section of the film where the black film was formed.

When a plane film adjoins a wire frame, the latter plays a role of the Plateau border, and capillary suction results in the flow component toward the wire. The film margins affected by such a flow can be subjected to the instability called marginal regeneration which is associated with the surfactant concentration-driven Marangoni effect [Berg et al. (2004); Berg et al. (2005); Mysels (1959); Mysels (1968); Nierstrasz and Frens (1999); Nierstrasz and Frens (2001)]. The marginal regeneration is always clearly visible in the form of “balloons” and “mushrooms” departing from the wire, which are the manifestations of the film thickness variations in the color interferometric images. It is emphasized that the images in Fig. 4.3 show that in the present

experiments with relatively thick films with mobile surfaces no signs of marginal regeneration were visible on the plane films. They were unaffected by the marginal instability probably because the gravity-driven flow dominated the capillary suction to the horizontal wires in the frame.

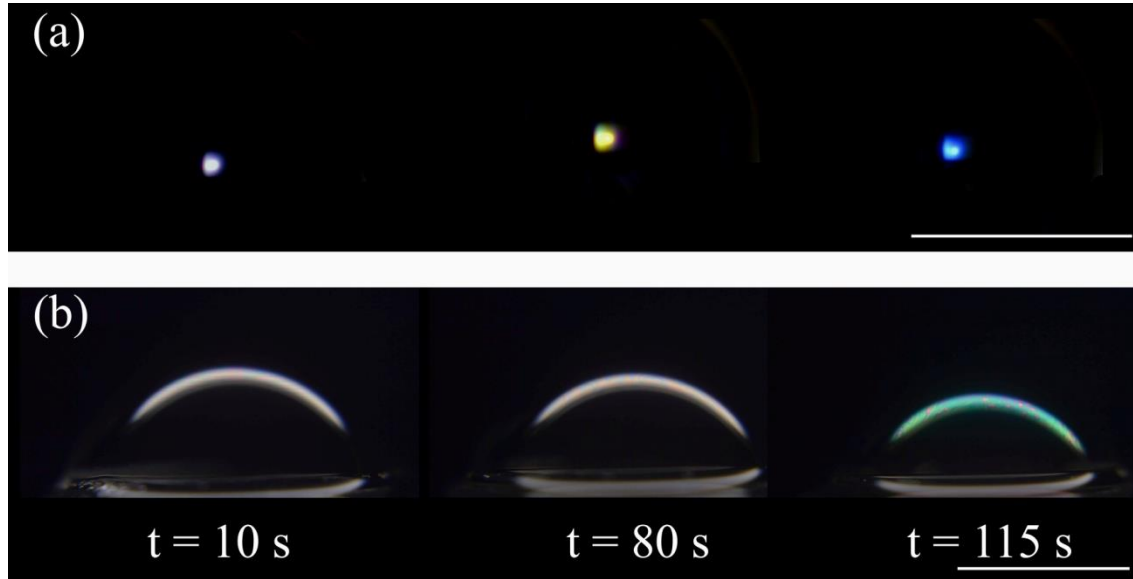


Figure 4.6. Drainage of D10.0 spherical bubble. The measurements of the film thickness at the bubble apex were done at different time moments using the interference color pattern seen in panel (a). (b) In a separate experiment, the side views for these moments were recorded. The scale bar is 1 cm for both sets of images.

In the case of bubbles in the setup in Fig. 4.2, the analysis of the images (Fig. 4.6) revealed that the bubble surface was perfectly spherical and its radius of curvature can be expressed as $a = H/2 + D^2/8H$ (see the inset in Fig. 4.2). However, unlike the planar films, the spherical bubble could not be imaged from the side because the incident light angle changed constantly due to the change of the normal projected from the film surface, which made

measurements of the film thickness inaccurate. As a result, the film thickness along the entire height of the bubble could not be measured. Therefore, in the experiments the light source and camera were kept directly above the bubble apex. Then, the film thickness at the apex of the bubble could be measured as the camera was parallel to the normal projected from the bubble surface at the apex, making the incidence angle $\theta = 0^\circ$.

4.3 Theoretical

In the present section a theory of gravity-driven drainage from surfactant-stabilized liquid films is developed. The theory describes stretching of the upper part of the film by the weight of the lower one. As a result of such stretching, concentration of surfactant molecules at the surface in the upper part of the film decreases compared to the lower one. Accordingly, surface tension in the upper part of the film increases compared to the lower one, and the associated concentration-driven Marangoni flow directed upward arises. This flow tends to diminish drainage and is identical to the surface elasticity, which decelerates gravity-driven drainage.

4.3.1 Drainage of plane soap film

Consider a vertical plane soap film suspended on a wide rectangular wire frame sketched in Fig. 4.7. Denote the coordinate reckoned in the drainage direction as x and the coordinate normal to it as y .

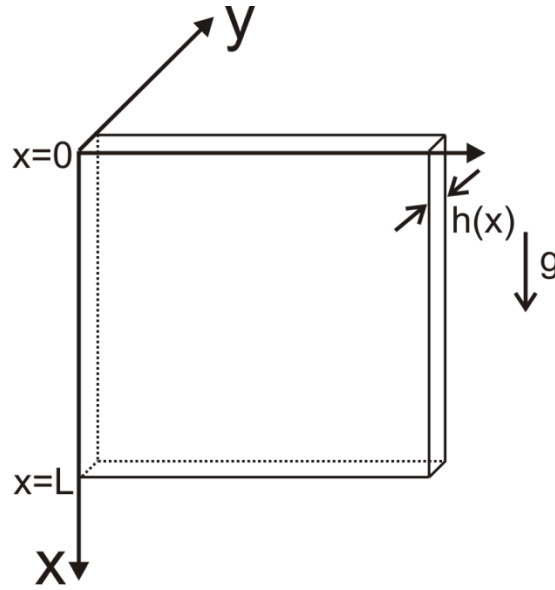


Figure 4.7. Sketch of vertical plane soap film on a frame.

As discussed below, quasi-one-dimensional approximation can be adopted to describe drainage of such films. Namely, the continuity equation reads

$$\frac{\partial h}{\partial t} + \frac{\partial uh}{\partial x} = 0 \quad (4.2)$$

where the film thickness is denoted as h , the longitudinal velocity as u , and time as t .

The drainage flow is relatively slow, which allows one to neglect the inertial effects. The normal viscous stresses in the film are also negligible. However, at the film surface acts shear stress $\sigma_{yx,surf}$. This stress appears due to a possible non-uniform distribution of surfactant at the film surface, i.e. due to the concentration Marangoni effect [Levich (1962); Edwards et al. (1991); Langevin and Sonin (1994)]. The corresponding longitudinal momentum balance reads

$$\sigma_{yx,surf} = -\frac{\rho gh}{2} \quad (4.3)$$

where ρ is the liquid density, and g is gravity acceleration. It is emphasized that a uniform surface tension does not contribute to this equation because in the case of a film surfaces

practically aligned with the x-axis, it equally pulls any film element in the opposite sides. Only, if the film is cut, surface tension being unbalanced as the cut line can produce fluid motion in the form of a moving and growing free rim causing the Taylor-Culick retraction [Taylor (1959) and Culick (1960)]. It is emphasized that Eq. 3 in de Gennes (2001) can be rearranged to our Eq. (4.3).

This stress is transmitted into the film bulk by viscous shear stresses, which tend to equilibrate the surface and bulk velocity. Such equilibration takes place at the distances of the order $\delta = \mu u / (\rho g h)$. With the characteristic values of the parameters corresponding to the present experiments ($\mu/\rho = 10^{-2} \text{ cm}^2/\text{s}$, $u = 10^{-2} \text{ cm/s}$ and $h = 10^{-4} \text{ cm}$), the value of δ is of the order of $\delta = 10^{-3} \text{ cm}$, which is larger than the film thickness h . This makes the velocity profile in the y-direction practically uniform, and thus the quasi-one-dimensional approximation $u = u(x, t)$ possible.

On the other hand, the shear stress $\sigma_{yx, \text{surf}}$ is determined by the surface elasticity ε of soap films, which is associated with the concentration Marangoni effect [Levich (1962); Edwards et al. (1991); Langevin and Sonin (1994)]. The corresponding surface elasticity (the Gibbs elasticity [Langevin and Sonin (1994); Karakashev et al. (2005)]) $\varepsilon = -\Gamma (\partial \sigma / \partial \Gamma)$ is associated with the dependence of the surface tension σ on the distribution of surfactant concentration Γ at the surface. If one follows a material surface element with an initial coordinate ξ which will be used as a Lagrangian parameter, stretching of the element can be expressed as $\partial \ell / \partial \xi$ where $d\xi$ is the initial length of the element and $d\ell$ is its current length. The elastic energy of a surface element with a unit width is then given by $dU = \varepsilon (\partial \ell / \partial \xi) d\xi$, which implies that no surfactant adsorption/desorption takes place at the surface during the experiment in agreement with the estimates in Langevin and Sonin (1994). In the expression for dU only the linear term of the

expansion in strain is accounted for with ε being a constant, which formally corresponds to small strains and linear elastic response. As usual in the phenomenological approach to rheology, if dictated by an experimental evidence, generalizations to a nonlinear elastic response could be done similarly to the nonlinear theory of elasticity [Lurie (2005)]. The elastic force $dF = \partial(dU)/\partial\xi$, and correspondingly, $\sigma_{yx,surf} = dF/dS = \varepsilon \partial^2 \ell / \partial \xi^2$, where the area of an element of the unit width $dS = d\xi$. Then, Eq. (4.3) can be transformed to the following form

$$-\frac{\rho g h}{2} = \varepsilon \frac{\partial^2 \ell}{\partial \xi^2} \quad (4.4)$$

The kinematic relation

$$\frac{d}{dt} \left(\frac{\partial \ell}{\partial \xi} \right) = \frac{\partial u}{\partial \xi} \quad (4.5)$$

allows one to transform the momentum balance Eq. (4.4) to the following form

$$-\frac{\rho g}{2\varepsilon} \frac{dh}{dt} = \frac{\partial^2 u}{\partial x^2} \quad (4.6)$$

The latter can be re-written as

$$\frac{\partial h}{\partial t} + u \frac{\partial h}{\partial x} = -\frac{2\varepsilon}{\rho g} \frac{\partial^2 u}{\partial x^2} \quad (4.7)$$

It is emphasized that Eqs. (4.6) and (4.7) can be also derived using as a starting point the equation of surfactant balance at the interface

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial \Gamma u}{\partial x} = 0 \quad (4.8)$$

together with the momentum balance Eq. (4.3) and the kinematic relation Eq. (4.5).

Note also, that Eq. (4.8) disregards adsorption or desorption of surfactant molecules at the film surface during the drainage process, which lasts of the order of 50-100 s. Since both the

bulk and surface liquid elements are equally stretched when a film is formed, the concentration gradient across the film is negligible, while surfactant molecules can be delivered to a depleted section of the surface only along the film. The characteristic times of the bulk and surface diffusion along the film are $\tau_{Db} \approx a^2 / D_b$ and $\tau_{Ds} \approx a^2 / D_s$, respectively, where D_b and D_s denote the bulk and surface diffusion coefficients, respectively. Taking for the estimate $D_b \approx 10^{-5} \text{ cm}^2/\text{s}$ and $D_s \approx 10^{-7} \text{ cm}^2/\text{s}$ as in Langevin and Sonin (1994), we find that in the present case $\tau_{Db} \approx 10^3 \text{ s}$ and $\tau_{Ds} \approx 10^5 \text{ s}$, much longer than the drainage process, indeed.

Combining Eqs. (4.2) and (4.7), we obtain the following expression for the film thickness h

$$h = \frac{2\varepsilon}{\rho g} \frac{\partial^2 u / \partial x^2}{\partial u / \partial x} \quad (4.9)$$

Integrating Eq. (4.2) from the top of the film at $x=0$, we recast the continuity equation to the following form

$$\frac{\partial}{\partial t} \int_0^x h dx + uh = 0 \quad (4.10)$$

Substituting Eq. (4.9) into Eq. (4.10), we obtain the following equation for u

$$\frac{\partial^2 u}{\partial t \partial x} + u \frac{\partial^2 u}{\partial x^2} = 0 \quad (4.11)$$

The latter can be expressed as the system of two equations of the first order

$$\frac{\partial f}{\partial t} + u \frac{\partial f}{\partial x} = 0 \quad (4.12)$$

$$f = \frac{\partial u}{\partial x} \quad (4.13)$$

Our problem on the film drainage involves four physical parameters: liquid density ρ , gravity acceleration g , surface elasticity ε , and the characteristic film thickness, say, the initial thickness at the film top h_0 . Two time scales can be constructed from these physical parameters

$$T = \frac{\varepsilon}{\rho(g h_0)^{3/2}} \quad (4.14)$$

and

$$\tau_g = \left(\frac{h_0}{g} \right)^{1/2} \quad (4.15)$$

The time scale T is related to the surface elasticity ε and is definitely relevant for the drainage process. The time scale τ_g does not depend on the surface elasticity and thus is irrelevant. Indeed, taking for the estimate $h_0 = 1 \mu\text{m}$, we find $\tau_g \sim 1\text{ms}$, whereas the duration of drainage from plane films is of the order of 50-100 s. Moreover, the viscous time scale (if one assumes that viscosity μ plays any role), $\tau_\mu = \mu / (\rho g h_0)$, is also incommensurate with the duration of the drainage process, since $\tau_\mu \sim 0.1\text{s}$. Therefore, the model of drainage assuming rigid film surfaces with the viscous friction-determined parabolic velocity profile of drainage flow [Mysels (1959)] is inapplicable in the present case.

Render Eqs (4.9), (4.12) and (4.13) dimensionless using T as the scale of t , h_0 as the scale of x and h , h_0/T as the scale of u , and T^{-1} as the scale of f . Then, these equations take the following dimensionless form

$$\bar{h} = E \frac{\partial^2 \bar{u} / \partial \bar{x}^2}{\partial \bar{u} / \partial \bar{x}} \quad (4.16)$$

$$\frac{\partial \bar{f}}{\partial \bar{t}} + \bar{u} \frac{\partial \bar{f}}{\partial \bar{x}} = 0 \quad (4.17)$$

$$\bar{f} = \frac{\partial \bar{u}}{\partial \bar{x}} \quad (4.18)$$

In Eq. (4.16) the dimensionless group E is given by

$$E = \frac{2\varepsilon}{\rho g h_0^2} \quad (4.19)$$

The hyperbolic Eq. (4.17) is solved by the method of characteristics and the solution reads

$$\bar{f} = \psi'(\xi) \quad (4.20)$$

$$\bar{x} = \xi + \int_0^{\bar{t}} \bar{u} d\bar{t} \quad (4.21)$$

where ξ is the $\bar{x}$ -coordinate of an individual fluid element at $\bar{t}=0$, and prime denotes the first derivative in ξ . It is emphasized that Eq. (4.20) means that $\partial u / \partial x = \partial u / \partial \xi$ on a material element, which was implied in Eq. (4.6).

At $\bar{t}=0$ the initial thickness distribution is known and given as $\bar{h} = \bar{h}_0(\xi)$. On the other hand, according to Eqs. (4.16) and (4.18), $\bar{h}_0(\xi) = E \left(d\bar{f} / d\xi \right) / \bar{f}$. Therefore, using Eq. (4.20), we find

$$\bar{f}(\xi) = \psi'(\xi) = \exp \left[\frac{1}{E} \int \bar{h}_0(\xi) d\xi \right] \quad (4.22)$$

and, in principle, the function $\psi(\xi)$ is established.

From Eq. (4.21) we find

$$1 = \frac{\partial \xi}{\partial \bar{x}} + \int_0^{\bar{t}} \frac{\partial \bar{u}}{\partial \bar{x}} d\bar{t} \approx \frac{\partial \xi}{\partial \bar{x}} + \int_0^{\bar{t}} \psi' d\bar{t} = \frac{\partial \xi}{\partial \bar{x}} + \psi' \bar{t} \quad (4.23)$$

It is emphasized that the approximate equality in Eq. (4.22) corresponds to the limit of small values of $\bar{t}$ (which will not be too restrictive, as the comparison with the experiments

shows below) and involves the usage of Eqs. (4.18) and (4.20). Therefore, from Eq. (4.23) we find

$$\frac{\partial \bar{\xi}}{\partial \bar{x}} = 1 - \bar{\psi}' \bar{t} \quad (4.24)$$

Then, from Eqs. (4.16), (4.18), (4.20) and (4.24) we find

$$\bar{h} = E \frac{\bar{\psi}'' (1 - \bar{t} \bar{\psi}')}{\bar{\psi}'} \quad (4.25)$$

Substituting Eq. (4.22) into Eq. (4.25), we arrive at

$$\bar{h}(\bar{x}, \bar{t}) = \bar{h}_0(\bar{\xi}) \left\{ 1 - \bar{t} \exp \left[\frac{1}{E} \int \bar{h}_0(\bar{\xi}) d\bar{\xi} \right] \right\} \quad (4.26)$$

$$\bar{x} = \int_0^{\bar{\xi}} \frac{d\bar{\xi}}{1 - \bar{t} \exp \left[E^{-1} \int \bar{h}_0(\bar{\xi}) d\bar{\xi} \right]} \quad (4.27)$$

At small $\bar{\xi}$, i.e. close to the top of the film, we can find from Eqs. (4.26) and (4.27)

$$\bar{h}(\bar{x}, \bar{t}) = (1 - \bar{t}) \exp \left(-\frac{\bar{x} \bar{t}}{E} \right) \quad (4.28)$$

Therefore, at small $\bar{x}$ close to the film top, $\bar{h}(\bar{x}, \bar{t}) \approx (1 - \bar{t})$, and thus the dimensional expression for the thickness at small x and t reads

$$h(x, t) = h_0 \left(1 - \frac{t}{T} \right) \quad (4.29)$$

It shows that close to the top of the film it is expected to rupture at the time moment $t=T$. That will be measured experimentally (see below) and thus reveal the value of the film elasticity with the help of Eq. (4.14).

4.3.2 Drainage of spherical soap bubble

Spherical soap bubble is sketched in Fig. 4.8. The continuity equation which replaces Eq. (4.2) of the plane film and expresses the mass balance in the case of drainage from a spherical film takes the following form

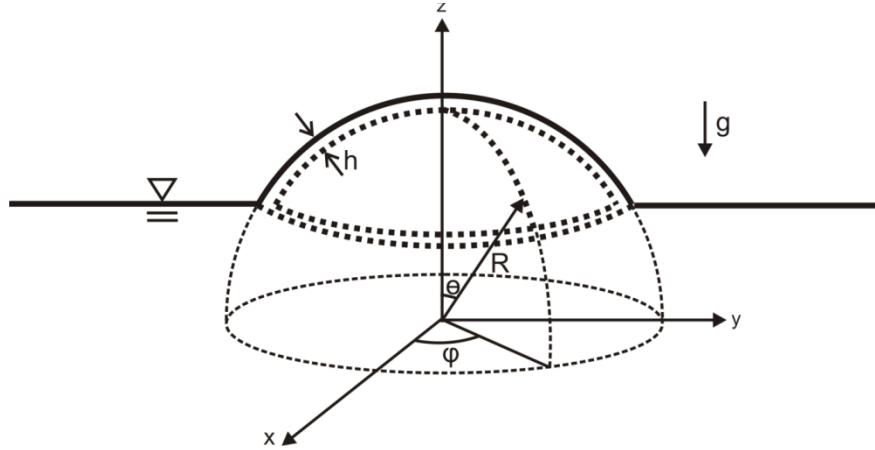


Figure 4.8. Sketch of spherical soap film. R denotes the bubble radius.

$$\frac{\partial h}{\partial t} + \frac{1}{R \sin \theta} \frac{\partial h v_{\theta} \sin \theta}{\partial \theta} = 0 \quad (4.30)$$

where v_{θ} is the flow velocity along the generatrix.

The momentum balance equation which replaces Eq. (4.3) of the plane film in the case of drainage from a spherical film reads

$$\sigma_{r\theta, \text{surf}} = -\frac{\rho g h}{2} \sin \theta \quad (4.31)$$

The uniform surface tension cannot contribute to Eq. (4.31) by the same reason as explained in relation to Eq. (4.3).

In the case of spherical films, a material element experiences bi-axial strain, with the principal strains being

$$\omega_{\theta\theta} = \frac{\partial \ell}{\partial \xi}, \quad \omega_{\varphi\varphi} = \frac{\sin \theta}{\sin \alpha} \quad (4.32)$$

which correspond to the two angular spherical coordinates θ and φ (cf. Fig. 4.8), and α being an initial value of the angular coordinate θ for an element (its Lagrangian parameter), with $\xi = R\alpha$.

The corresponding elastic energy of a material element of the film is

$$dU = \varepsilon (\omega_{\theta\theta} + \omega_{\varphi\varphi}) d\xi 2\pi R \sin \theta \quad (4.33)$$

which implies that no surfactant adsorption/desorption takes place at the surface during the experiment following the estimates of Langevin and Sonin (1994). The elastic force $dF = \partial(dU)/\partial \xi$, and correspondingly, the shear stress at the film surface

$$\sigma_{r\theta, \text{surf}} = \frac{dF}{dS} = \frac{dF}{2\pi R \sin \alpha d\xi} = \frac{\varepsilon}{\sin \alpha} \frac{\partial}{\partial \xi} \left[\sin \theta (\omega_{\theta\theta} + \omega_{\varphi\varphi}) \right] \quad (4.34)$$

where dS is the element surface area.

Then, Eqs. (4.31) and (4.34) yield

$$-\frac{\rho g h}{2} \sin \theta = \frac{\varepsilon}{\sin \alpha} \frac{\partial}{\partial \xi} \left[\sin \theta (\omega_{\theta\theta} + \omega_{\varphi\varphi}) \right] \quad (4.35)$$

The kinematic relations associated with time differentiation, which follow from Eq. (4.32) read

$$\frac{d\omega_{\theta\theta}}{dt} = \frac{d}{dt} \left(\frac{\partial \ell}{\partial \xi} \right) = \frac{\partial v_{\theta}}{R \partial \theta}, \quad \frac{d\omega_{\varphi\varphi}}{dt} = \frac{\cos \theta}{\sin \alpha} \frac{d\theta}{dt} = \frac{\cos \theta}{\sin \alpha} \frac{v_{\theta}}{R} \quad (4.36)$$

Then, Eqs. (4.35) and (4.36) yield

$$-\frac{\rho g}{2\varepsilon} \frac{dh}{dt} = \frac{1}{R \sin \theta} \frac{\partial}{\partial \theta} \left[\frac{1}{R \sin \theta} \frac{\partial (v_{\theta} \sin \theta)}{\partial \theta} \right] \quad (4.37)$$

The latter equation can also be derived using the equation which governs surfactant concentration at the film surface in the spherical case

$$\frac{\partial \Gamma}{\partial t} + \frac{1}{R \sin \theta} \frac{\partial \Gamma v_{\theta} \sin \theta}{\partial \theta} = 0 \quad (4.38)$$

which replaces Eq. (4.8) of the planar case.

In the Eulerian framework Eq. (4.37) takes the following form

$$\frac{\partial h}{\partial t} + \frac{v_{\theta}}{R} \frac{\partial h}{\partial \theta} = - \frac{2\varepsilon}{\rho g R \sin \theta} \frac{\partial}{\partial \theta} \left[\frac{1}{R \sin \theta} \frac{\partial}{\partial \theta} (v_{\theta} \sin \theta) \right] \quad (4.39)$$

which replaces Eq. (4.7) of the planar case.

The latter equation in combination with the continuity Eq. (4.30) yields the following expression for the film thickness h

$$h = \frac{2\varepsilon}{\rho g} \frac{\partial}{\partial \theta} \left[\frac{1}{R \sin \theta} \frac{\partial (v_{\theta} \sin \theta)}{\partial \theta} \right] / \frac{\partial (v_{\theta} \sin \theta)}{\partial \theta} \quad (4.40)$$

In the case of drainage from spherical films this equation replaces Eq. (4.9).

Using Eqs. (4.30) and (4.40), one derives the following equation for v_{θ}

$$\frac{\partial^2 (v_{\theta} \sin \theta)}{\partial \zeta \partial t} + \frac{v_{\theta} \sin \theta}{R} \frac{\partial^2 (v_{\theta} \sin \theta)}{\partial \zeta^2} = 0 \quad (4.41)$$

where $\zeta = -\cos \theta$. This equation is a spherical counterpart of Eq. (4.11).

Equation (4.40) is equivalent to the following system of two equations of the first order

$$\frac{\partial f}{\partial t} + \frac{v_{\theta}}{R} \frac{\partial f}{\partial \theta} = 0 \quad (4.42)$$

$$f = \frac{1}{\sin \theta} \frac{\partial (v_{\theta} \sin \theta)}{\partial \theta} \quad (4.43)$$

which replace Eqs. (4.12) and (4.13) of the planar case.

Render v_{θ} and f by R/T , and time t by T . Then, Eqs. (4.40), (4.42) and (4.43) take the following dimensionless form

$$\bar{h} = \frac{h_0}{R} E \frac{\partial}{\partial \theta} \left[\frac{1}{\sin \theta} \frac{\partial (\bar{v}_\theta \sin \theta)}{\partial \theta} \right] / \frac{\partial (\bar{v}_\theta \sin \theta)}{\partial \theta} \quad (4.44)$$

$$\frac{\partial \bar{f}}{\partial \bar{t}} + \bar{v}_\theta \frac{\partial \bar{f}}{\partial \theta} = 0 \quad (4.45)$$

$$\bar{f} = \frac{1}{\sin \theta} \frac{\partial (\bar{v}_\theta \sin \theta)}{\partial \theta} \quad (4.46)$$

The approximate solution of Eq. (4.45) at small values of $\bar{t}$ is found similarly to the planar case as

$$\bar{f} = \overline{f(\xi)} = \psi'(\xi) = \exp \left[\frac{1}{(h_0/R)E} \int \overline{h_0(\xi)} \sin \xi d\xi \right] \quad (4.47)$$

which replaces Eq. (4.22).

Then, Eq. (4.44) yields

$$\bar{h} = \overline{h_0(\xi)} \left[1 - \overline{v'_\theta(\xi)} \bar{t} \right] \quad (4.48)$$

while from Eq. (4.46) it follows that

$$\frac{d\overline{v_\theta}}{d\xi} = \frac{d}{d\xi} \left[\frac{1}{\sin \xi} \int \psi'(\xi) \sin \xi d\xi \right] \quad (4.49)$$

At small ξ close to the bubble apex, $\psi'(\xi) \approx 1$, and according to Eq. (4.49), $\overline{v'_\theta(\xi)} \approx 1/2$.

Therefore, at small $\bar{t}$ and ξ the film thickness given by Eq. (4.48) reduces to

$$\bar{h} = \overline{h_0(\xi)} \left(1 - \frac{\bar{t}}{2} \right) \quad (4.50)$$

The dimensional form of Eq. (4.50) reads

$$h(x, t) = h_0 \left(1 - \frac{t}{2T} \right) \quad (4.51)$$

This equation shows that drainage from spherical films is slower than drainage from plane films described by Eq. (4.29). This stems from the fact that the effect of the driving force, gravity, on the flow is stronger in the plane films, since they are oriented vertically, whereas the spherical films are inclined at the most part of their generatrix.

4.4 Results and discussion

4.4.1 Drainage of plane soap film

Solutions with different concentrations of the cationic surfactant DTAB and the anionic surfactant SDS were used in experiments with drainage of the plane films. For DTAB solution D3.5, the top part of the plane film turned black (Fig. 4.9a) and the black film advanced downwards. The black film was present for about half the length of the film along the wire frame at the time of bursting. For DTAB solution D5.0 (Fig. 4.9b) the black film reached further down the film at the instant of bursting, but the color bands were still seen at the bottom of the film. In the case of DTAB solution D10.0 (Fig. 4.9c), the entire film turned black just before the instant of bursting. For DTAB solution D12.0 (Fig. 4.9d), the entire film turned black, and had a sufficient stability to last for about 60 s after the black film was formed before bursting.

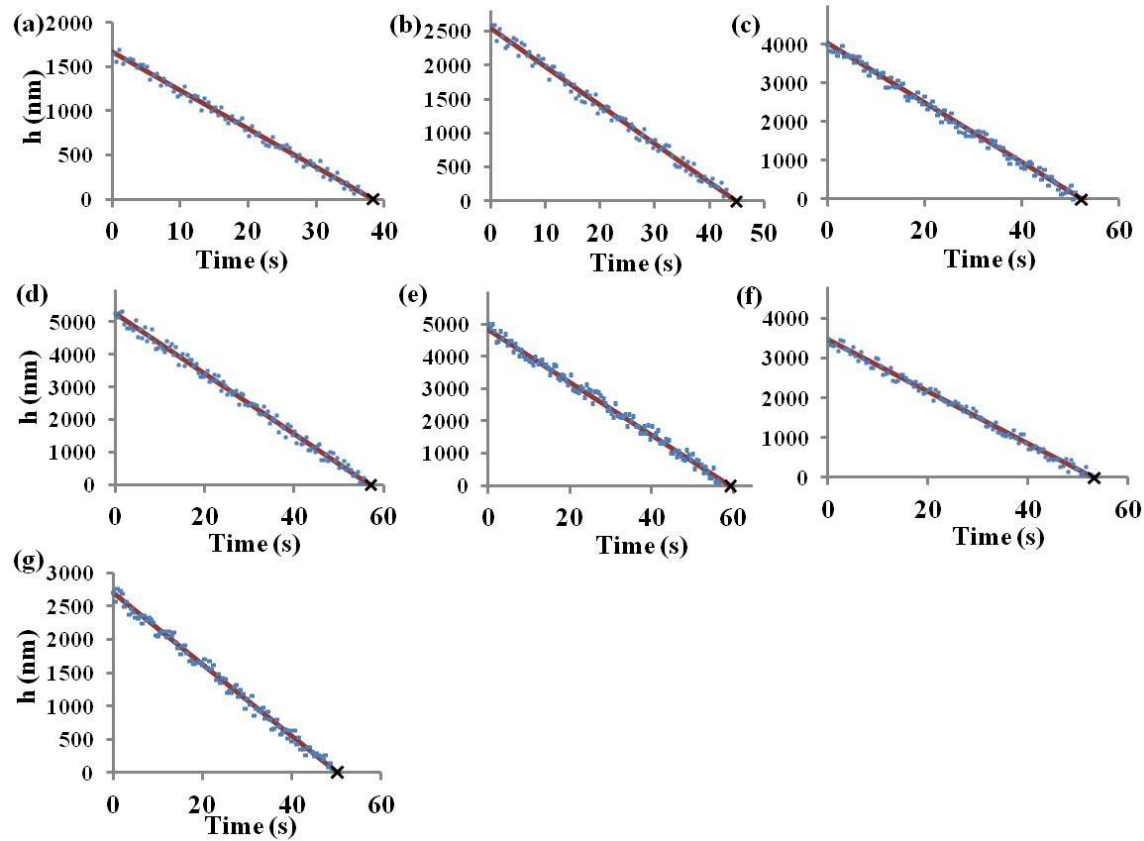


Figure 4.9. Drainage of DTAB solution films: (a) D3.5, (b) D5.0, (c) D10.0, (d) D12.0, (e) D15.0, (f) D18.0 and (g) D20.0. The data correspond to the film top. The experimental results are shown by symbols. The inclined straight lines correspond to the theoretical result, Eq. (4.29).

The data in Fig. 4.9 allow one to find the characteristic drainage time T as the time moment when h approaches zero, as follows from Eq. (4.29). The latter perfectly agrees with the experimental data. Then, Eq. (4.14) is used to find the corresponding values of the surface elasticity ϵ , since the other parameters in it are known. The results for the DTAB solutions are summarized in Table 4.1, where, in particular, the measured values of the film elasticity ϵ are listed.

Table 4.1. Plane DTAB solution films. The film lifetime is denoted t ; t_b denotes the time at which black film sets in at the top of the wire frame; t_{be} denotes the time at which black film covers the entire wire frame. The x column corresponds to the position in the film (reckoned from the top) to which the leading edge of the black film reached at the moment of bursting. The initial film thickness at the top is denoted $h_i=h_0$, and at the bottom - h_{bi} ; the drainage time $-T$. The values of the surface elasticity ε were found from T using Eq. (4.14).

Sol.	t (s)	t_b (s)	x (cm)	t_{be} (s)	$h_i=h_0$ (nm)	h_{bi} (nm)	T (s)	ε (g/s ²)
D3.5	63	38	2.6	-	1650.75	1853.56	38.37	2.49
D5.0	73	44	2.9	-	2601.92	2930.96	44.89	5.78
D10.0	98	51	4	90	4013.32	4388.94	52.17	12.87
D12.0	117	55	4	106	5267.63	5652.14	55.91	20.74
D15.0	124	58	4	111	4995.81	5109.52	59.16	20.27
D18.0	120	52	4	101	3488.66	3859.41	53.04	10.60
D20.0	105	49	4	92	2710.35	2998.82	50.13	6.86

For the anionic SDS solutions SD2.0 to SD10.0 (Figs. 4.10a-4.10e, respectively) similar trends were observed as those in Fig. 4.9 for DTAB. In all the cases, black films were formed at the top and the films turned completely black for SD6.0, SD8.0 and SD10.0.

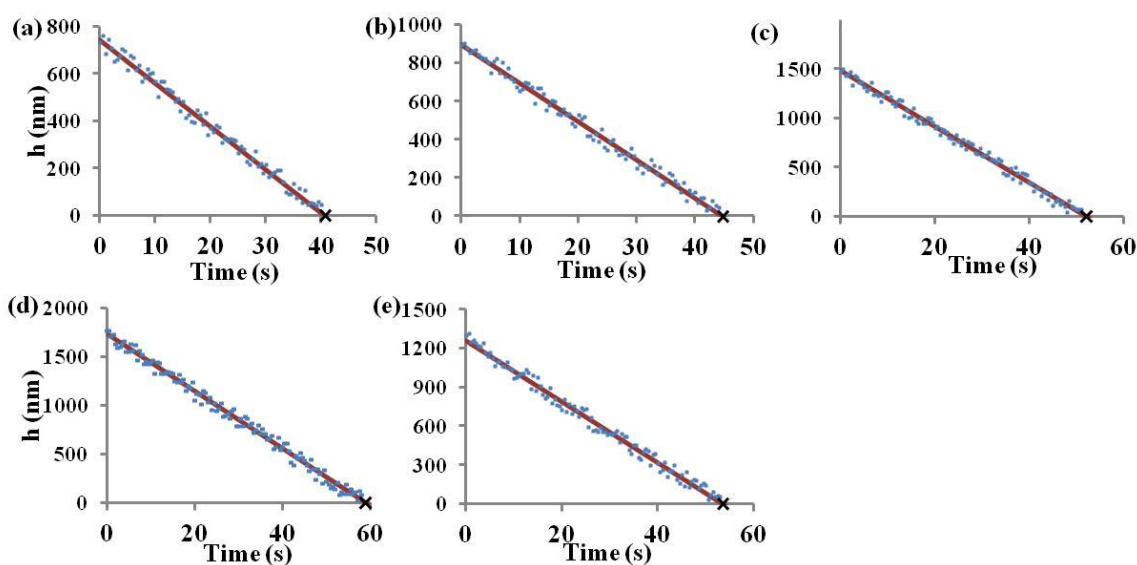


Figure 4.10. Drainage of SDS solution films: (a) SD2.0, (b) SD4.0, (c) SD6.0, (d) SD8.0, and (e) SD10.0. The data correspond to the film top. The experimental results are shown by symbols. The inclined straight lines correspond to the theoretical result, Eq. (4.29).

The values of the cut-off time T were established using the experimental data in Fig. 4.8. Then, the film elasticity ϵ was calculated from Eq. (4.14). The results for the SDS solutions are summarized in Table 4.2, where, in particular, the measured values of the film elasticity ϵ are listed.

Table 4.2. Plane SDS solution films. The film lifetime is denoted t ; t_b denotes the time at which black film sets in at the top of the wire frame; t_{be} denotes the time at which black film covers the entire wire frame. The x column corresponds to the position in the film (reckoned from the top) to which the leading edge of the black film reached at the moment of bursting. The initial film thickness at the top is denoted $h_i=h_0$, and at the bottom - h_{bi} ; the drainage time - T . The values of the surface elasticity ε were found from T using Eq. (4.14).

Sol.	T (s)	t_b (s)	x (cm)	t_{be} (s)	$h_i=h_0$ (nm)	h_{bi} (nm)	T (s)	ε (g/s ²)
SD2.0	65	39	2.05	-	734.45	983.85	40.65	0.79
SD4.0	79	44	3.8	-	892.71	1136.98	44.71	1.16
SD6.0	102	51	4.0	98	1481.94	1796.88	51.96	2.88
SD8.0	117	58	4.0	105	1770.29	1942.13	58.89	4.26
SD10.0	104	53	4.0	97	1259.48	1548.37	53.52	2.32

For the cationic and anionic surfactant solutions with concentrations below the corresponding cmc (D3.5, D5.0, D10.0, D12.0, D15.0, SD2.0, SD4.0, SD6.0 and SD8.0) adding more surfactant (not above cmc) increased the electrostatic repulsive molecular forces when the film thinned down to the level of a black film, stabilizing the latter and thereby increasing the

overall lifetime of the films. Of them, for the films of D10.0, D12.0, D15.0, SD6.0 and SD8.0 the entire film turned black before bursting, indicating a strong influence of forces associated with the electric part of the disjoining pressure during the last stage of drainage. However, the time of the onset of the black film did not increase significantly with the increase in concentrations of DTAB and SDS. This shows that the initial gravity-driven drainage flow is not affected strongly by the surfactant concentration below cmc, and the stabilization mechanisms can affect the process only shortly when the films thin to a certain critical thickness.

Note that the results in Tables 4.1 and 4.2 show that for the films formed from solutions with surfactant concentrations above cmc (D18.0, D20.0 and SD10.0), lower surface elasticity values were measured than for the corresponding solutions at cmc. This formally stems from the fact that the thinnest initial films were created from micellar solutions as is seen in Figs. 4.9 and 4.10, and nevertheless, their characteristic drainage times T were rather close to those of the corresponding films at the below-cmc concentrations. Then, according to Eq. (4.14), the surface elasticity is diminished. It looks like the surfactant gradient along the surface diminishes when films are initially formed from the above-cmc solutions (since due to stretching the surface concentration in a stretched film still can be lower than the one corresponding to an optimal packing).

The theoretical result, Eq. (4.29), revealed a linear decrease in the film thickness during drainage near the film top, which is fully confirmed by the experimental data in Figs. 4.9 and 4.10. It is emphasized that a linear decrease of the film thickness was also observed experimentally for all other cross-sections x at the same rate dh/dt as the one predicted in Eq. (4.29).

Despite DTAB and SDS being two radically different surfactants, the former being cationic and the latter anionic, almost identical values were observed for the drainage time of their films. However, the initial thicknesses of the films formed with DTAB solutions were much larger than those of the films of SDS solutions. For the thicker DTAB films the increase in weight was compensated by a higher surface elasticity, which made their drainage time similar to that of the SDS films.

Solutions with different concentrations of non-ionic surfactants C_8E_4 and non-ionic copolymer Pluronic P-123 were also used in experiments with drainage of plane films. For C_8E_4 solutions below cmc, an increase in the surfactant concentration led to an increased film lifetime. The films of C0.1, C0.5, C1.0, C7.5 (all below cmc of 7.5 mM) and C10.0 (above cmc) (Figs. 4.11a-4.11e, respectively) turned completely black before bursting, indicating strong stabilization influence of molecular forces. However, unlike for the plane films formed from the ionic surfactant solutions, the onset time of the black film formation t_b significantly increased with the increase in concentration. Using the measured values of T and Eq. (4.14) to evaluate the surface elasticity ϵ , it was found that C_8E_4 revealed higher values of ϵ than ionic surfactants (cf. the data in Table 4.3 with those of Tables 4.1 and 4.2). The drainage of the films formed from C_8E_4 solutions was slower than that of the ionic surfactant films. All films of the ionic surfactants studied turned black nearly about the same time depending on the concentration of the surfactant, which determined the total lifetime of the film. For the plane films of the non-ionic C_8E_4 surfactant, stability of the black films was not affected by the surfactant concentration. The stability of the black films of the non-ionic C_8E_4 surfactant was low and these black films rapidly burst. The review in Stubenrauch and von Klitzing (2003) revealed the results which show that non-ionic surfactants, albeit with chains longer than that of C_8E_4 , are

prone to the specific adsorption of hydroxyl (OH^-) to the film surfaces. The surfaces thus charged repel each other by electrostatic repulsive forces on the range up to about 100 nm, which adds a stabilizing effect. However, in the present case of a relatively short-chain non-ionic C_8E_4 surfactant, such stabilization effect on the black-film stage (below 100 nm) was not observed, and the black films rapidly burst. On the other hand, the slower drainage from the non-ionic surfactant films compared to the drainage from ionic surfactant films encompassed film thicknesses in the range from 100 to 6000 nm (cf. Fig. 4.11) where any electrostatic repulsive forces associated with specific adsorption of hydroxyl would be negligible. Therefore, the slower drainage from the non-ionic surfactant films in the present case can be attributed to a higher surface elasticity, rather than to the electrostatic repulsion. Note also, that even though the formation of the black film was delayed for the non-ionic surfactant compared to the ionic ones, the overall lifetime of both types of the films was not very different.

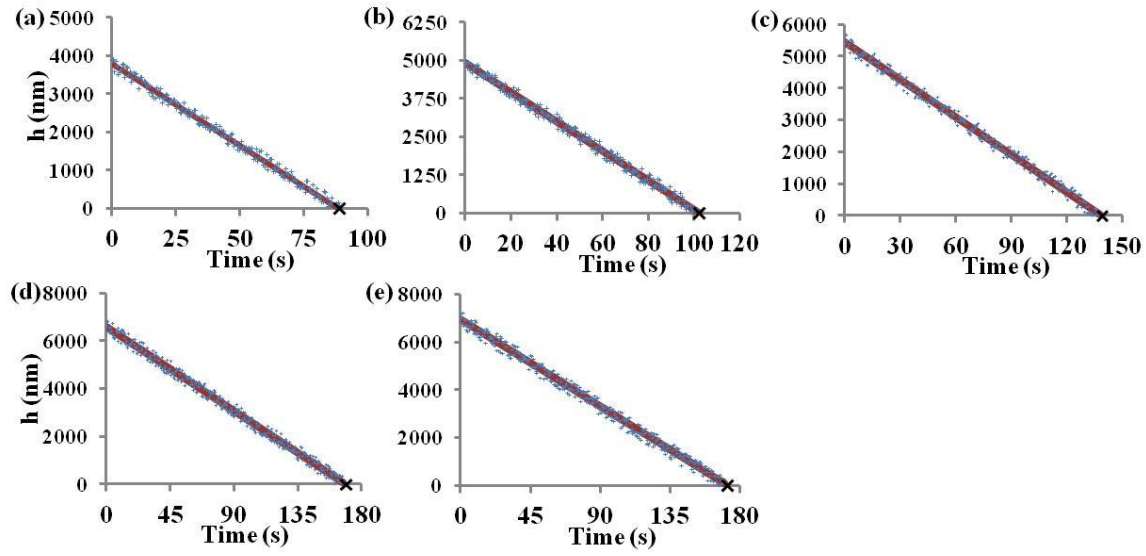


Figure 4.11. Drainage of C_8E_4 solution films: (a) C0.1, (b) C0.5, (c) C1.0, (d) C7.5, and (e) C10.0. The data correspond to the film top. The experimental results are shown by symbols. The inclined straight lines correspond to the theoretical result, Eq. (4.29).

Table 4.3. Plane films of the non-ionic C₈E₄ solutions. The film lifetime is denoted t ; t_b denotes the time at which black film sets in at the top of the wire frame; t_{be} denotes the time at which black film covers the entire wire frame. The x column corresponds to the position in the film (reckoned from the top) to which the leading edge of the black film reached at the moment of bursting. The initial film thickness at the top is denoted $h_i=h_0$, and at the bottom - h_{bi} ; the drainage time – T . The values of the surface elasticity ϵ were found from T using Eq. (4.14).

Sol.	t (s)	t_b (s)	x (cm)	t_{be} (s)	$h_i=h_0$ (nm)	h_{bi} (nm)	T (s)	ϵ (g/s ²)
C0.1	98	89	4	96	3761.62	4014.28	88.88	19.89
C0.5	114	102	4	110	4896.28	5207.64	102.3	34.00
C1.0	151	138	4	144	5432.91	5861.72	139	54.00
C7.5	190	167	4	182	6617.34	6940.23	169.03	88.27
C10	189	170	4	183	6943.55	7086.22	172.09	99.59

Pluronic P-123 has a very low cmc of 0.052 mM [Alexandridis et al. (1994)] and solutions of concentrations lower than cmc could not be tested due to the inaccuracy of measuring such low quantities of surfactant. Drainage of plane films was observed for P0.052, P0.1 and P0.5 solutions (Figs. 4.12a – 4.12c, respectively). For all the concentrations there was no difference between the lifetimes of the films or in their surface elasticities (cf. Table 4.4).

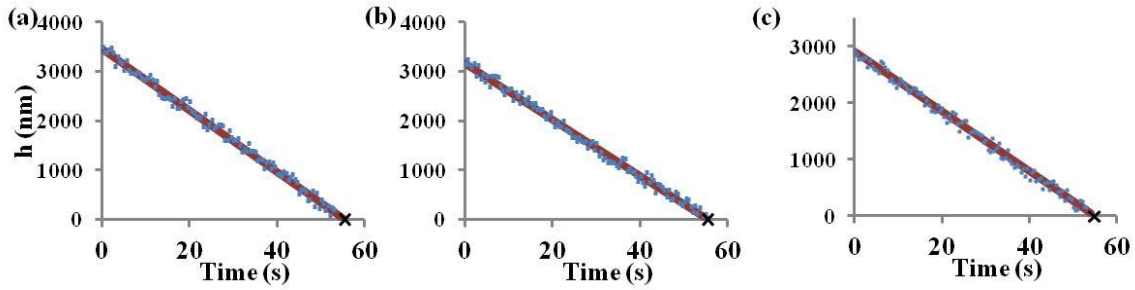


Figure 4.12. Drainage of Pluronic P-123 solution films: (a) P0.052, (b) P0.1 and (c) P0.5. The data correspond to the film top. The experimental results are shown by symbols. The inclined straight lines correspond to the theoretical result, Eq. (4.29).

Table 4.4. Plane films of the non-ionic Pluronic P-123 solutions. The film lifetime is denoted t ; t_b denotes the time at which black film sets in at the top of the wire frame; t_{be} denotes the time at which black film covers the entire wire frame. The x column corresponds to the position in the film (reckoned from the top) to which the leading edge of the black film reached at the moment of bursting. The initial film thickness at the top is denoted $h_i=h_0$, and at the bottom - h_{bi} ; the drainage time - T . The values of the surface elasticity ε were found from T using Eq. (4.14).

Sol.	t (s)	t_b (s)	x (cm)	t_{be} (s)	$h_i=h_0$ (nm)	h_{bi} (nm)	T (s)	ε (g/s ²)
P0.052	78	55	4	67	3461.76	3872.93	55.31	10.93
P0.1	72	55	4	65	3163.52	3574.22	55.39	9.56
P0.5	70	54	4	64	2934.55	3126.84	54.66	8.43

For both non-ionic surfactants (C_8E_4 and Pluronic P-123) black films typically appeared after a longer period of time compared to those of the cationic and anionic ionic surfactants DTAB and SDS. Also, the increased values of the drainage time T indicated typically higher values of the surface elasticity of the non-ionic surfactants. This is associated with the fact that in the absence of mutual electric repulsion, a higher surface concentration of the non-ionic surfactant molecules could be reached compared to the ionic ones, which facilitates higher surface gradients and a stronger Marangoni effect.

4.4.2 Drainage of Spherical Soap Bubble

In the experiments single bubbles were formed from Pantene Shampoo solution PS5.0, and four cationic DTAB solutions D5.0, D10.0, D12.0, and D15.0. The experimental data were obtained at the bubble apex at the incidence angle $\theta = 0^\circ$, as mentioned in the section which describes the experimental method. The results on the drainage of spherical bubbles are illustrated in Fig. 4.13 (for the Pantene Shampoo solution PS5.0) and Fig. 4.14 (for the DTAB solutions D5.0, D10.0, D12.0, and D15.0). The latter figure shows that spherical bubbles lasted longer than the corresponding plane films. Figures 4.14a, 4.14b, 4.14c and 4.14d for spherical bubbles should be compared with the corresponding Figs. 4.9b, 4.9c, 4.9d and 4.9e for plane films of DTAB, respectively.

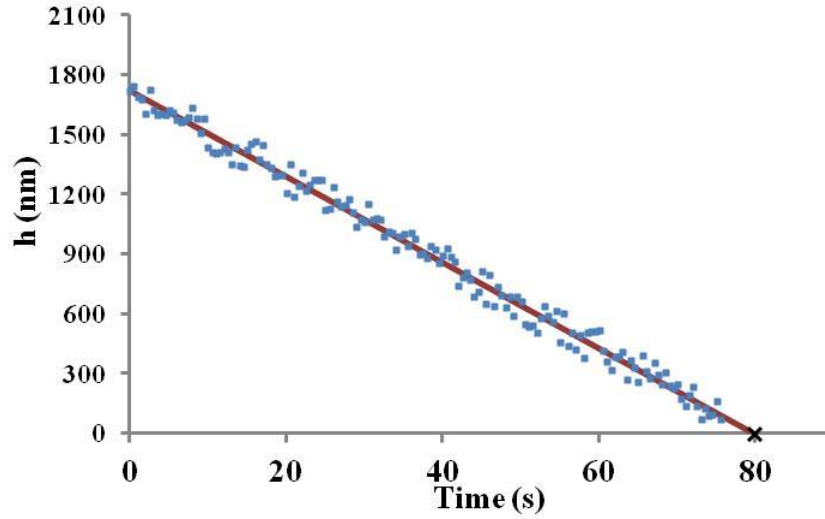


Figure 4.13. Drainage at the top of a spherical bubble of Pantene Shampoo solution PS5.0. The data correspond to the film top (at $\theta = 0^\circ$). The experimental results are shown by symbols. The inclined straight line corresponds to the theoretical result, Eq. (4.51).

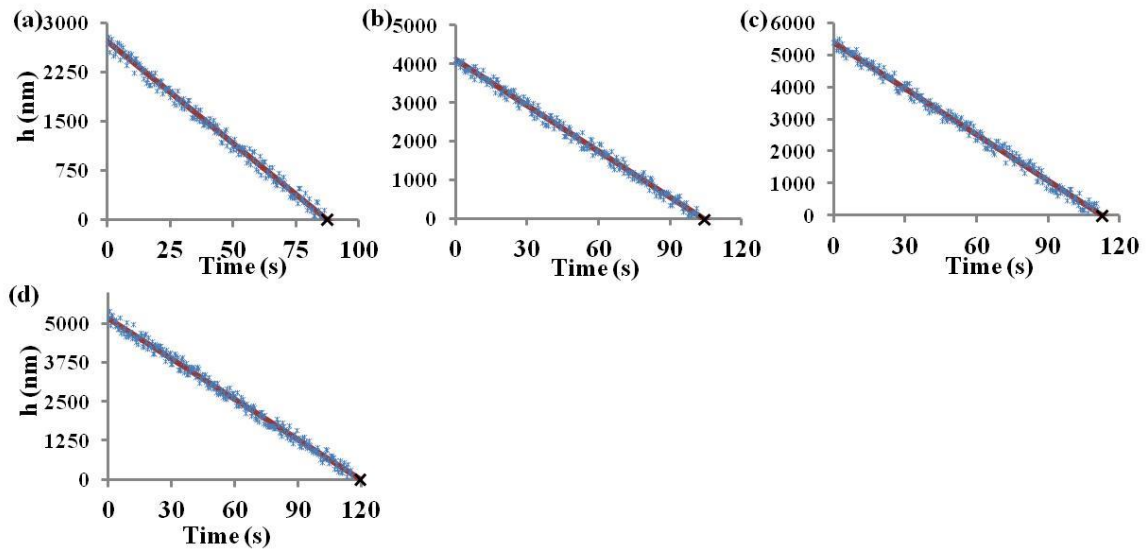


Figure 4.14. Drainage at the top of spherical bubbles of DTAB solutions: (a) D5.0, (b) D10.0, (c) D12.0, and (d) D15.0. The data correspond to the film top (at $\theta = 0^\circ$). The experimental results are shown by symbols. The inclined straight line corresponds to the theoretical result, Eq. (4.51).

The experimental observation that the lifetime of spherical bubbles is about two times longer than the lifetime of the corresponding plane films is in agreement with the predictions of Eqs. (4.29) and (4.51). The results in Figs. 4.13 and 4.14 allow measuring the drainage time $2T$, which can be used to elucidate the surface elasticity ε from Eq. (4.14). The data for the spherical bubbles are summarized in Table 4.5, including the values of the bubble surface elasticity ε . These values of ε are in good agreement with those found from drainage of plane films of the corresponding surfactant films.

Table 4.5. Spherical bubbles of Pantene Shampoo solution and DTAB solutions. The bubble lifetime is denoted t ; t_b denotes the time at which black film sets in at the bubble apex. The initial film thickness at the top is denoted $h_i=h_0$, and the drainage time $-2T$. The values of the surface elasticity ε were found from T using Eq. (4.14).

Sol.	t (s)	t_b (s)	$h_i=h_0$ (nm)	$2T$ (s)	T (s)	ε (g/s ²)
PS5.0	85	78	1722.87	79.73	39.87	2.77
D5.0	95	86	2690.31	87.15	43.58	5.89
D10.0	118	102	4121.66	103.97	51.99	13.35
D12.0	132	110	5384.94	112.46	56.23	21.56
D15.0	136	117	5207.73	119.31	59.66	21.75

It took longer time for spherical bubbles to thin down to a level of a black film than for the corresponding plane films. However, after being formed, black films on spherical bubbles were destabilized faster than the black films on the corresponding plane films. For spherical bubbles, a small black spot appears at the top of the bubble, as the thickness approaches that of the black film and the bubble bursts very soon after that.

4.4.3 Comparison with data from literature

Tables 4.6 and 4.7 contain the results of the present work for the surface elasticity ε of the two ionic surfactants in comparison with the data available in literature [Karakashev and Ivanova (2010a); Sonin et al. (1994); Noskov et al. (1998) and Prins et al. (1967)] measured by the other methods. In particular, the values of Sonin et al. (1994) were of the same order but higher than the present results (cf. Table 4.6). The surface elasticity values measured for anionic surfactant SDS (cf. Table 4.7) were in reasonable agreement with those of Karakashev and Ivanova (2010a) and Noskov et al. (1998) measured by the micro-interferometry method in the Scheludko cell and using the longitudinal surface waves, and lower than the one in Prins et al. (1967) measured using the Wilhelmy plate technique. We found that the surface elasticity values are increasing till the solution cmc contrary to the decreasing trend measured with longitudinal wave viscometer [Rao et al. (1982)]. Surface wave devices operating at lower frequencies consider surface convection to be negligible and surfactant adsorption – desorption and diffusion processes to be predominant, whereas for a soap film in the drainage process, surface convection is more important than the rest [Langevin and Sonin (1994)]. Surfactant solutions above cmc have micelles formed which contribute to the mass exchange between the surface layer and the bulk phase [Noskov et al. (1999)], resulting in a decrease in surface elasticity, as the present results show. The measured surface elasticity values at cmc of the ionic solutions are significantly lower than those for non-ionic surfactants [Karakashev et al. (2010b)]. The increase in surfactant surface diffusion due to repulsion of identical charges and weakening of the Marangoni effect [Karakashev and Ivanova (2010a)] causes faster drainage of the ionic surfactant films.

Table 4.6. Comparison of surface elasticity ε measured for different concentrations of cationic DTAB solutions with data in literature.

DTAB solution concentrations	3.5 mM	5 mM	10 mM	12 mM	15 mM	18 mM	20 mM
Present work	2.49	5.78	12.87	20.74	20.27	10.6	6.86
Sonin et al. (1994) (fitted values ε_f)	32	38	60	-	40	-	38

Table 4.7. Comparison of surface elasticity ε measured for different concentrations of the anionic SDS solutions with data in literature.

SDS solution concentrations	1 mM	2 mM	4 mM	6 mM	8 mM	10 mM
Present work	-	0.79	1.16	2.88	4.26	2.32
Prins et al. (1967) (the thickest film)	-	-	27 $\pm$ 1	-	-	-
Karakashev et al. (2010a)	2.99	-	-	-	-	-

The values of the surface elasticity ε measured for in the present work for the non-ionic surfactant C_8E_4 solutions are in reasonable agreement with those of Karakashev and Ivanova (2010a) and Karakashev et al. (2010b) measured for the lower concentrations (cf. Table 4.8). The values measured here are of the same order as those measured for another non-ionic surfactant $C_{12}G_2$ in Georgieva et al. (2009) and Santini et al. (2007). The values of the surface elasticity ε measured for Pluronic P-123 are quite comparable with the values measured in Georgieva et al. (2009) for the other Pluronics, namely Pluronic F-68 and Pluronic F-127 (Table 4.9).

Table 4.8. Comparison of surface elasticity ε measured for different concentrations of the non-ionic C_8E_4 solutions with data in literature.

C_8E_4 solution concentrations	0.1 mM	0.5 mM	1.0 mM	7.5 mM	10 mM
Present work	19.89	34	54	88.27	99.59
Karakashev et al. (2010a) and (2010b)	21.1	-	211	-	1060

Table 4.9. Comparison of surface elasticity ε measured for different concentrations of the non-ionic Pluronic P-123 solutions with data in literature.

Solution concentrations	0.052 mM	0.1 mM	0.5 mM	0.6 mM	1.0 mM
Pluronic P-123 (Present work)	10.93	9.56	8.43	-	-
Pluronic F-68 Georgieva et al. (2009)	-	-	-	21±1.6	-
Pluronic F-127 Georgieva et al. (2009)	-	-	-	-	22.1±1.6

The surface elasticity of a longer non-ionic surfactant $C_{12}E_6$ measured in Stubenrauch et al. (2009) in the concentration range $0.1 \leq c / \text{cmc} \leq 1$ (with c being surfactant concentration) belong to the range 30 to 40 g/s^2 , whereas our data in Tables 4.3 and 4.8 for a shorter non-ionic surfactant C_8E_4 reveal $19.89 \leq \varepsilon \leq 54 \text{ g/s}^2$ in the range $0.013 \leq c / \text{cmc} \leq 0.13$ and $\varepsilon = 88.27 \text{ g/s}^2$ at $c/\text{cmc}=1$. This shows that our data for C_8E_4 is in good agreement with the data for $C_{12}E_6$ at relatively low surfactant concentration and probably overestimates ε at cmc, since ε is expected to increase with chain length Stubenrauch et al. (2009).

4.5 Conclusions

We developed a method of measuring the surface elasticity of surfactant films using gravity-driven drainage from plane vertical films suspended on a wire frame or from a spherical bubble located on the free surface of a liquid pool. The method is based on the theory proposed in this work. The physical pattern of the drainage due to gravity and the effect of the surface elasticity on it is the following. The upper part of the film is stretched by the weight of the film suspended on it. As a result, surfactant concentration is diminished at the surface of the upper part of the film, and surface tension there is higher than in the lower section of the film which is stretched less. The higher surface tension in the upper part of the film results in the Marangoni stress directed upward which opposes gravity-driven drainage. Therefore, the duration of the drainage process is determined by the competition of gravity and the Marangoni stress and could be employed to measure the surface elasticity ε . Moreover, the usage of relatively thick films allows the exclusion of a potentially stabilizing electrostatic forces for practically the entire duration of drainage from the ionic and non-ionic surfactant films (the latter can be prone to specific adsorption of hydroxyl at the film surface).

The surface elasticity values measured in plane films of cationic surfactant DTAB and anionic surfactant SDS increased with an increase in surfactant concentration until cmc was reached, and were found to be maximal at cmc. Below cmc, an increase in the surfactant concentration in the bulk was accompanied by an increase in the surfactant concentration gradient at the film surface, thereby increasing the surface elasticity. Above cmc, the results suggest that the surfactant gradient along the surface diminishes when films are initially formed (since due to stretching, the surface concentration in a stretched film still can be lower than the one corresponding to an optimal packing), and the surface elasticity is lower than the one at cms.

Similar trends were observed with plane films of non-ionic surfactants C_8E_4 and Pluronic P-123. Due to its small cmc value, the experiments with Pluronic P-123 could not be done for concentrations below cmc. However, similarly to the ionic surfactant, the surface elasticity values for Pluronic P-123 decreased with an increase in its concentration above cmc. Higher surface elasticity values for non-ionic surfactant C_8E_4 were measured as compared to the values for the ionic surfactants DTAB and SDS, and the values increased as the surfactant concentration increased.

The spherical bubbles formed with DTAB solutions lasted almost twice the time of the corresponding plane films because the effect of gravity is less pronounced in the drainage from spherical bubbles (note, that the flow is horizontal near the apex and inclined over the rest of the generatrix). The surface elasticity values of DTAB solutions measured for plane films and spherical bubbles were close to each other, indicating that surface elasticity plays the principal role in drainage of thin films, as well as the self-consistency of our two methods of measurements based on plane or spherical films.

CHAPTER 5

SUPERSPREADERS VERSUS “COUSIN” NON-SUPERSPREADERS: DISJOINING PRESSURE IN GRAVITATIONAL FILM DRAINAGE

This chapter has been previously published in Sett et al. (2014a).

Reprinted with permission from [Sett, S., Sahu, R. P., Sinha-Ray, S., & Yarin, A. L. (2014). Superspreaders versus “cousin” non-superspreaders: Disjoining pressure in gravitational film drainage. *Langmuir*, 30(10), 2619-2631]. Copyright 2014 American Chemical Society.

5.1 Introduction

This work aims at gravitational drainage of vertical films of the aqueous solutions of the superspreaders and their “cousin” non-superspreaders, studied using the setup similar to the one described in Sett et al. (2013). Even though superspreader solutions do not contact with any hydrophobic solid surfaces in the present case of gravitational drainage, their behavior is radically different from that of the “cousin” non-superspreaders and the ordinary surfactants. Namely, a dramatic deceleration of the drainage process at the later stage is observed, which makes superspreader films much more stable than their non-superspreader counterparts. The reason of the unusual behavior of superspreaders in the case of gravitational drainage is traced to their disjoining pressure. Disjoining pressure is associated with the internal energy-related part of the free energy, in distinction from the osmotic pressure, which is associated with the entropy-related part of the free energy [Derjaguin et al. (1987)]. The disjoining pressure strongly depends on the film thickness h when $h < 100$ nm, and the dependence (the scaling or the oscillatory character) is determined by the inter-surface repulsion mechanisms in the film on the

microscopic level [Derjaguin et al. (1987); Israelachvili et al. (1992); Nikolov et al. (1989) and Basheva et al. (2007)]. For example, the electrostatic repulsion in the DLVO theory, the van der Waals attraction and repulsion, as well as the steric repulsion and micelle ordering, result in drastically different dependences of the disjoining pressure on the film thickness h [Derjaguin et al. (1987); Israelachvili (1992); Nikolov et al. (1989); Basheva et al. (2007); Alexander (1977) and de Gennes (1987)].

Disjoining pressure was measured using Scheludko [Scheludko (1967) and Exerova and Kruglyakov (1998)] and/or Mysels-Jones [Basheva et al. (2007) and Mysels and Jones (1966)] cells for many ordinary cationic, anionic and non-ionic surfactants. In the present work we introduce an alternative technique, gravitational film drainage, and apply it to superspreaders and their “cousin” non-superspreaders. The following section describes the materials and the experimental setup and method. Then, the experimental results are presented. After that, the theoretical section is given, which is followed by the comparison with the experimental data and discussion. Conclusions are drawn at the end.

5.2 Experimental

5.2.1 Materials

The following trisiloxane-(poly)ethoxylate surfactants were used in drainage experiments. SILWET L-77 (superspreader) and SILWET L-7607 (the “cousin” non-superspreader), both obtained from Momentive, were used as received. In addition, BREAK-THRU S 278 (superspreader) and BREAK-THRU S 233 (the “cousin” non-superspreader), obtained from Evonik Industries were used as received.

5.2.2 Solution preparation

Trisiloxane surfactants SILWET L-77, SILWET L-7607, BREAK-THRU S 278 and BREAK-THRU S 233 were used to prepare solutions as follows. Using the superspreader SILWET L-77, 0.1 ml, 0.2 ml, 0.5 ml and 1 ml of the surfactant was added to 100 ml of deionized water (ASTM Type II). The resulting solutions were denoted as L-77-0.1, L-77-0.2, L-77-0.5, and L-77-1.0, respectively. Using the “cousin” non-superspreader SILWET L-7607, 0.1 ml, 0.2 ml, 0.5 ml and 1 ml of the surfactant was added to 100 ml of deionized water (ASTM Type II), and the resulting solutions were denoted as L-7607-0.1, L-7607-0.2, L-7607-0.5, and L-7607-1.0, respectively. Using the superspreader BREAK-THRU S 278 and the “cousin” non-superspreader BREAK-THRU S 233, solutions were prepared similarly. The BREAK-THRU S 278 solutions were denoted as S 278-0.1, S 278-0.2, S 278-0.5, and S 278-1.0. The BREAK-THRU S 233 solutions were denoted as S 233-0.1, S 233-0.2, S 233-0.5, and S 233-1.0.

5.2.3 Experimental setup and method

The experimental setup and method used to study drainage of vertical plane surfactant films is described elsewhere [Sett et al. (2013)]. In brief, Fig. 5.1 depicts the schematic which shows how the container with a surfactant solution is raised using the linear actuator to create a film supported by the fixed aluminum wire frame (4 cm x 4 cm x 0.087 cm). The container is then lowered and the film which stays on the frame is photographed using a CCD camera (Phantom Miro 4), while the data are stored in the computer. It was found that fully reliable and self-consistent data can be acquired for film thicknesses above 30 nm [Sett et al. (2013)]

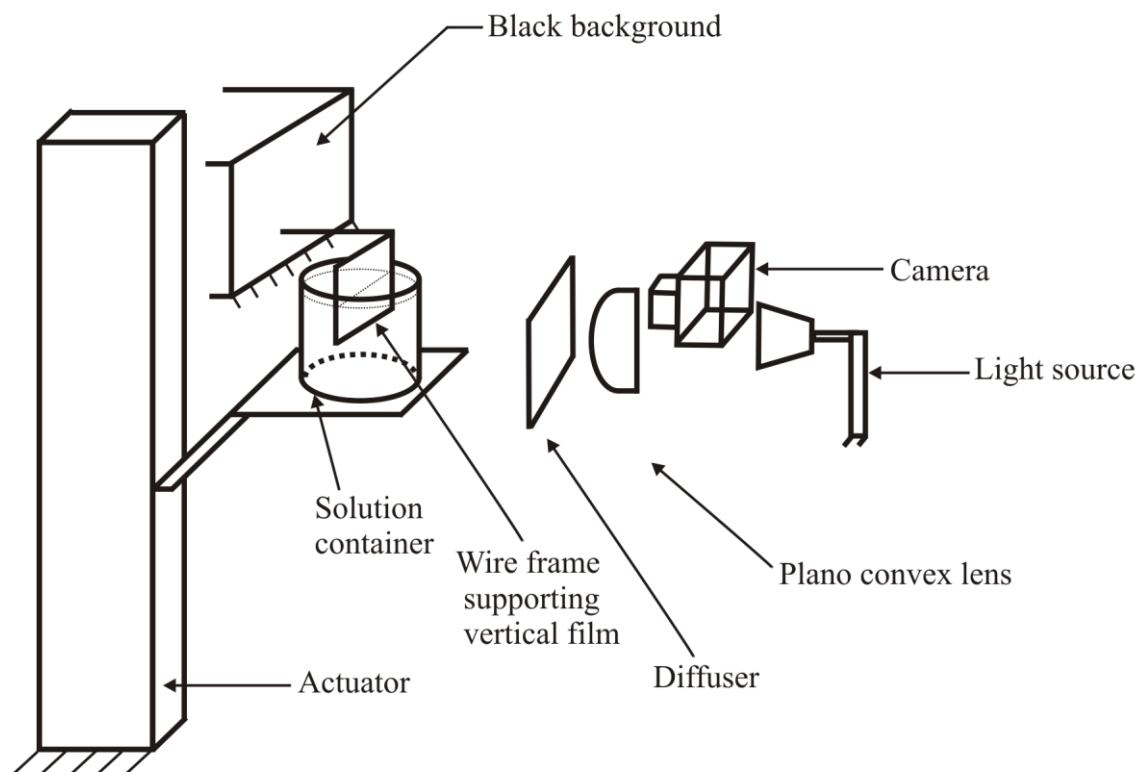


Figure 5.1. Schematic of the experimental setup.

The film thickness at the top was measured right below the top wire and 2 cm from the left wire, so the side wires did not have any effect on the film thickness. The local film thickness h was calculated using the interferometric formula [Sett et al. (2013); Karakashev et al. (2005); Karakashev and Nguyen (2009); Karakashev and Ivanova (2010a); Karakashev et al. (2011) and Karakashev et al. (2008a)].

5.3 Experimental results

The critical micelle concentration (cmc) of each of the four surfactants was determined by measuring the surface tension using the Wilhelmy plate apparatus (KRUSS Tensiometer K 12) [Rao et al. (1982) and Danov et al. (2004)] with the plate dimensions of 20 mm x 10 mm. The

data in Fig. 5.2 show that at the concentration 0.007 %v/v, for SILWET L-77, SILWET L-7607, BREAK-THRU S 278 and BREAK-THRU S 233 the surface tensions had saturated. This value was considered as the cmc value corresponding to these surfactants. The concentration of all the solutions used in the drainage experiments was above their critical micelle concentration.

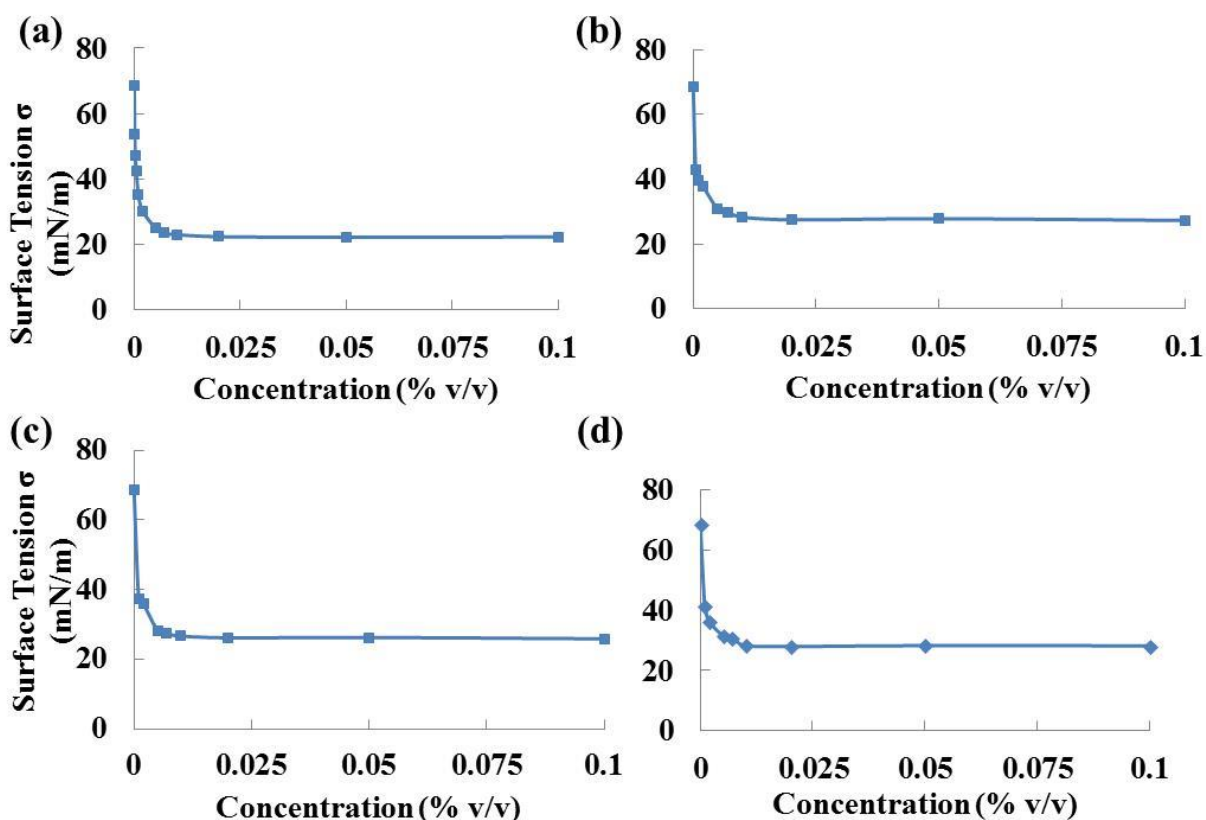


Figure 5.2. Surface tension measured using the Wilhelmy plate technique for: (a) SILWET L-77, (b) SILWET L-7607, (c) BREAK-THRU S 278, and (d) BREAK-THRU S 233.

Dynamic Light Scattering (DLS) was used to measure the aggregate sizes formed in solutions of SILWET L-77, SILWET L-7607, BREAK-THRU S 278, and BREAK-THRU S 233 at concentration 0.5 %v/v above cmc.

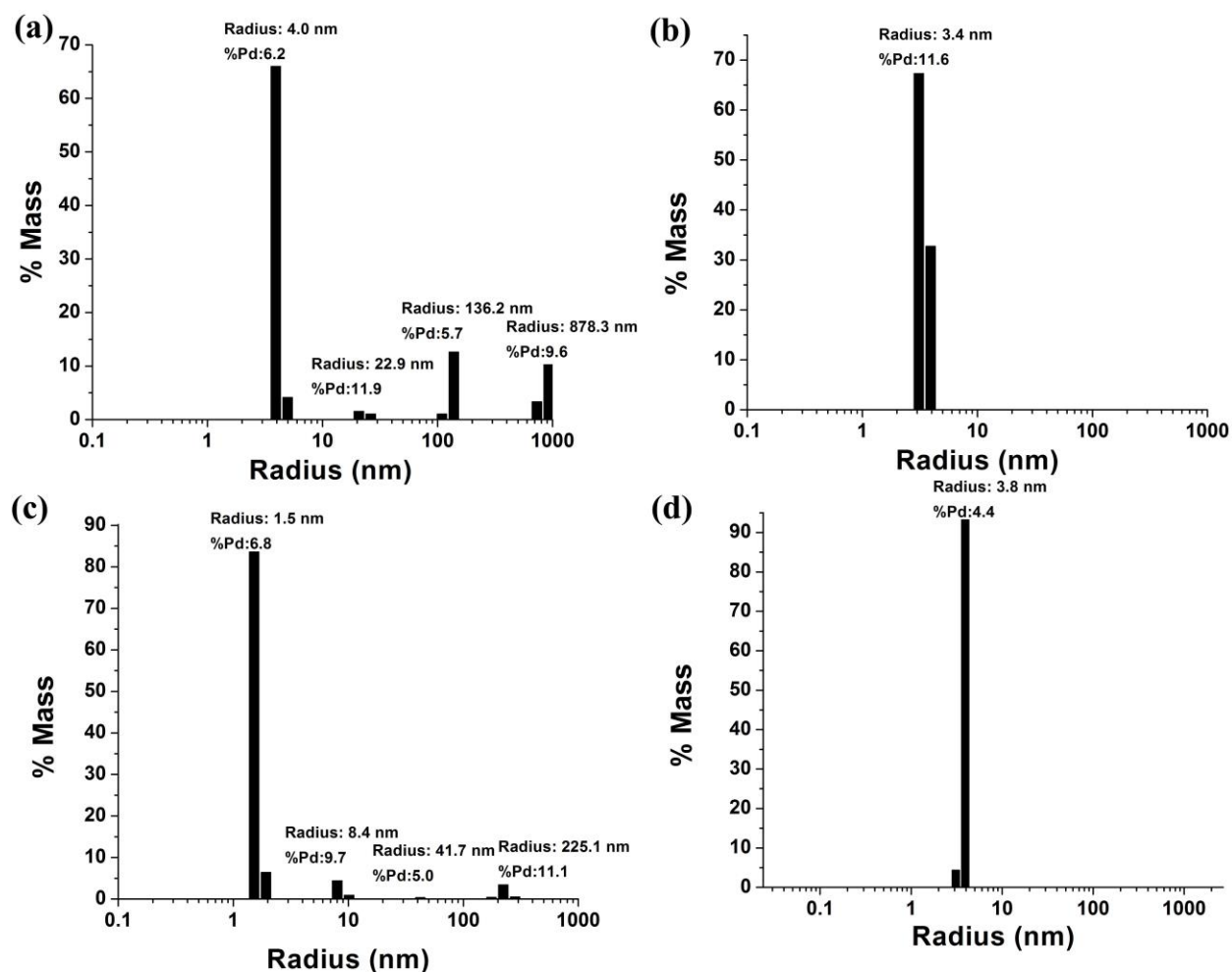


Figure 5.3. Aggregate size distribution for 0.5 %v/v solutions of: (a) SILWET L-77, (b) SILWET L-7607, (c) BREAK-THRU S 278, and (d) BREAK-THRU S 233. %Pd stands for the percentage of polydispersity which is a measure of standard deviation and is indicative of the distribution of each peak. %Mass is the percentage of mass of aggregates of a particular size present in the solution.

The solutions prepared from the superspreaders SILWET L-77 and BREAK-THRU S 278 were turbid in appearance, and the turbidity was found to increase with concentration. It is evident from Fig. 5.3 that the superspreader solutions contain aggregates which are two orders of magnitude larger than their counterpart non-superspreader. The aggregate structures in the

superspreader solutions combine and form larger entities (Figs. 5.3a and 5.3c) known as mesomorphic phases [Particle Sciences Technical Brief (2012)]. These are anisotropic structures causing solution turbidity and resulting in light scattering. Increasing surfactant concentration increases the number of such aggregates, and thus, turbidity. On the contrary, solutions prepared from the “cousin” non-superspreaders SILWET L-7607 and BREAK-THRU S 233 stayed clear. They formed smaller aggregates/micelles (Figs. 5.3b and 5.3d) that are too small to cause any significant light scattering [Particle Sciences Technical Brief (2012)]. The size of aggregates formed in surfactant solutions depends on the critical packing parameter P [Israelachvili (1992) and Venzmer and Wilkowski (1998)]

$$P = \frac{V}{a_0 \ell_c} \quad (5.1)$$

where V is the chain volume, a_0 is the optimal aggregate-water interfacial area (the hydrocarbon/water interfacial area), and ℓ_c is the critical chain length.

For surfactants with the hydrophilic head group larger than the hydrophobic part ($P < 1$), curved aggregates such as spherical or cylindrical micelles are formed. For comparable sizes of hydrophilic and hydrophobic parts, $P = 1$, surfactant bilayer aggregates are formed [Israelachvili (1992) and Venzmer and Wilkowski (1998)].

For trisiloxane surfactants, the length of poly(ethylene oxide) increases from 7.5 for SILWET L-77 to 16 for SILWET L-7607. A similar increase in the length of poly(ethylene oxide) is found when BREAK-THRU S 278 and BREAK-THRU S 233 are compared. The small hydrophilic head group in the superspreaders SILWET L-77 and BREAK-THRU S 278 results in formation of larger aggregates (vesicles and bilayers) and turbid solutions as compared to the smaller micellar aggregates of the non-superspreaders SILWET L-7607 and BREAK-THRU S

233, and their clear solutions. This is in agreement with a well-established fact that surfactants having shorter hydrophilic chains form large aggregates, while those with longer chains form smaller aggregates [Venzmer (2011) and Hill (1999)].

Solutions with different concentrations of the superspreaders SILWET L-77 and BREAK-THRU S 278, and their non-superspreader counterparts SILWET L-7607 and BREAK-THRU S 233, respectively, were used in the gravitational drainage experiments. For SILWET L-77 solution L-77-0.1, it was observed that initially the interference color bands were formed. These color bands were not uniform horizontally and each color strip was of uneven thickness. With time, the visible colors in the upper part of the wire frame mixed with one another, indicating non-uniform film thickness in the horizontal direction. Towards the bottom of the wire frame, the film became turbid with time, and no distinct colors could be seen in a while. After 55 s from the formation of the film, the topmost part of the film turned black, where the measured thickness was ~ 50 nm (Fig. 5.4a). The top part of the film remained black for the remaining time. The black domain was confined to the topmost part and did not spread downward with time. The color intermittency over the entire film further increased gradually till the film burst after 105 s (Fig. 5.4a, the inset image). It is emphasized that the “abstract” color patterns in all the superspreader solutions as shown in Fig. 5.4 (the inset images) are dramatically different from the regular horizontal color bands observed before for the ordinary cationic, anionic and non-ionic surfactants [Sett et al. (2013)]. As it is shown below, the “abstract” color patterns of the superspreader solutions are also very different from those of the cousin non-superspreaders.

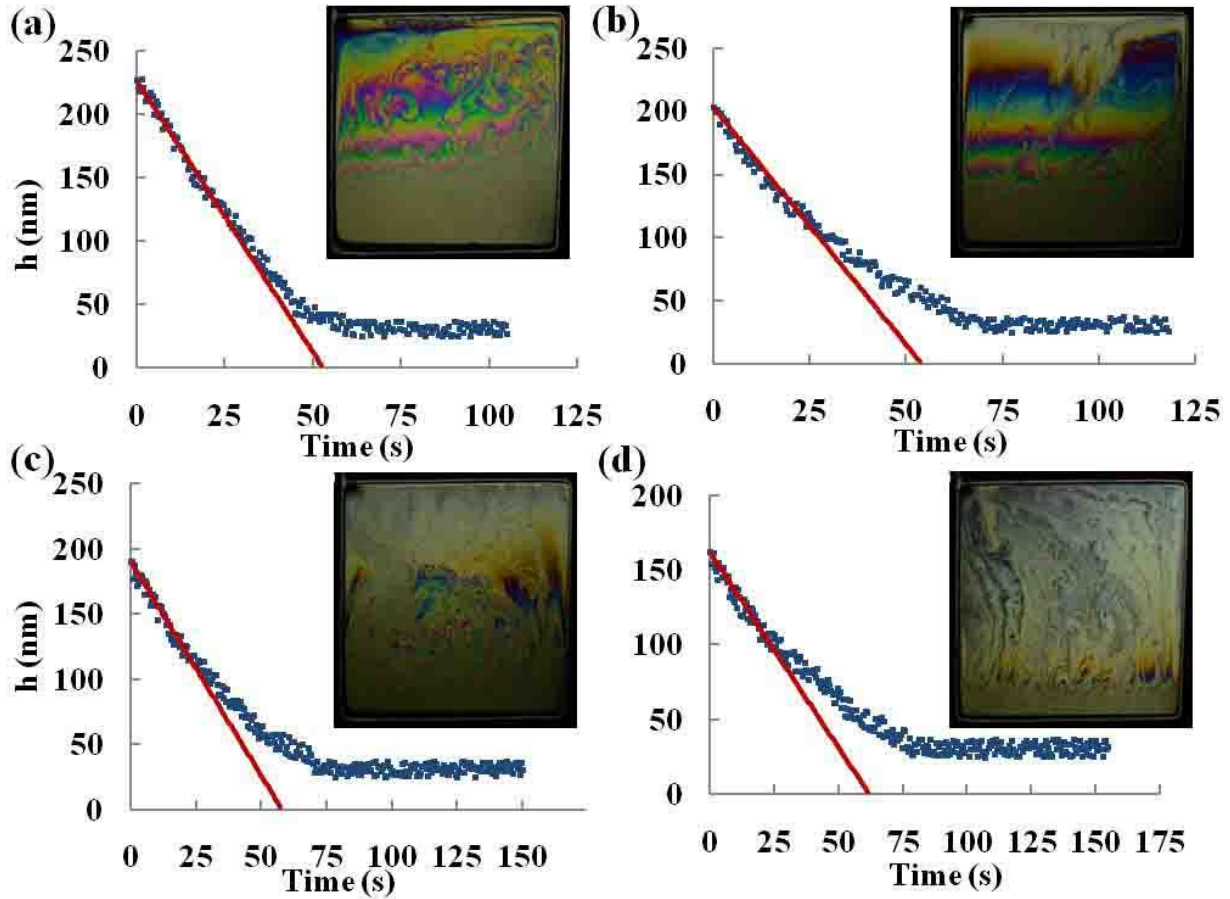


Figure 5.4. Drainage of the plane films of the superspreader SILWET L-77 solutions: (a) L-77-0.1, (b) L-77-0.2, (c) L-77-0.5, and (d) L-77-1.0. The data correspond to the film top. The experimental results are shown by symbols. The inclined straight lines correspond to the theoretical prediction of Sett et al. (2013), Eq. (5.16) in the present work. The inset images show the interference patterns just prior to the film bursting.

For SILWET L-77 solution L-77-0.2, similar observations were done. The black film had been formed at the film top after 65 s (Fig. 5.4b). It descended down with time and a considerable part of the film at the top was black when the film burst after 118 s (Fig. 5.4b, the inset image). For SILWET L-77 solution L-77-0.5, after the initial color intermittency led to an

uneven color distribution, plumes were seen to rise from the bottom, indicating that the thickness distribution is uneven and highly transient. The plumes made the bottom part of the film blurred and no distinct colors were seen in these regions. The top part of the film turned black after 72 s (Fig. 5.4c) and the black domain advanced downward with time. The black film occupied at about one half of the film length along the wire frame at the time of bursting after 150 s (Fig. 5.4c, the inset image).

It should be emphasized that the color intermittency in the horizontal direction over the superspreader films in Fig. 5.4 according to the interferometric formula [Sett et al. (2013); Karakashev et al. (2005); Karakashev and Nguyen (2009); Karakashev and Ivanova (2010a); Karakashev et al. (2011) and Karakashev et al. (2008a)] corresponds to the film thickness variation in the horizontal direction Δh on the scale of $\Delta h = \Delta \lambda / (2\pi n)$, with $\Delta \lambda$ being the wavelength difference between the two colors, and n being the refractive index ($n=1.333$). In the worst case of red color replaced by blue color or vice versa $\Delta h \approx 23.8 \text{ nm}$, which would result in variance close to $\pm 10 \text{ nm}$ about the mean. In reality, the color intermittency is less than in the worst case, and the results shown in Fig. 5.4 reveal the following accuracies corresponding to the thinnest films stabilized by the superspreader: Fig. 5.4(a): $36 \pm 4 \text{ nm}$ (L-77-0.1), Fig. 5.4(b): $35 \pm 3 \text{ nm}$ (L-77-0.2), Fig. 5.4(c): $36 \pm 3 \text{ nm}$ (L-77-0.5), and Fig. 5.4(d): $35 \pm 3 \text{ nm}$ (L-77-1.0). This shows that the accuracy is sufficient even at the lowest data branches for the highly intermittent films of superspreader solutions. Note also, that measurements were done only when distinct colors were fully recognizable, whereas turbid areas near the bottom of the wire frame were never used.

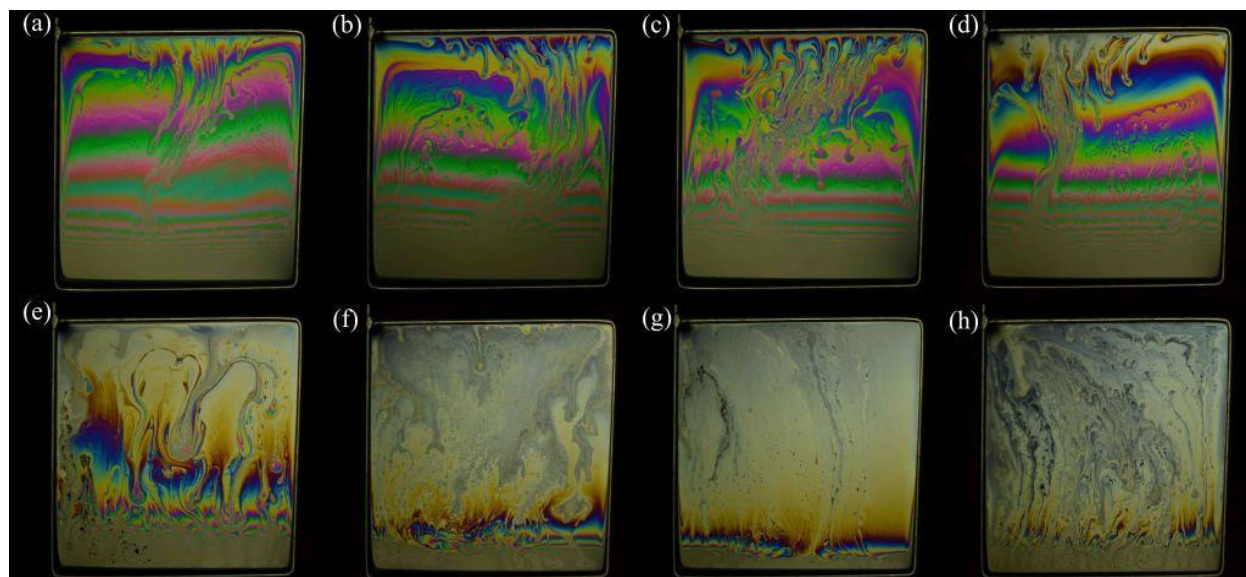


Figure 5.5. Drainage of the superspreader SILWET L-77-1.0 film at: (a) $t = 0$ s, (b) $t = 25$ s, (c) $t = 50$ s, (d) $t = 70$ s, (e) $t = 90$ s, (f) $t = 110$ s, (g) $t = 130$ s, and (h) $t = 155$ s.

The time evolution of the film of the superspreader SILWET L-77 solution L-77-1.0 is illustrated in Fig. 5.5. In such a film, the number of rising plumes increased and eventually could be seen covering the entire film. “Turbulent”-like patterns seen on the film were also much larger compared to the lower concentration films. The black film formed at the top after 78 s (Fig. 5.4d, the inset image, and Fig. 5.5e), increased with time and covered the entire film at the moment of bursting (Fig. 5.4d, the inset image, and Fig. 5.5h).

Even though the superspreader films looked pretty agitated and transient (Fig. 5.4, the inset image, and Fig. 5.5), they showed a remarkable stabilization at the latter stage of their existence, as is seen in Fig. 5.4. They were stabilized at thicknesses ~ 35 nm where they stopped thinning linearly in time [Sett et al. (2013)], and their thinning was practically arrested for a long time. This is dramatically different from the observations of drainage of the ordinary cationic,

anionic and non-ionic surfactants (refs 6 and 26 and references therein, and the cousin non-superspreaders discussed below).

For the second superspreader studied in this work, BREAK-THRU S 278, similar trends were observed to those in Fig. 5.4 for the superspreader SILWET L-77. The corresponding results for solutions S 278-0.1 to S 278-1.0 are presented in Fig. 5.6. With the increase in the surfactant concentration, the length of the black section at the film top at the time of bursting increases and reaches the maximum for S 278-1.0 (Fig. 5.6, the inset images). Even for BREAK-THRU S 278 solution S 278-1.0 (Fig. 5.6d, the inset image), the black film did not spread over the entire film length, in distinction from the superspreader SILWET L-77 in Fig. 5.4d (the inset image). Also, “plumes” were seen to rise from the bottom of the wire frame for BREAK-THRU S 278 solution S 278-0.2 (Fig. 5.6b, the inset image) and the intensity of these plumes increased for S 278-0.5 (Fig. 5.6c, the inset image) and S 278-1.0 (Fig. 5.6d, the inset image).

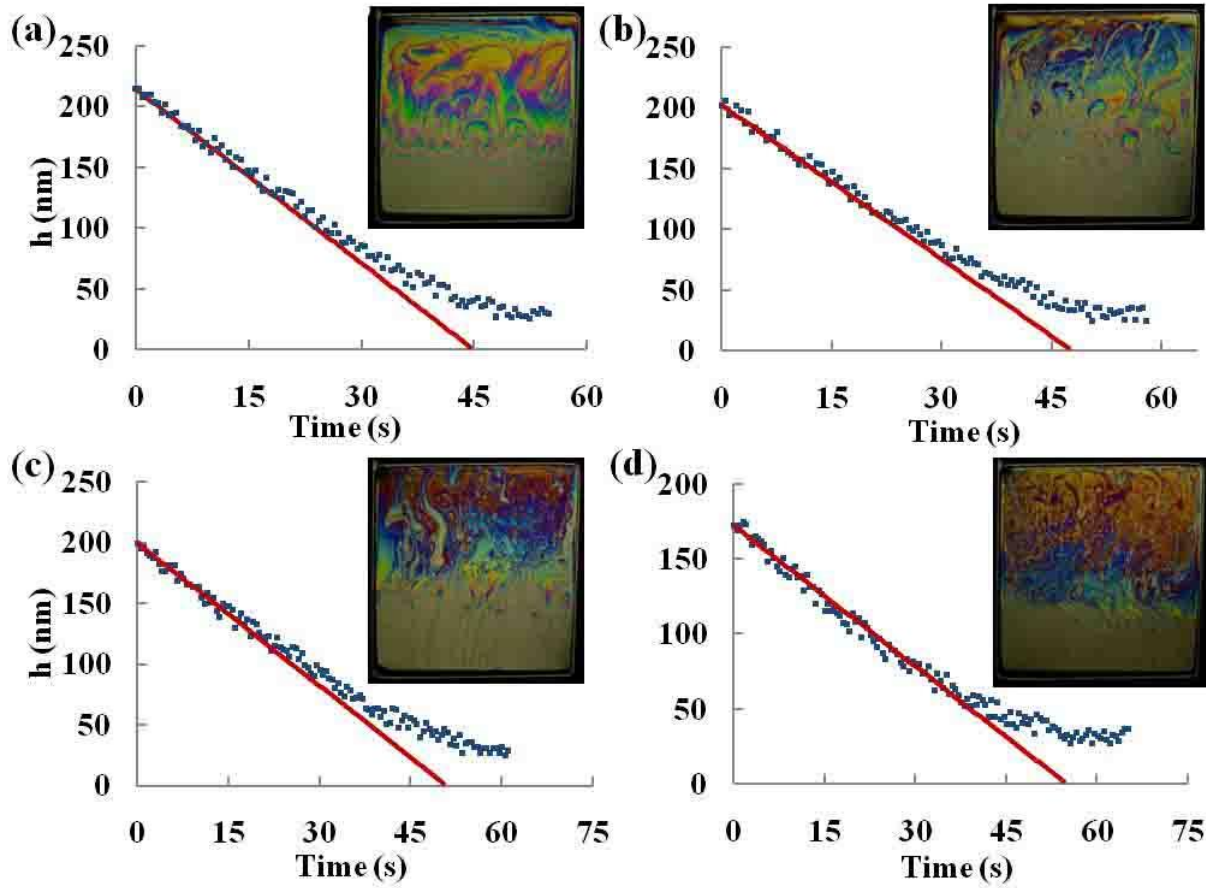


Figure 5.6. Drainage of the superspreader BREAK-THRU S 278 solution films: (a) S 278-0.1, the lowest branch corresponds to 34 ± 2 nm; (b) S 278-0.2, the lowest branch corresponds to 35 ± 4 nm; (c) S 278-0.5, the lowest branch corresponds to 34 ± 3 nm; and (d) S 278-1.0, the lowest branch corresponds to 33 ± 3 nm. The data correspond to the film top. The experimental results are shown by symbols. The inclined straight lines correspond to the theoretical prediction of Sett et al. (2013), Eq. (5.16) in the present work. The inset images show the interference patterns just prior to the film bursting. It is emphasized that due to the vigorous “turbulent”-like motion, the lower half of the film becomes so hazy that colors cannot be seen in that region. Colors can only be seen in the top part of the film, in distinction from Fig. 5.4 (the inset images) and Fig. 5.5 where colors are seen in the entire film. Only in Fig. 5.5h the lower part of the film (close to the bottom wire frame) does turn hazy, somewhat similar to those in the present figure. Perhaps, the

lower part of the film is turbid in the present case because of the larger aggregates suspended mostly in the lower portion of the film. This is similar to milk turbidity due to the Tyndall effect.

Figure 5.7 shows that the experimental data for the non-superspreaders SILWET L-7607 is in good agreement with Eq. (5.16) (see the theoretical part below) which reveals a linear decrease in the film thickness during the gravitational drainage near the film top. This is similar to the cationic, anionic and non-ionic surfactants studied earlier [Sett et al. (2013) and Lucassen (1981)], and is drastically different from the results for the “cousin” superspreader SILWET L-77 shown in Fig. 5.4.

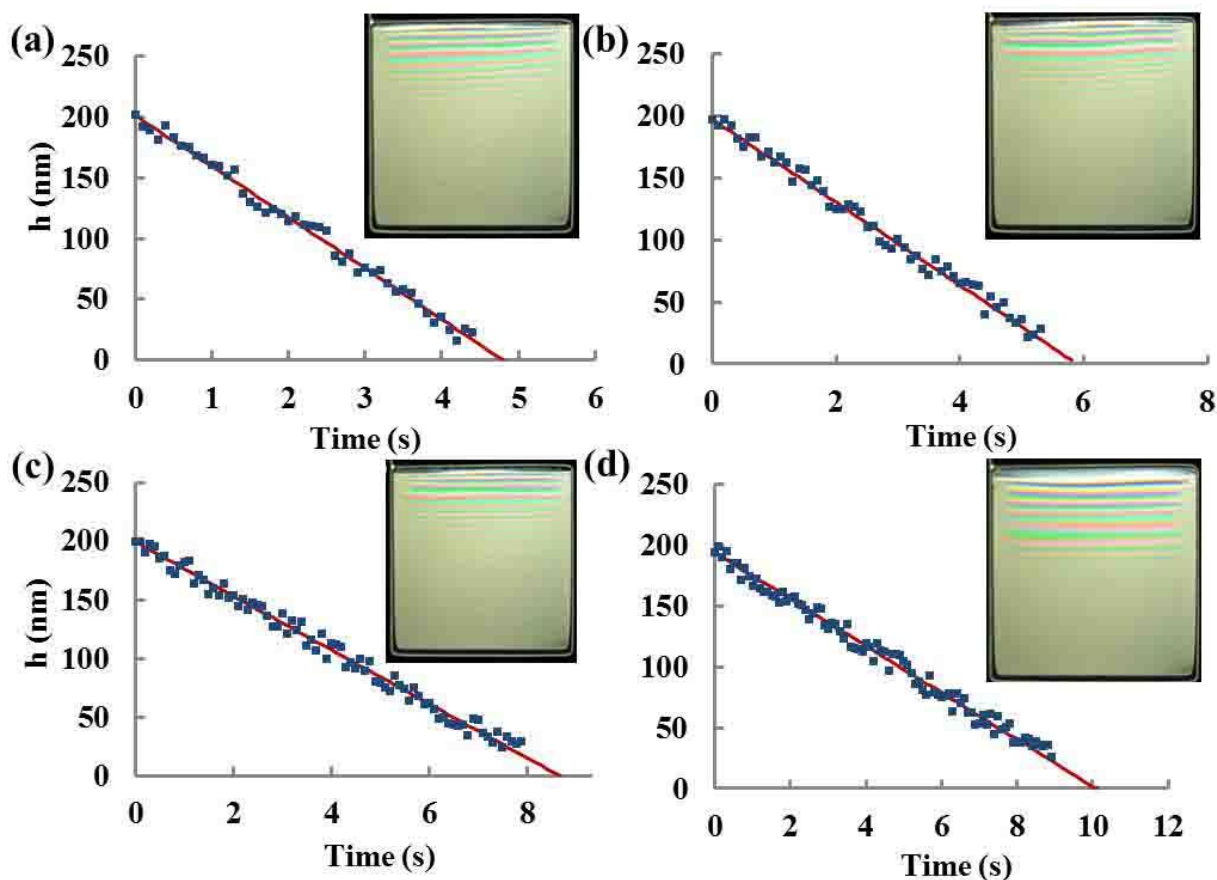


Figure 5.7. Drainage of the non-superspreader SILWET L-7607 solution films: (a) L-7607-0.1, (b) L-7607-0.2, (c) L-7607-0.5, and (d) L-7607-1.0. The data correspond to the film top. The experimental results are shown by symbols. The films burst in about 5-10 s. The inclined straight lines correspond to the theoretical prediction of Sett et al. (2013), Eq. (5.16) in the present work. The inset images show the interference patterns just prior to the film bursting.

For the non-superspreader SILWET L-7607 solution L-7607-0.1, the films burst just after the top part turned black (Fig. 5.7a, the inset image). The length of the black film part on top of the film increased only slightly with the increase in the surfactant concentration, in distinction from the “cousin” superspreader SILWET L-77 (cf. Fig. 5.4, the inset images, and Fig. 5.5). In

fact, only for SILWET L-7607 solution L-7607-1.0, there was a noticeable increase in the black film length at the time of bursting (Fig. 5.7d, the inset image).

Gravitational drainage of plane vertical films of the non-superspreader BREAK-THRU S 233 solutions S 233-0.1, S 233-0.2, S 233-0.5, and S 233-1.0 revealed a linear decrease in the film thickness (Fig. 5.8) with no stabilization characteristic of the superspreader counterpart BREAK-THRU S 278 (Fig. 5.6).

Solutions of the non-superspreader BREAK-THRU S 233 revealed similar regular horizontal interference color strips like those of the non-superspreader SILWET L-7607 solutions (Fig. 5.7, the inset images) or the solutions of the ordinary cationic, anionic and non-ionic surfactants studied in Sett et al. (2013) and Lucassen (1981) and references therein. On the other hand, such film patterns are drastically different from those for both superspreaders SILWET L-77 (Fig. 5.4, the inset images, and Fig. 5.5) and BREAK-THRU S 278 (Fig. 5.6, the inset image). Only the small top parts of the non-superspreader BREAK-THRU S 233 films turned black before the bursting (Fig. 5.8, the inset images).

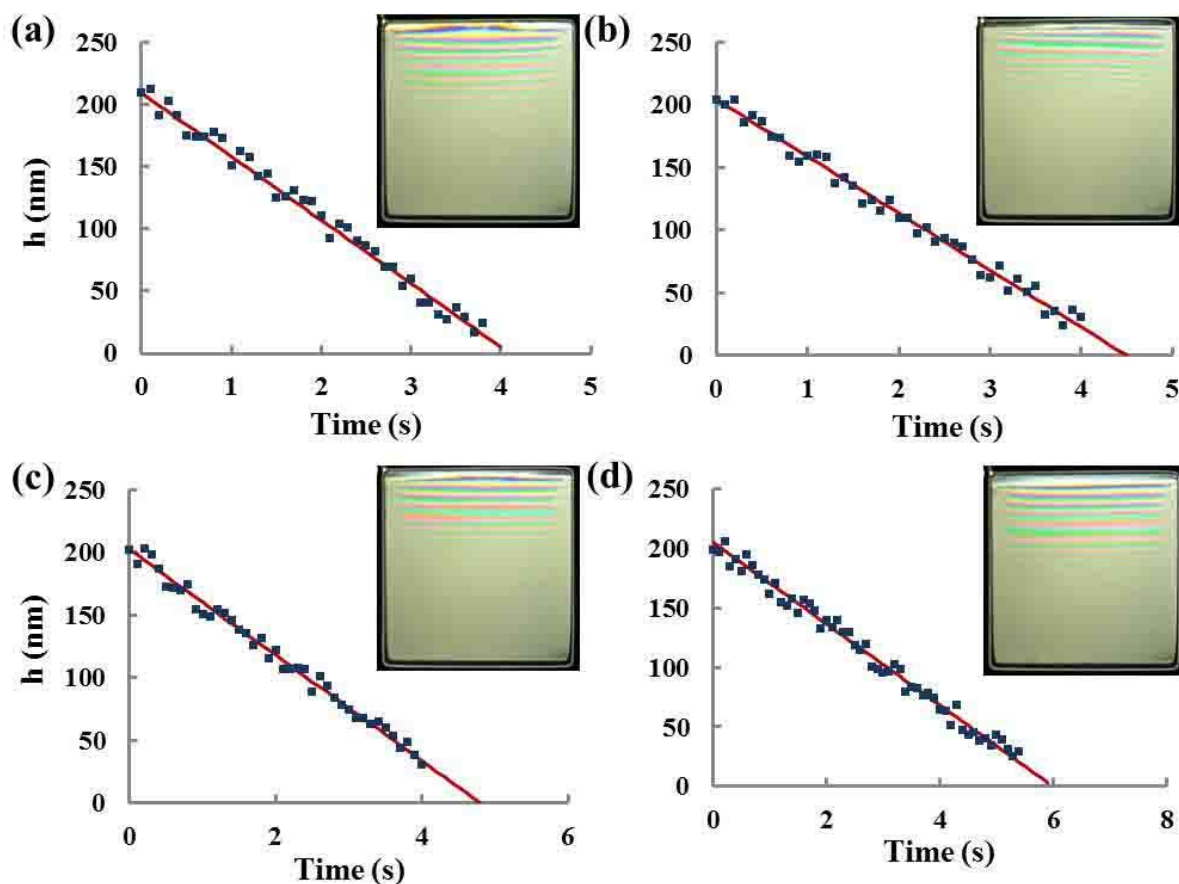


Figure 5.8. Drainage of the non-superspreader BREAK-THRU S 233 solution films: (a) S 233-0.1, (b) S 233-0.2, (c) S 233-0.5, and (d) S 233-1.0. The data correspond to the film top. The experimental results are shown by symbols. The films burst in about 4-6 s. The inclined straight lines correspond to the theoretical prediction of Sett et al. (2013), Eq. (5.16) in the present work. The inset images show interference patterns just prior to the film bursting.

Overall, the thin films formed from the superspreader solutions were stable for a much longer time in comparison with the cousin non-supspreaders and the ordinary surfactants [Sett et al. (2013) and Lucassen (1981)], albeit also much more “vigorous (Figs. 5.4, 5.5, and 5.6, the inset images, versus Figs. 5.7 and 5.8, the inset images). The thinning of the superspreader films was practically arrested at the latter stage, whereas the “cousin” non-superspreader films

continued to drain (Figs. 5.4 and 5.6 versus Figs. 5.7 and 5.8). The thin films formed by the superspreaders (cf. Figs. 5.9a and 5.9c) revealed a “turbulent”-like motion (a pretty stable motion) visibly different from the marginal regeneration [Berg et al. (2005); Mysels (1968); Mysels (1959); Nierstrasz and Frens (1999), Nierstrasz and Frens (2001) and Berg et al. (2004)], which is a destabilizing effect. On the other hand, the non-superspreader films (cf. Figs. 5.9b and 5.9d) revealed the ordered drainage pattern characteristic of the ordinary surfactants [Sett et al. (2013) and Lucassen (1981)].

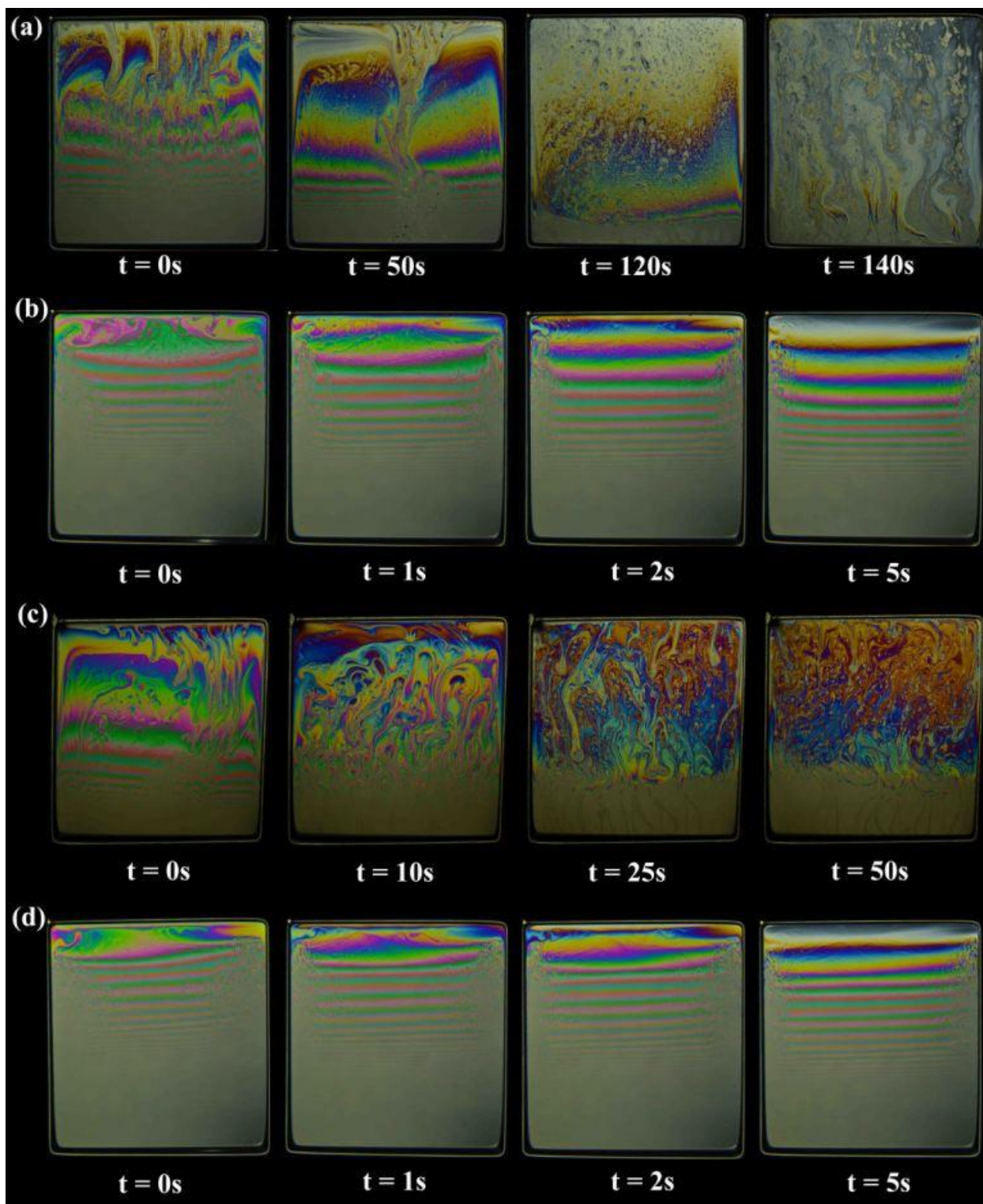


Figure 5.9. Drainage of (a) the superspreader Silwet L-77, and (b) its “cousin” non-superspreader Silwet L-7607. Drainage of the superspreader (c) BREAK-THRU S 278, and (d) its “cousin” non-superspreader BREAK-THRU S 233.

5.4 Theoretical

5.4.1 Effect of disjoining pressure on drainage rate

Gravitational drainage of a vertical plane film of surfactant solution suspended on a wide rectangular wire frame sketched in Fig. 5.10 was theoretically studied in Sett et al. (2013) for the cases where the films were sufficiently thick for the disjoining pressure to be neglected. The theory accounts for the surfactant concentration gradient-driven Marangoni flow determined by the surface elasticity and directed upward, which decelerates the gravity-driven drainage. In addition, in the present work a generalization for the case where the disjoining pressure is important is proposed. The need for such generalization is motivated by the experimental data for the superspreaders, which revealed dramatic stabilization of the drainage process at the latter stages in Figs. 5.5 (for SILWET L-77) and 5.6 (for BREAK-THRU S 278).

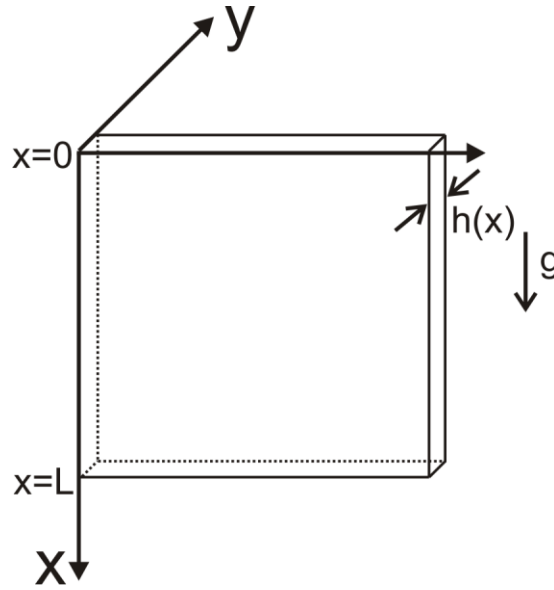


Figure 5.10. Sketch of a plane vertical surfactant film on a wire frame.

In Fig. 5.10 the coordinate reckoned in the drainage direction is denoted as x and the coordinate normal to it as y . The quasi-one-dimensional mass balance equation for the film drainage without accounting for the disjoining pressure [Sett et al. (2013)] can be written as

$$\frac{dh}{dt} = \frac{\partial h}{\partial t} + u \frac{\partial h}{\partial x} = -h \frac{\partial u}{\partial x} \quad (5.2)$$

with h being the film thickness, u being the longitudinal velocity component, t being time, and dh/dt being the material time derivative.

The normal stresses in viscous liquid in the film read

$$\sigma_{xx} = -p + 2\mu \frac{\partial u}{\partial x}, \quad \sigma_{yy} = -p + 2\mu \frac{\partial v}{\partial y} \quad (5.3)$$

with p being pressure, v being the transversal velocity component, and μ being the viscosity.

In the quasi-one-dimensional approximation the stress σ_{yy} is constant across the film, and thus, $\sigma_{yy} = -p_\gamma - p_{disj}$ where p_γ and p_{disj} are the capillary and disjoining pressure. Then, pressure in the film is found as

$$p = p_\gamma + p_{\text{disj}} - 2\mu \frac{\partial u}{\partial x} \quad (5.4)$$

where use is made of the fact that due to the continuity equation $\partial v / \partial y = -\partial u / \partial x$.

Combining the first Eq. (5.3) and Eq. (5.4) yields

$$\sigma_{xx} = 4\mu \frac{\partial u}{\partial x} - p_\gamma - p_{\text{disj}} \quad (5.5)$$

and, correspondingly, the total normal force in the film cross-section reads

$$\sigma_{xx} h + 2\gamma = 4\mu h \frac{\partial u}{\partial x} - p_\gamma h - p_{\text{disj}} h + 2\gamma \quad (5.6)$$

with γ being the surface tension.

In the inertialess approximation the quasi-one-dimensional momentum balance equation reads

$$\frac{\partial \sigma_{xx} h}{\partial x} + \frac{\partial 2\gamma_0}{\partial x} + 2\sigma_{yx,\text{surf}} + \rho g h = 0 \quad (5.7)$$

where, γ_0 represents an invariable part of the surface tension (if any) and, as usual [Sett et al. (2013); de Gennes (2001) and Levich (1962)], the variable part of the surface tension associated with the concentration Marangoni effect determines the shear stress acting at the film surface $\sigma_{yx,\text{surf}}$. In addition, ρ denotes the liquid density and g is the gravity acceleration.

In the almost uniform films of low viscosity aqueous surfactant solutions the contribution of the first term on the left in Eq. (5.7) is negligibly small [Sett et al. (2013); Lucassen (1981) and de Gennes (2001)], the capillary pressure is absent, also $\partial \gamma_0 / \partial x \equiv 0$, and Eq. (5.7) reduces to the following form

$$\sigma_{yx,\text{surf}} = -\frac{\rho g h}{2} + \frac{1}{2} \frac{\partial p_{\text{disj}} h}{\partial x} \quad (5.8)$$

which generalizes Eq. (3) of Sett et al. (2013), or Eq. (12) of Lucassen (1981), or Eq. (3) of de Gennes (2001) on the cases where the disjoining pressure is important. It is emphasized that the theoretical approach to gravitational drainage of surfactant films developed in Sett et al. (2013) and de Gennes (2001) fully accounts for the surfactant concentration gradient-driven Marangoni effect and the associated surface elasticity of such films.

Taking the material time derivative d/dt of Eq. (5.8) and accounting for the relation of $\sigma_{yx,surf}$ with the surface elasticity (the Gibbs elasticity corresponding to the Marangoni effect) $\varepsilon = -\Gamma(\partial\gamma/\partial\Gamma)$, one arrives at the following expression

$$-\frac{\rho g}{2\varepsilon} \frac{dh}{dt} = \frac{\partial^2 u}{\partial x^2} - \frac{1}{2\varepsilon} \frac{d}{dt} \left(\frac{\partial p_{disj} h}{\partial x} \right) \quad (5.9)$$

where ε is associated with the dependence of the surface tension γ on the distribution of surfactant concentration Γ at the surface.

Using the mass balance Eq. (5.2), we rearrange Eq. (5.9) to the following form

$$h = \frac{2\varepsilon}{\rho g} \frac{\partial^2 u / \partial x^2}{\partial u / \partial x} - \frac{1}{\rho g} \frac{d \left[\partial (p_{disj} h) / \partial x \right] / dt}{\partial u / \partial x} \quad (5.10)$$

This equation generalizes Eq. (9) of Sett et al. (2013) on the cases where the disjoining pressure is important. Note that

$$\frac{d}{dt} \left(\frac{\partial p_{disj} h}{\partial x} \right) = \frac{d}{dh} \left(\frac{\partial p_{disj} h}{\partial x} \right) \frac{dh}{dt} = \frac{d}{dh} \left(\frac{\partial p_{disj} h}{\partial x} \right) \left(-h \frac{\partial u}{\partial x} \right) \quad (5.11)$$

where use was made of Eq. (5.2). Then, Eq. (5.10) takes the form

$$h = \frac{2\varepsilon}{\rho g} \frac{\partial^2 u / \partial x^2}{\partial u / \partial x} \left[1 - \frac{1}{\rho g} \frac{d}{dh} \left(\frac{\partial p_{disj} h}{\partial x} \right) \right]^{-1} \quad (5.12)$$

The characteristic length scale along the film is $\varepsilon/(\rho gh)$ [note that it is of the order of 1 cm in the present case]. Using this length scale, the following approximation is made

$$\frac{d}{dh} \left(\frac{\partial p_{\text{disj}} h}{\partial x} \right) \approx - \frac{\rho g h}{\varepsilon} \frac{dp_{\text{disj}} h}{dh} \quad (5.13)$$

whereas Eq. (5.12) approximately takes the following form

$$h = \left[\frac{2\varepsilon}{\rho g} \frac{\partial^2 u / \partial x^2}{\partial u / \partial x} \right] [1 - F(h) / \varepsilon] \quad (5.14)$$

with

$$F(h) = h \frac{d}{dh} [p_{\text{disj}}(h) h] \quad (5.15)$$

The first multiplier on the right-hand side in Eq. (5.14) describes gravitational drainage without accounting for the effect of the disjoining pressure [Sett et al. (2013)], whereas the second one is the correction associated with the disjoining pressure. Without the effect of the disjoining pressure the film thickness at the top of the film linearly diminishes in time as

$$h(x, t) = h_0 \left(1 - \frac{t}{T} \right) \quad (5.16)$$

where h_0 is the initial film thickness at the top, and the characteristic time scale T is given by

$$T = \frac{\varepsilon}{\rho (g h_0)^{3/2}} \quad (5.17)$$

Accounting for the effect of the disjoining pressure, we obtain from Eqs. (5.14) and (5.16) the following expression for the film thickness at the top

$$\bar{h} = (1 - \bar{t}) M(\bar{h}) \quad (5.18)$$

where the dimensionless film thickness $\bar{h} = h / h_0$, the dimensionless time $\bar{t} = t / T$, and the dimensionless function $M(\bar{h})$ is found using Eq. (5.15) as

$$M(\bar{h}) = 1 - \bar{h} \frac{d}{d\bar{h}} \left[\overline{p_{\text{disj}}}(\bar{h}) \bar{h} \right] \quad (5.19)$$

In the latter equation the disjoining pressure is rendered dimensionless by ε/h_0 .

It is emphasized that the function $M(\bar{h})$ can be calculated from the deviation of the experimental data for the film thicknesses of the superspreader solutions from the linear red lines in Figs. 5.4 and 5.6, i.e. plotting $M(\bar{h}) = \bar{h}/(1-\bar{t})$ versus $\bar{h}$. Then, the disjoining pressure responsible for the drastic deceleration of the gravitational film drainage is found as

$$\overline{p_{\text{disj}}}(\bar{h}) = \frac{1}{\bar{h}} \int_{\bar{h}}^1 \frac{[M(\bar{h}) - 1]}{\bar{h}} d\bar{h} \quad (5.20)$$

which implies that the initial film thickness is large enough to have a negligible disjoining pressure, i.e. $\overline{p_{\text{disj}}}(1) = 0$. Note that evaluating the integral in Eq. (5.20), we account for the fact that $\bar{h} < 1$.

5.5 Discussion: experiments versus theory

The data in Fig. 5.4 for the film thickness of the superspreader SILWET L-77 solutions during gravitational drainage was used to find the characteristic time T of the process before the disjoining pressure becomes significant (cf. Eqs. (5.16) and (5.17)). Then, using the difference between the measured data and the linear decrease in the film thickness, the function M (cf. Eq. (5.18)) is established as $M(\bar{h}) = \bar{h}/(1-\bar{t})$. After that the disjoining pressure is found from Eq. (5.20). The results for the superspreader SILWET L-77 solutions are summarized in Table 5.1.

Table 5.1. Superspreader SILWET L-77 solution films. The film lifetime is denoted t ; t_b denotes the time at which black film sets in at the top of the wire frame. The x column corresponds to the position at the film center (reckoned from the top) to which the black film reached at the moment of bursting. The initial film thickness at the top is denoted $h_i=h_0$; the characteristic drainage time is denoted as T . The values of the surface elasticity ε were found from T using Eq. (5.17).

Sol.	t (s)	t_b (s)	x (cm)	$h_i=h_0$ (nm)	T (s)	ε (g/s ²)
L-77-0.1	105	55	0.15	227.03	53	0.176
L-77-0.2	118	65	1.25	202.86	54	0.151
L-77-0.5	150	72	1.95	190.89	58	0.148
L-77-1.0	155	78	3.10	161.15	62	0.124

The corresponding distributions of $\bar{M}(h)$ and the disjoining pressure are shown in Figs. 5.11(a) – 5.11(p), for the superspreader SILWET L-77 – 0.1, L-77 – 0.2, L-77 – 0.5, and L-77 – 1.0 solutions, respectively. In addition, the log-log plots of the measured disjoining pressure versus the film thickness for these superspreader solutions are shown in Figs. 5.12(a)-5.12(d) to demonstrate the repeatability of the results and evaluate the variance. The scaling exponents found using Figs. 5.12(a)-5.12(d) are listed in Table 5.2.

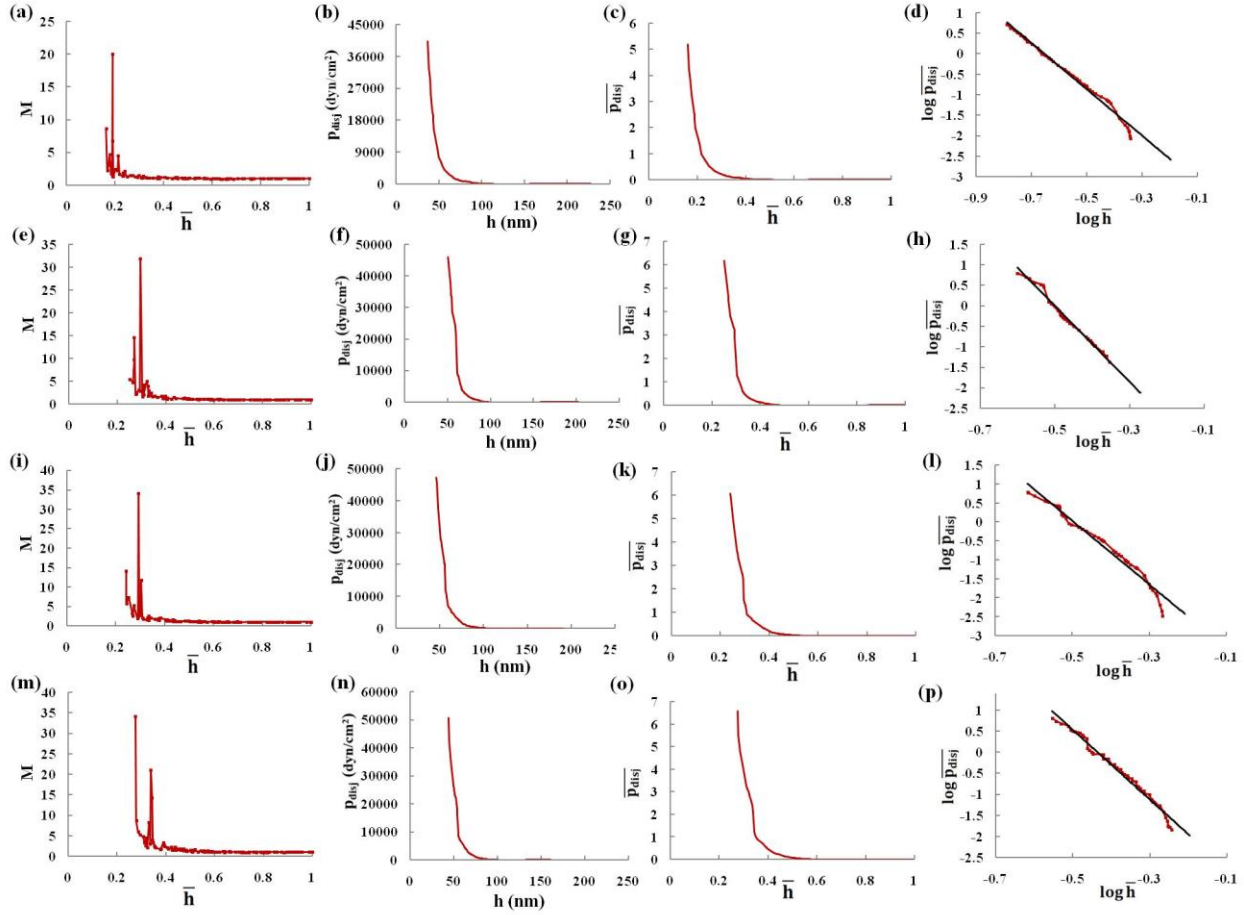


Figure 5.11. The dependences of M and p_{disj} on the film thickness h for the superspreader SILWET L-77 solutions. L-77-0.1 solution: (a) Function M , (b) the dimensional disjoining pressure, (c) the dimensionless disjoining pressure, (d) scaling of the disjoining pressure: the experimental data is shown in red, the straight line used to determine the exponent in the scaling law is black. The dependences of M and p_{disj} on the film thickness h for the superspreader SILWET L-77-0.2 solution, L-77-0.5 solution, and L-77-1.0 solution are shown similarly in panels (e)-(h), (i)-(l), and (m)-(p), respectively.

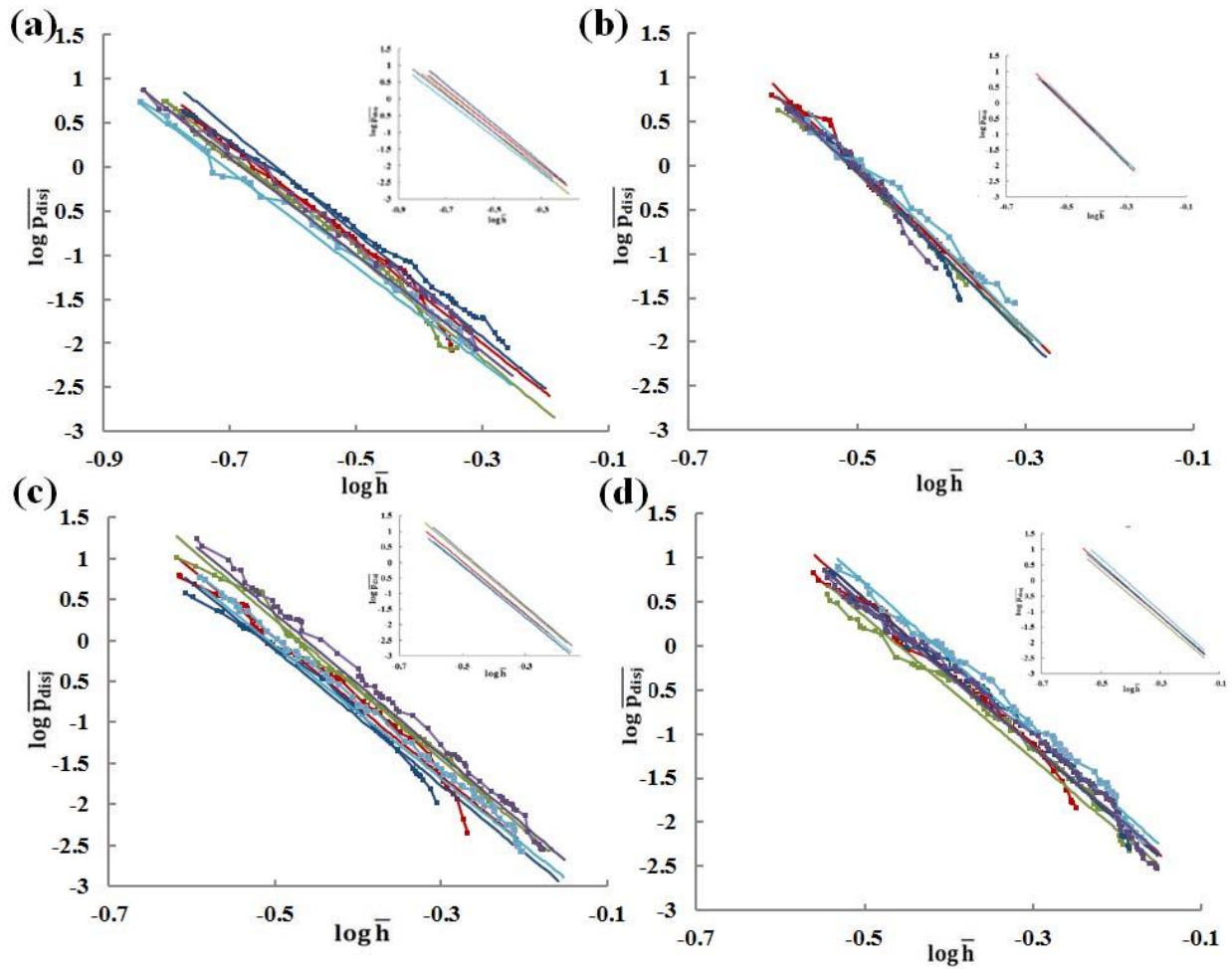


Figure 5.12. Disjoining pressure versus the film thickness for SILWET L-77 solutions of different concentration: (a) L-77-0.1, (b) L-77-0.2, (c) L-77-0.5, and (d) L-77-1.0. The experimental data is shown with symbols spanned with lines and fitted by continuous straight lines of the corresponding color to determine the exponent in the scaling law. The different colors represent different experimental trials where the initial film thickness varied. The data from Figs. 5.11d, 5.11h, 5.11l and 5.11p is shown in red. The inserts show the straight lines corresponding to the scaling laws separately.

Table 5.2. Scaling exponents for the disjoining pressure of the superspreader SILWET L-77 solutions found using the slope of the scaling laws shown in Figs. 5.12a-5.12d.

Solution	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Average exponent
L-77-0.1	-6.38	-6.59	-6.62	-6.15	-6.21	-6.39 ± 0.21
L-77-0.2	-10.7	-10.53	-10.81	-10.95	-10.39	-10.67 ± 0.22
L-77-0.5	-8.66	-8.8	-8.49	-8.37	-8.88	-8.64 ± 0.21
L-77-1.0	-9.37	-9.15	-9.44	-9.56	-9.12	-9.33 ± 0.19

The data for the superspreader BREAK-THRU S 278 in Fig. 5.6 was processed similarly to those for the superspreader SILWET L-77. The results for the linear drainage time T and the corresponding surface elasticity ε of BREAK-THRU S 278 are summarized in Table 5.3.

Table 5.3. Superspreader BREAK-THRU S 278 solution films. The film lifetime is denoted t ; t_b denotes the time at which black film sets in at the top of the wire frame. The x column corresponds to the position at the film center (reckoned from the top) to which the black film reached at the moment of bursting. The initial film thickness at the top is denoted $h_i=h_0$; the characteristic drainage time is T . The values of the surface elasticity ε were found from T using Eq. (5.17).

Sol.	t (s)	t_b (s)	x (cm)	$h_i=h_0$ (nm)	T (s)	ε (g/s ²)
S 278-0.1	51	48	0.10	214.21	45	0.137
S 278-0.2	53	50	0.25	202.26	48	0.134
S 278-0.5	61	54	1.00	199.52	51	0.139
S 278-1.0	65	56	2.20	172.26	55	0.121

The distributions of $\bar{M}(h)$ and the disjoining pressure found using the data in Fig. 5.6 are shown in Figs. 5.13(a)–5.13(p) for the superspreader solutions BREAK-THRU S 278-0.1, S 278-0.2, S 278-0.5 and S 278-1.0, respectively. In addition, the log-log plots of the measured disjoining pressure versus the film thickness for these superspreader solutions are shown in Figs. 5.14(a)-5.14(d) to demonstrate the repeatability of the results and evaluate the variance. The scaling exponents found using Figs. 5.14(a)-5.14(d) are listed in Table 5.4.

It is emphasized that the values of the disjoining pressure found in Figs. 5.11 and 5.13 are in the range up to 6×10^4 dyn/cm², which is to be compared to the values up to 15×10^4 dyn/cm² measured for the micellar solutions of two non-ionic surfactants Brij 35 and Tween 20 using the Scheludko capillary cell or the Mysels-Jones porous-plate cell [Basheva et al. (2007)].

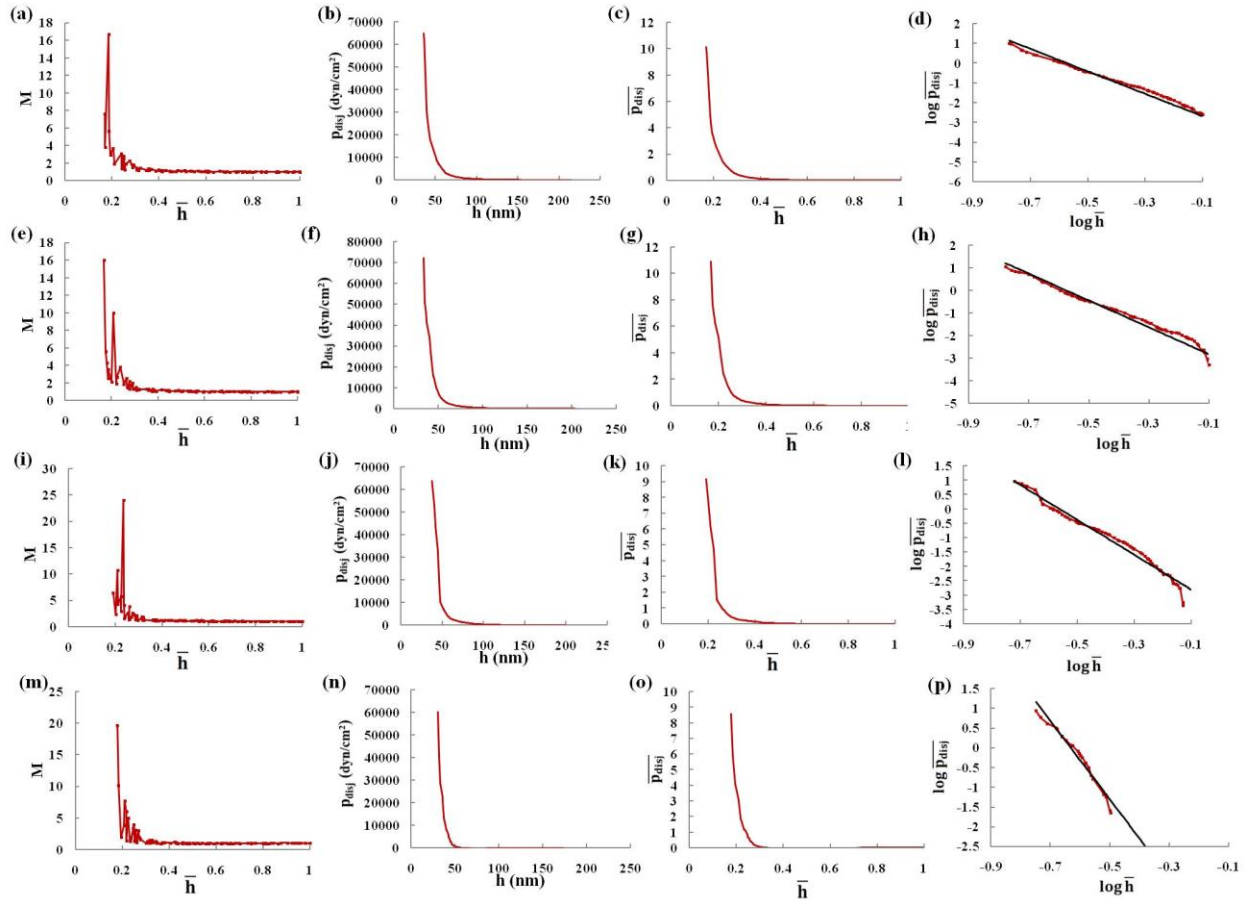


Figure 5.13. The dependences of M and p_{disj} on the film thickness h for the superspreader BREAK-THRU S 278 solutions. S 278-0.1 solution: (a) Function M , (b) the dimensional disjoining pressure, (c) the dimensionless disjoining pressure, (d) scaling of the disjoining pressure: the experimental data is shown in red, the straight line used to determine the exponent in the scaling law is black. The dependences of M and p_{disj} on the film thickness h for the

superspreader BREAK-THRU S 278-0.2 solution, S 278-0.5 solution, and S 278-1.0 solution are shown similarly in panels (e)-(h), (i)-(l) and (m)-(p), respectively.

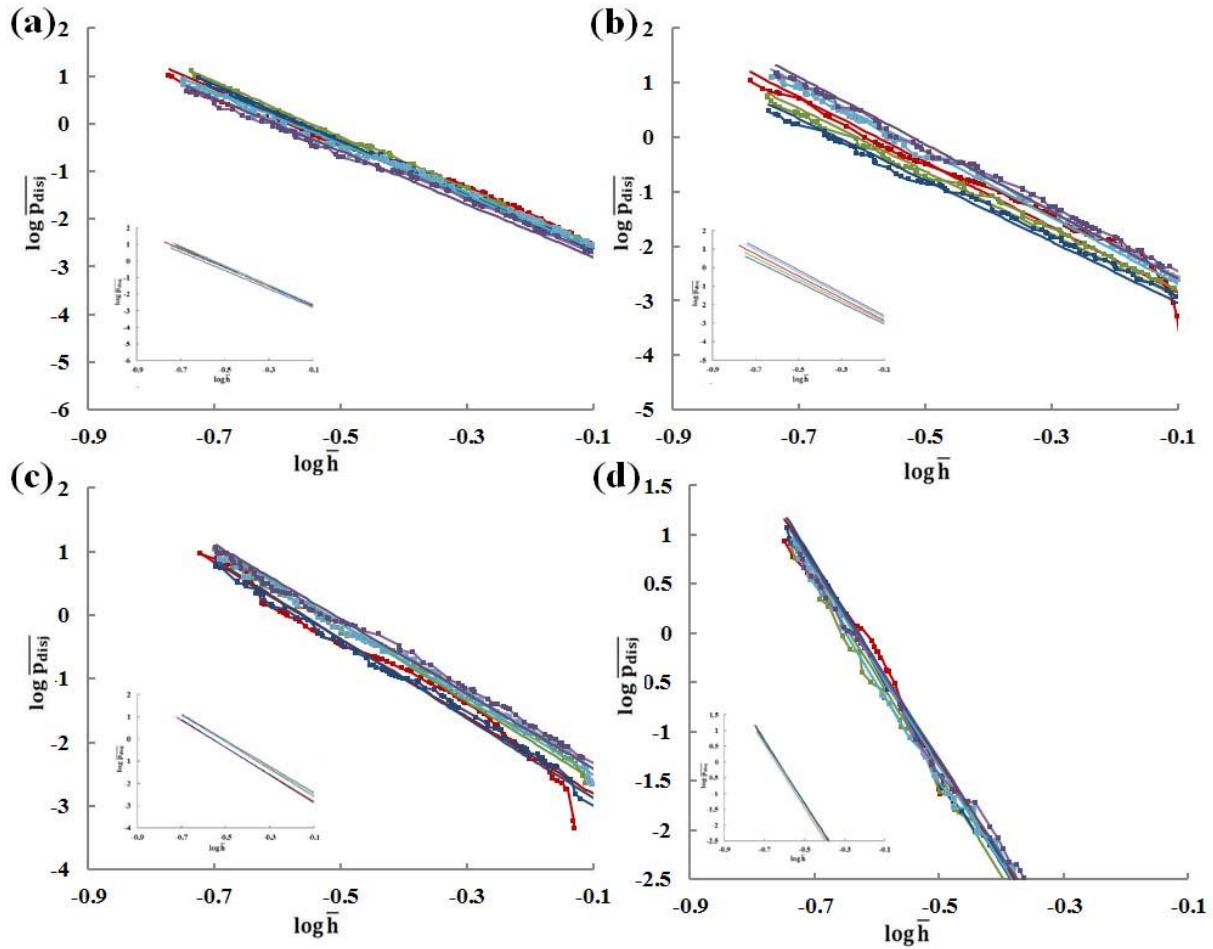


Figure 5.14. Disjoining pressure versus the film thickness for BREAK-THRU S 278 solutions of different concentration: (a) S 278-0.1, (b) S 278-0.2, (c) S 278-0.5, and (d) S 278-1.0. The experimental data is shown with symbols spanned with lines and fitted by continuous straight lines of the corresponding color to determine the exponent in the scaling law. The different colors represent different experimental trials where the initial film thickness varied. The data from Figs. 5.13d, 5.13h, 5.13l and 5.13p is shown in red. The inserts show the straight lines corresponding to the scaling laws separately.

Table 5.4. Scaling exponents for the disjoining pressure of the superspreader BREAK-THRU S 278 solutions found using the slope of the scaling laws shown in Figs. 5.14(a)-5.14(d).

Solution	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Average exponent
S 278-0.1	-5.69	-5.85	-5.88	-5.46	-5.55	-5.68 ± 0.18
S 278-0.2	-5.96	-5.75	-5.63	-6.14	-6.11	-5.92 ± 0.22
S 278-0.5	-6.07	-6.14	-6.25	-5.95	-5.88	-6.06 ± 0.15
S 278-1.0	-11.39	-11.56	-11.3	-11.71	-11.25	-11.44 ± 0.19

The results in Table 5.2 show that for the sufficiently concentrated 0.2-1.0 v/v% superspreader SILWET L-77 solutions the measured scaling exponents are close to -9 or -10. On the other hand, for the most dilute solution of 0.1 v/v%, the measured exponent -6.39 ± 0.21 . The results in Table 5.4 show that for the superspreader BREAK-THRU S 278 only 1.0 v/v% solution revealed the scaling exponent of a high magnitude -11.44 ± 0.19 , the other solutions of the superspreader BREAK-THRU S 278 (0.1-0.5 v/v%) revealed the measured exponent close to -6.

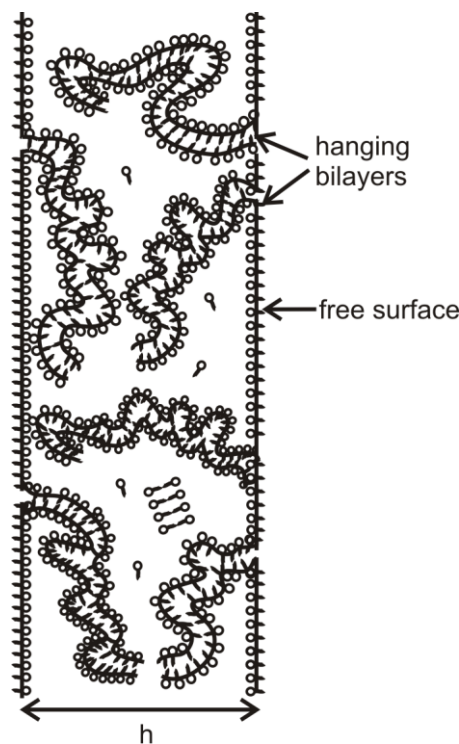


Figure 5.15. Sketch of fluffy surfaces of the film formed by long hanging superspreader bilayers.

The DLS results in Fig. 5.3 imply that in the films formed from the superspreader solutions of sufficient concentration (definitely above cmc) there are bilayer aggregates of sizes larger than the film thickness h . This can be viewed as the presence of multiple sections of bilayer aggregates hanging from the free surface Venzmer (2011) and forming fluffy surfaces of the film as sketched in Fig. 5.15. Steric repulsions of the entropic origin can certainly decelerate thinning of such films. However, the scaling exponents in Tables 5.2 and 5.4 differ from the predictions for any of the entropic steric repulsions, e.g. those discussed in Derjaguin et al. (1987) and Israelachvili (1992). It should be emphasized that in the present case of solutions of non-ionic superspreaders in deionized water formation of double layers characteristic of electrolytes is excluded, and thus there is no stabilizing electric forces.

In distinction from the superspreaders, the corresponding non-superspreaders SILWET L-7607 and BREAK-THRU S 233 revealed the linear drainage pattern (Fig. 5.7 and Fig. 5.8 respectively) and regular horizontal interferometric color bands (Fig. 5.9 and Fig. 5.8) with practically no stabilization associated with the disjoining pressure. Such horizontal uniformity of color bands was neither seen for the plane films of the superspreader SILWET L-77 (Fig. 5.4, the inset images, and Fig. 5.5) solutions, nor for the superspreader BREAK-THRU S 278 (Fig. 5.6) solutions. Therefore, for the non-superspreaders the only parameter of interest to be elucidated from the present measurements is the surface elasticity ε which is found from the measured values of the characteristic time T using the data in Figs. 5.7 and 5.8, similarly to Sett et al. (2013). The results for the non-superspreader SILWET L-7607 solutions are summarized in Table 5.5, and for the non-superspreader BREAK-THRU S 233 in Table 5.6.

Table 5.5. Non-superspreader SILWET L-7607 solution films. The film lifetime is denoted t ; t_b denotes the time at which black film sets in at the top of the wire frame. The x column corresponds to the position at the film center (reckoned from the top) to which the black film reached at the moment of bursting. The initial film thickness at the top is denoted $h_i=h_0$; the characteristic drainage time is T . The values of the surface elasticity ε were found from T using Eq. (5.17).

Sol.	t (s)	t_b (s)	x (cm)	$h_i=h_0$ (nm)	T (s)	ε (g/s ²)
L-7607-0.1	5	4	0.1	201.45	4.8	0.013
L-7607-0.2	7	5	0.1	197.14	5.9	0.016
L-7607-0.5	10	8	0.1	199.62	8.7	0.024
L-7607-1.0	11	9	0.25	194.35	10.1	0.027

Table 5.6. Non-superspreader BREAK-THRU S 233 solution films. The film lifetime is denoted t ; t_b denotes the time at which black film sets in at the top of the wire frame. The x column corresponds to the position at the film center (reckoned from the top) to which the black film reached at the moment of bursting. The initial film thickness at the top is denoted $h_i=h_0$; the characteristic drainage time is T . The values of the surface elasticity ε were found from T using Eq. (5.17).

Sol.	t (s)	t_b (s)	x (cm)	$h_i=h_0$ (nm)	T (s)	ε (g/s ²)
S 233-0.1	4	3.8	0.05	209.64	4.1	0.012
S 233-0.2	4	3.8	0.1	204.37	4.5	0.013
S 233-0.5	5	4.9	0.1	202.16	4.8	0.013
S 233-1.0	7	5	0.2	205.55	6	0.017

The difference between the superspreaders and the “cousin” non-superspreaders is only in the length of the poly(ethylene oxide) group. Yet, they show radically different drainage behavior, both morphologically and by duration. For example, the drainage of the superspreader SILWET L-77 and BREAK-THRU S 278 films is by an order of magnitude longer than the drainage of their non-superspreader counterparts SILWET L-7607 and BREAK-THRU S 233. The thinning of the superspreader films was practically arrested by the disjoining pressure at the latter stages of gravitational drainage, whereas the “cousin” non-superspreader films drained

without any visible inhibition and lasted for only a short time. Morphologically, the interferometric patterns of the superspreader films during the drainage revealed a “turbulent”-like motion. On the contrary, the “cousin” non-superspreader films showed horizontal interference bands, indicating ordered drainage pattern characteristic of the ordinary surfactants [Sett et al. (2013) and Lucassen (1981)].

5.6 Conclusions

Gravitational drainage of vertical films suspended on a rectangular wire frame is established as a relatively simple method of measurement of disjoining pressure. The effect of the disjoining pressure is in drastic deceleration of the later stage of the drainage process where the film thickness deviates (at about $h < 100$ nm) from the linear decrease sustained by the interplay of gravity and surface elasticity, and practically stabilizes at about ~ 35 nm. Gravitational drainage of two superspreaders SILWET L-77 and BREAK-THRU S 278 was dramatically stabilized in this manner, even though their interferometric patterns were highly dynamic and “turbulent”-like. The significant disjoining pressure revealed by the superspreaders is associated with the fluffy surfaces of the film formed by long superspreader bilayers hanging from the free surfaces (sketched in Fig. 5.15). The ability to form long bilayer elements was attributed in the literature to the shorter length of poly(ethylene oxide) group in superspreaders compared to their non-superspreader “cousin” non-superspreaders SILWET L-7607 and BREAK-THRU S 233. The present work showed that these non-superspreaders do not possess any significant disjoining pressure in the ~ 35 -100 nm range of the film thickness. Therefore, the non-superspreader gravitational drainage proceeds uninhibited, the thickness decrease is fully controlled by gravity and surface elasticity, and is not different from the ordinary surfactants.

The scaling law for the disjoining pressure of the sufficiently concentrated superspreader solutions are $p_{\text{disj}}(h) \sim h^{-m}$ (with $m \approx 9-11$), as well as $p_{\text{disj}}(h) \sim h^{-s}$ (with $s \approx 6$) for more dilute solutions (in both cases concentrations were above cmc). These scaling laws differ from those known for the entropic steric repulsions.

CHAPTER 6

FOAMABILITY ENHANCEMENT USING TRISILOXANE SURFACTANTS

6.1 Introduction

The present Chapter aims at studying the foamability and foam stability of foam generated from surfactant mixture solutions of the United States Gypsum Corporation (USG) stable soap and different trisiloxane surfactants. The experimental technique involves measuring the amount of liquid drained, as well as the rate of drainage as functions of time, using the gravity settler setup similar to the one described in Jun et al. (2012).

6.2 Experimental materials and methods

6.2.1 Materials

To study the foamability and foam stability of surfactant mixtures, four different trisiloxane-(poly)ethoxylate surfactants were used with USG stable soap. They are SILWET L-77 (superspreader), SILWET L-7607 (the “cousin” non-superspreader), both obtained from Momentive, BREAK-THRU S278 (superspreader) and BREAK-THRU S233 (the “cousin” non-superspreader), both obtained from Evonik Industries. Sodium dodecyl sulfate (SDS) with molecular weight $M_w = 288.38$ Da - an anionic surfactant was obtained from Sigma Aldrich. The United States Gypsum Corporation provided USG stable soap, a surfactant widely used in wallboard manufacturing. All the chemicals were used as received.

6.2.2 Experimental method

The foam column experiments were conducted as in Jun et al. (2012). For foam generation, a fixed volume of surfactant solution in water (200 mL in present case) was taken in a mixing bowl. Using hand mixer, foam was generated by mixing the solution for three minutes. The foam was then poured into a long hose (the inside diameter was 0.4 cm) and placed inside the gravity settler. The gravity settler was filled from the bottom up as shown in Fig. 6.1. As the level of foam increased, the funnel-hose system was raised accordingly so that the foam exiting the hose would be at the top. When the foam was filled to the top of the cylinder, the cylinder was capped, which effectively prevented loss of liquid vapor or gas from the settler during the entire experiment. The time to fill the settler with foam averaged about 1 min, during which no drained liquid was visible. The sizes of the settler were 2.58 cm in diameter and 104 cm tall. The drained liquid height was measured using a CCD camera and a backlight arrangement as shown in Fig. 6.2.

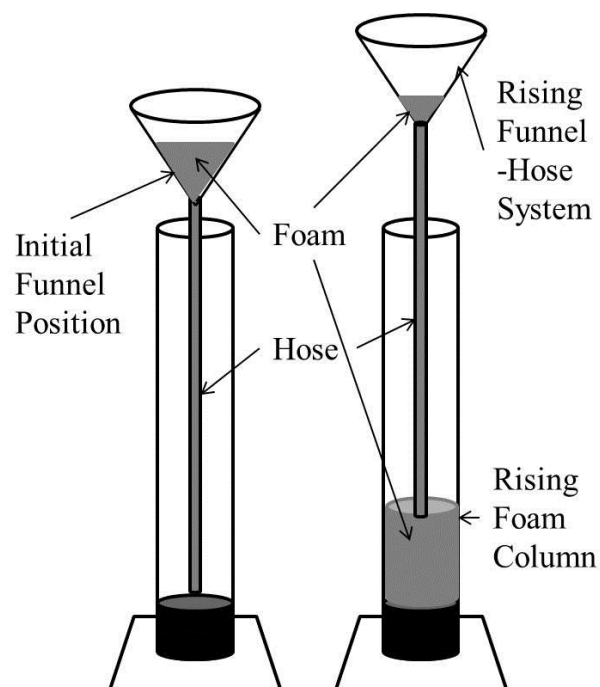


Figure 6.1. Filling gravity settler using the funnel-hose system. The system is raised with the foam height so that the foam exiting the hose is at the top of the foam column.

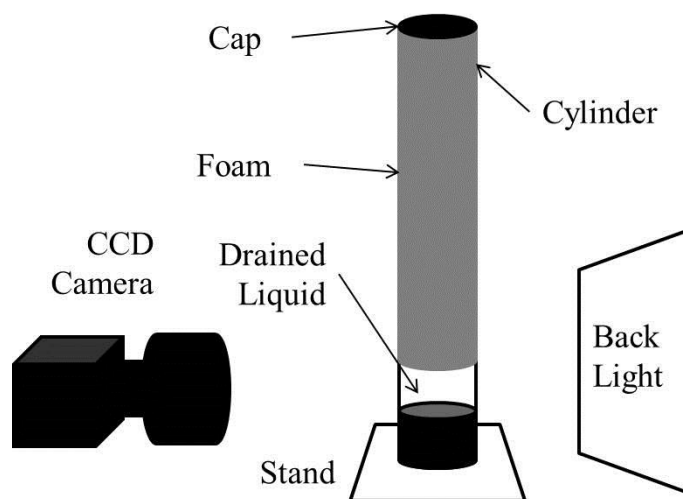


Figure 6.2. Sketch of the experimental setup.

Different concentrations of anionic surfactant sodium dodecyl sulfate (SDS) and non-ionic trisiloxane-(poly)ethoxylate surfactants SILWET L-77, SILWET L-7607, BREAK-THRU S 278 and BREAK-THRU S 233 were added separately to aqueous solutions containing 0.5 %v/v USG stable soap for generating foam. 0.5 %v/v of USG stable soap was added to 2 mM, 4 mM, 6 mM, 8 mM, 10 mM and 12 mM aqueous SDS solutions to measure foamability of USG stable soap with ordinary surfactants. For each of the trisiloxane surfactants, the solutions were prepared at different concentrations of 0.025 %v/v, 0.05 %v/v, 0.1 %v/v, 0.2 %v/v, 0.5 %v/v and 1 %v/v while the USG stable soap concentration was kept constant at 0.5 %v/v in the solution for all cases.

The amount of liquid drained was measured in time. The height of the drained liquid/foam interface was measured by counting pixels in the images recorded by the CCD camera and using the external diameter cylinder as a reference scale. Each pixel corresponded to approximately 0.07 mm. Several images taken during one of the drainage experiments of 0.5 %v/v SILWET L-77 with 0.5 %v/v USG stable soap are shown in Fig. 6.3. The consecutive images show the increase in the volume of liquid drained at the bottom of the cylinder with time.

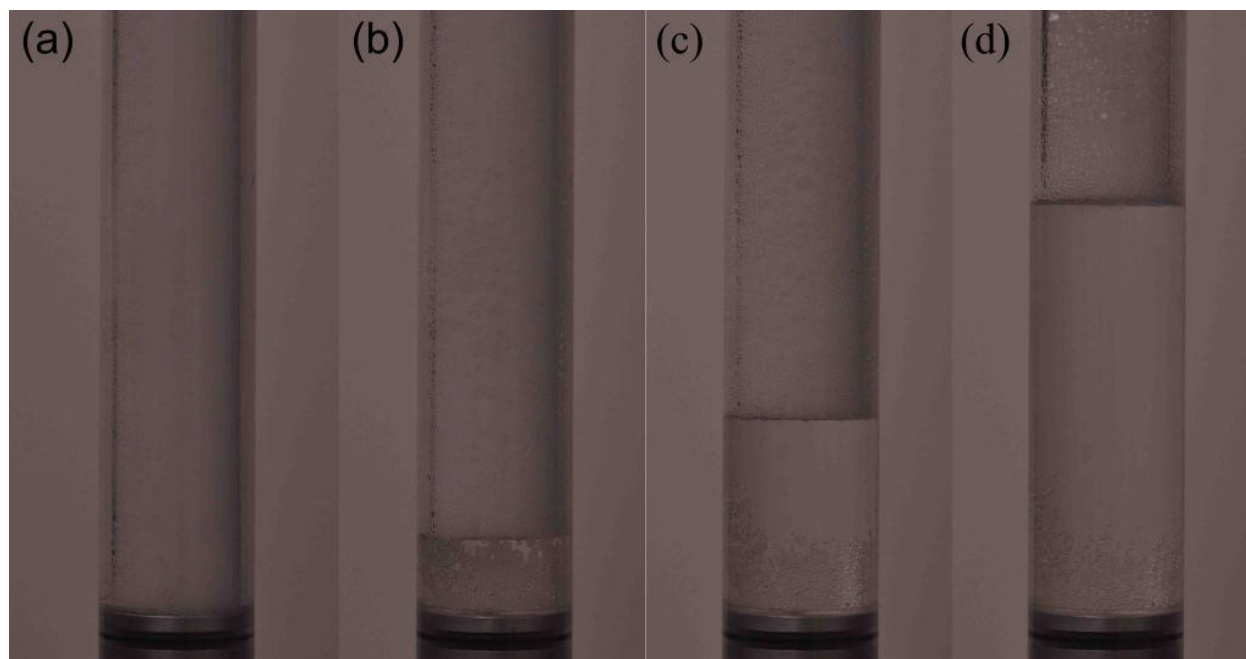


Figure 6.3. Images taken during drainage of 0.5 %v/v SILWET L-77 with 0.5 %v/v USG stable soap foam. The images (a)-(d) correspond to 1.5 min, 5 min, 15 min and 1 h (the end of draining).

6.3 Results and discussion

The rate of drainage as a function of time was calculated from the measured amount of drained liquid in time. The volume of the liquid drained at any instant of time is rendered dimensionless by the total volume of liquid that is present in the gravity settler at the end of drainage process. The dimensionless volume of liquid drained and its evolution with time indicate the stability as well as the rate of drainage. Figures 6.4a–6.4d show the dimensionless volume of liquid in time for different concentrations of trisiloxane surfactants SILWET L-77, SILWET L-7607, BREAK-THRU S 278 and BREAK-THRU S 233 with 0.5 %v/v USG stable soap, respectively. The data points in blue represent the drainage data for the 0.5 %v/v USG stable soap only. It is evident from the figures that with an addition of small amount of either of

the four trisiloxane surfactants increases the stability of the foam significantly, as it takes longer time to reach the plateau corresponding to the dimensionless volume of drained liquid equal to one. Moreover, it was found that a further increase in the concentration of the trisiloxane surfactants irrespective of the superspreader and its “cousin” non-superspreader does not have significant impact on the stability as is evident from Fig. 4, where the drainage data marked in different colors corresponding to different concentrations of the trisiloxane surfactants overlap with each other.

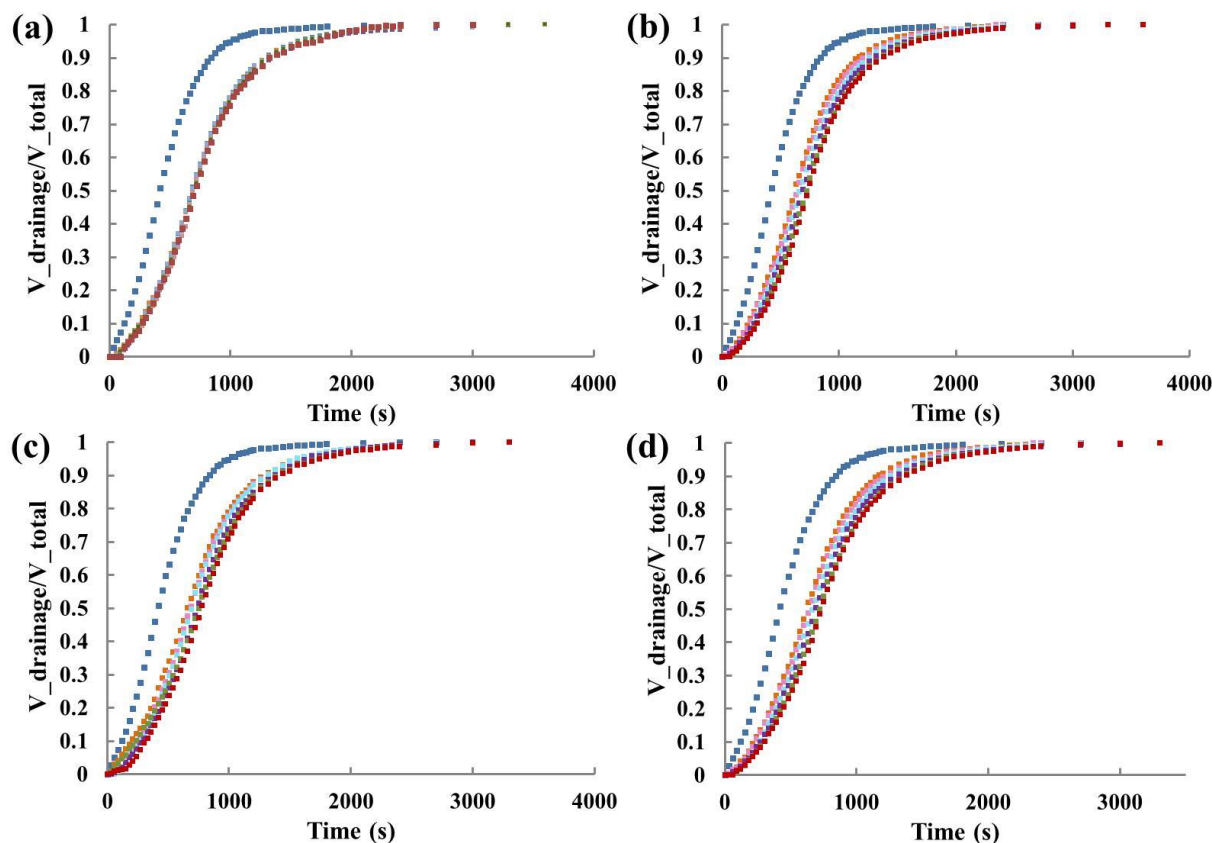


Figure 6.4. Dimensionless volume of liquid drained as function of time from foam generated with a mixture of USG Stable Soap and (a) SILWET L-77, (b) SILWET L-7607, (c) BREAK-THRU S 278, and (d) BREAK-THRU S 233. Different colors represent different concentrations of the trisiloxane surfactant, with blue, orange, pink, faded blue, purple, green and red representing 0, 0.025 %v/v, 0.05 %v/v, 0.1 %v/v, 0.2 %v/v, 0.5 %v/v and 1 %v/v, respectively. The USG stable soap concentration was 0.5 %v/v in all cases.

The volume of liquid drained in time from foam column for mixtures of USG stable soap with different concentrations of trisiloxane surfactants SILWET L-77, SILWET L-7607, BREAK-THRU S 278 and BREAK-THRU S 233 are shown in Figs. 6.5a-6.5d, respectively. Adding a very small percentage of 0.025 %v/v of superspreader SILWET L-77 or BREAK-

THRU S 278 reduces the total volume of liquid at the end of the drainage by 53%, as seen in Fig. 6.5a and Fig. 6.5c. With a further increase in concentration of the superspreader, there was a further reduction in the final volume of liquid in the gravity settler. However, the decrease in liquid volume from 0.025 %v/v to 0.05 %v/v, from 0.05 %v/v to 0.1 %v/v and so forth were not as significant in comparison to the case when 0.025 %v/v was added initially to the solution containing only 0.5 %v/v USG stable soap. The decrease in volume of liquid in case of “cousin” non-superspreader SILWET L-7607 or BREAK-THRU S 233 was more gradual as the concentration of the trisiloxane was increased from 0 to 1 %v/v as seen in Fig. 6.5b and Fig. 6.5d respectively.

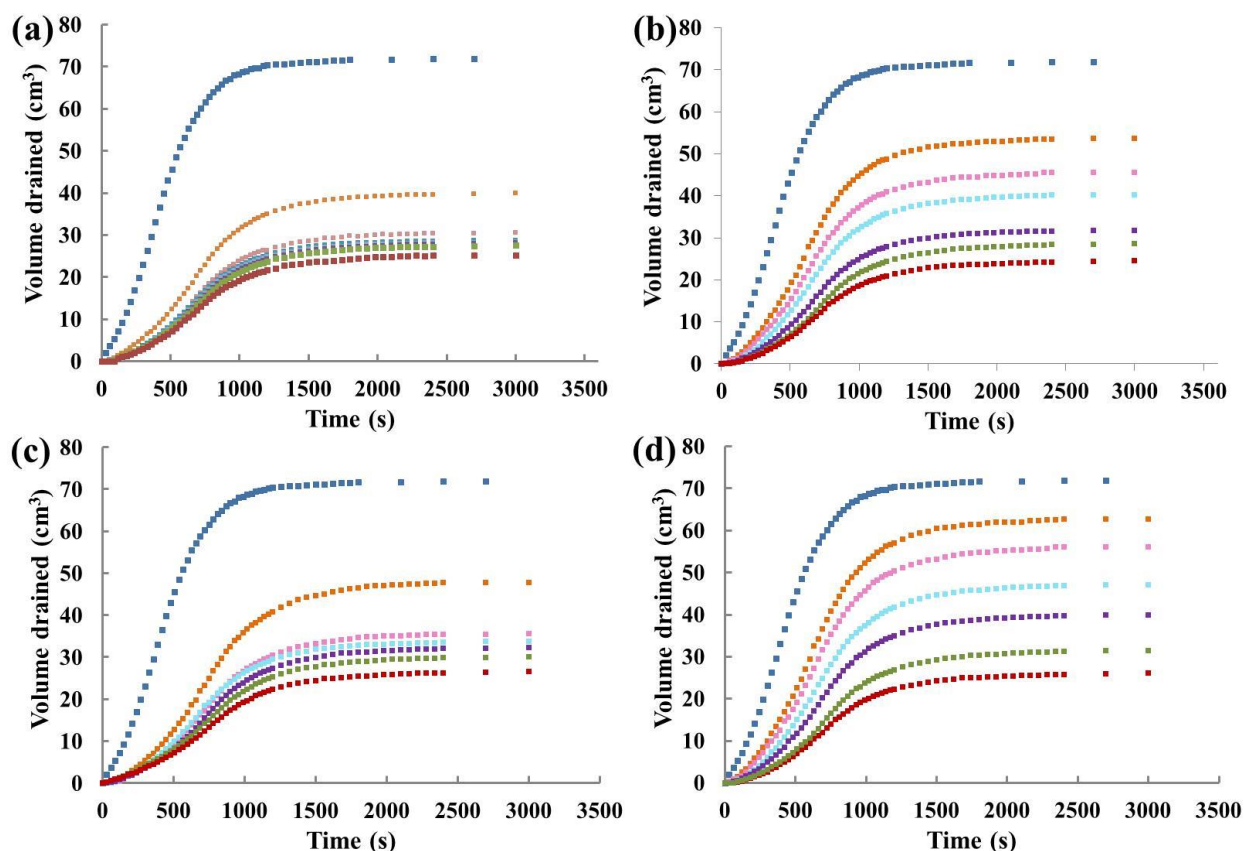


Figure 6.5. Volume of liquid drained as function of time from foam generated with a mixture of USG Stable Soap and (a) SILWET L-77, (b) SILWET L-7607, (c) BREAK-THRU S 278, and (d) BREAK-THRU S 233. The different colors represent the different concentration of the trisiloxane surfactant with blue, orange, pink, faded blue, purple, green and red representing 0, 0.025 %v/v, 0.05 %v/v, 0.1 %v/v, 0.2 %v/v, 0.5 %v/v and 1 %v/v, respectively. The USG stable soap concentration was 0.5 %v/v in all cases.

Foamability is defined as the total volume of foam generated in a fixed period of time from a fixed volume of liquid. The initial volume of the different surfactant solutions used to generate the foam was kept constant at 200 mL. The foam generated was then poured and the gravity settler was filled to the top as discussed in the experimental section. The total volume of

liquid in the gravity settler at the end of drainage experiment thus allowed us to calculate the total volume of foam generated from 200 mL of solution, and accordingly the foamability of the surfactant mixture solution. A smaller volume of liquid at the end of drainage process implies a higher foamability of the initial surfactant mixture solution. The foamability data for different trisiloxane surfactants at different concentrations with 0.5 %v/v USG stable soap is depicted in Fig. 6.6.

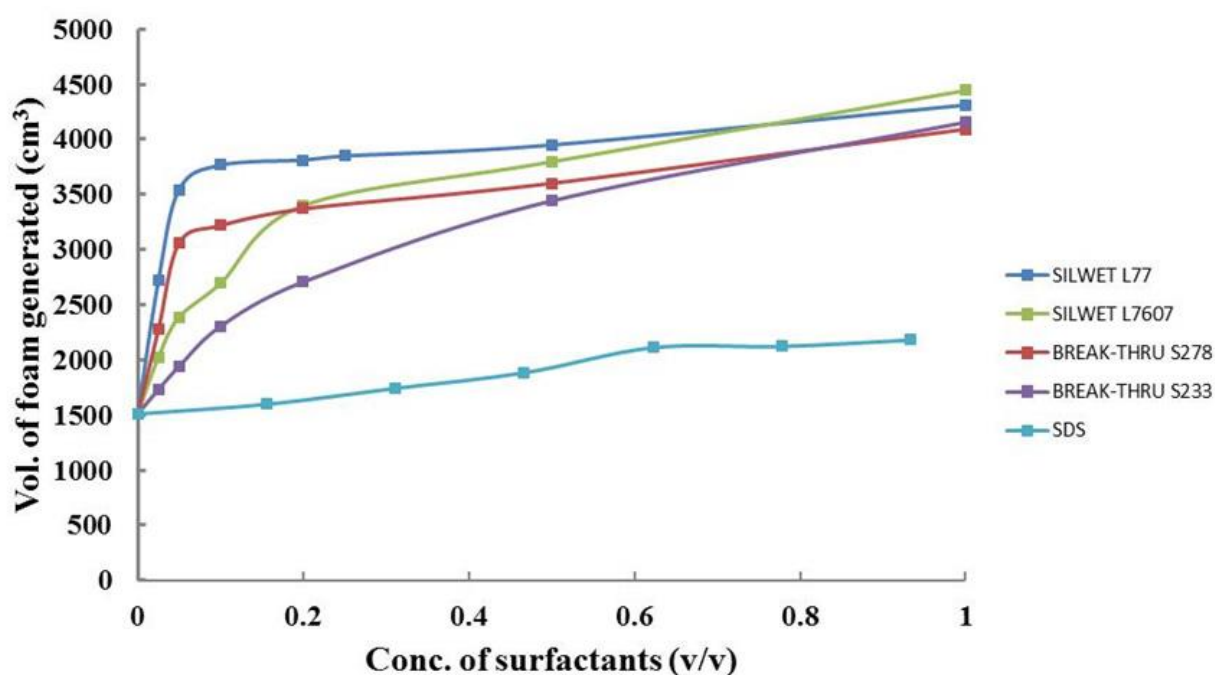


Figure 6.6. Foamability of trisiloxane surfactants at different concentrations with 0.5 %v/v USG stable soap. For comparison with ordinary surfactant, foamability of anionic surfactant SDS is shown with 0.5 %v/v USG stable soap.

The ordinary anionic surfactant, SDS, revealed a very small increase in foamability of the surfactant solution mixture and reached its maxima at 8 mM (0.6235 %v/v), which is the critical micelle concentration (cmc) [Berg et al. (2005) and Mysels (1986)] of SDS. Thereafter,

increasing the concentration of SDS did not have any impact on the foamability. Trisiloxane surfactants have a cmc of 0.007% (v/v) as mentioned in Sett et al (2014a). Hence the concentrations of trisiloxane surfactants for all the foam column experiments was above their corresponding cmc. The foamability of the solution doubled on addition of only 0.025 %v/v of superspreader SILWET L-77 and BREAK-THRU S 278. The increase in foamability was much more gradual on the addition of non- superspreaders SILWET L-7607 and BREAK-THRU S 233. At 1 %v/v concentration of the trisiloxane surfactants, the foamability of superspreader and its “cousin” non-superspreader was almost identical as seen in Fig. 6.5.

6.4 Conclusions

The foamability of 0.5 %v/v USG stable soap was greatly enhanced by addition of trisiloxane surfactants, in particular the superspreaders. On the addition of very small amount of superspreaders SILWET L-77 and BREAK-THRU S 278 to 0.5 %v/v USG stable soap solution, the foamability (Figs. 6.5 and 6.6) as well as the stability of foam (Fig. 6.4) increased significantly after which the increase was not so significant. In contrast, with the addition of non-superspreaders SILWET L-7607 and BREAK-THRU S 233, the foamability increase was more gradual. The stability of the foams in the latter case was similar to those of the superspreaders. Among the two superspreaders, SILWET L-77 was found to possess a higher foamability.

CHAPTER 7

DRAINAGE OF SODIUM DODECYL SULFATE SURFACTANT MIXED WITH SUPERSPREADER TRISILOXANE-(POLY)ETHOXYLATE

This chapter has been previously published in Sett et al. (2014b).

Reprinted with permission from [Sett, S., Sahu, R. P., Pelot, D. D., & Yarin, A. L. (2014). Enhanced Foamability of Sodium Dodecyl Sulfate Surfactant Mixed with Superspreader Trisiloxane-(poly) ethoxylate. *Langmuir*, 30(49), 14765-14775]. Copyright 2014 American Chemical Society.

7.1 Introduction

The present work aims at studying drainage from the plane vertical films of two-surfactant mixture solutions and relating the results to those for the foamability and foam stability. Two different surfactants, namely the anionic SDS and non-ionic superspreader SILWET L-77, and their mixtures at different mixing ratios are used. Foamability of the ordinary surfactant solution (SDS), which forms ordinary spherical micelles, increases till the critical micelle concentration (cmc). However, the nonionic trisiloxane surfactant, which forms bilayer aggregates, shows foamability enhancement with increasing concentration even beyond its cmc. In the present work, mixtures of a widely used ordinary surfactant, SDS and trisiloxane surfactant SILWET L-77 (superspreader) were used to investigate whether a further enhancement of foamability could be attained. The methods developed by the present group for the investigation of plane vertical film drainage [Sett et al. (2013) and Sett et al. (2014a)] and the foam column drainage [Jun et al. (2012)] are applied in this work.

7.2 Experimental

7.2.1 Materials

The following surfactants were used in drainage and gravity settler experiments. Trisiloxane-(poly)ethoxylate SILWET L-77 (superspreader), which is a nonionic surfactant, was obtained from MOMENTIVE™. Sodium dodecyl sulfate (SDS) with molecular weight $M_w = 308.34$ Da, an anionic surfactant, was obtained from Sigma Aldrich. Both surfactants were used as received.

7.2.2 Solution preparation

SDS and trisiloxane SILWET L-77 were used to prepare solutions as follows. Using SDS, 2 mM, 4 mM, 6 mM, 8 mM, 10 mM, and 12 mM aqueous solutions were prepared by adding the surfactant to deionized water (ASTM Type II) at 25° C and denoted S2.0, S4.0, S6.0, S8.0, S10.0, and S12.0, respectively. Using the superspreader SILWET L-77, 0.1 ml, 0.2 ml, 0.5 ml, 1.0 ml, 1.5 ml, and 2.0 ml of the surfactant was added to 100 ml of deionized water (ASTM Type II) at 25° C, and the resulting solutions were denoted as L0.1, L0.2, L0.5, L1.0, L1.5, and L2.0, respectively. Mixture solutions containing SDS and SILWET L-77 were prepared as follows. Different volumes of superspreader SILWET L-77 were added to 4 mM aqueous solution of SDS to obtain surfactant ratio of SDS to SILWET L-77 as 1:0.5, 1:1, 1:2, 1:5, and 1:10 [cf. Table 7.1]. They were denoted as SL4-0.5, SL4-1.0, SL4-2.0, SL4-5.0, and SL4-10.0, respectively. Similarly, aqueous solutions having the surfactant ratios of SDS to SILWET L-77 of 1:0.5, 1:1, 1:2, 1:5, and 1:10 were prepared with 8 mM and 12 mM SDS solutions. They were denoted as SL8-0.5, SL8-1.0, SL8-2.0, SL8-5.0, and SL8-10.0 for the 8 mM SDS/SILWET L-77 solutions and as SL12-0.5, SL12-1.0, SL12-2.0, SL12-5.0, and SL12-10.0 for the 12 mM SDS/SILWET L-

77 solutions [cf. Table 7.1]. All the solutions were prepared and kept at room temperature of 25° C.

The solutions prepared from superspreader SILWET L-77 were turbid in appearance, and the turbidity was found to increase with the increase in the superspreader concentration. The solutions prepared from SDS were clear, but on the addition of SILWET L-77, they turned more and more turbid as the superspreader concentration increased. Turbidity of solutions containing superspreader results from large aggregates formed by superspreader molecules [Sett et al. (2014a); Venzmer (2011); Venzmer and Wilkowski (1998) and Hill (1999)]. These anisotropic structures cause light scattering resulting in solution turbidity [Particle Sciences Technical Brief (2012)]. The turbidity of these solutions was simply a phenomenon worth of mentioning. However, it was not used for characterization of the solutions or films, and thus was not measured.

Table 7.1. Concentration of SILWET L-77 in 4 mM, 8 mM, and 12 mM SDS aqueous solutions for mixing ratios of SDS to SILWET L-77 1:0.5, 1:1, 1:2, 1:5, and 1:10. The solution labels are given in parenthesis.

SDS Solution		4 mM	8 mM	12 mM
Conc. of SDS (g/l)		1.153	2.306	3.459
SDS to SILWET L-77 ratios (ml/l)	1:0.5	0.577 (SL4-0.5)	1.153 (SL8-0.5)	1.729 (SL12-0.5)
	1:1	1.153 (SL4-1.0)	2.306 (SL8-1.0)	3.459 (SL12-1.0)
	1:2	2.306 (SL4-2.0)	4.612 (SL8-2.0)	6.918 (SL12-2.0)
	1:5	5.765 (SL4-5.0)	11.53 (SL8-5.0)	17.295 (SL12-5.0)
	1:10	11.53 (SL4-10.0)	23.06 (SL8-10.0)	34.59 (SL12-10.0)

7.2.3 Surface tension measurement

Surface tension of mixed solutions of SDS with SILWET L-77 was measured using the Wilhelmy plate apparatus (KSV Nima Instruments) with the plate having a width of 10.3 mm. The data in Fig. 7.1 shows that for all three concentrations of SDS (4 mM, 8 mM, and 12 mM), at the SILWET L-77 concentration of about 0.003 %v/v the surface tension values had saturated. This concentration was considered as the cmc of SILWET L-77 in the 4 mM, 8 mM and 12 mM SDS/SILWET L-77 mixture solutions. Note that the cmc for mixture solutions is lower than either the cmc of SILWET L-77 alone, which is 0.007 %v/v [Sett et al. (2014a)], or that of SDS alone, which is 8 mM [Berg et al. (2005) and Mysels (1986)] (0.231 %v/v). The concentrations of all the solutions used in the present experiments with plane film drainage and gravity settler were above the cmc of the SDS/SILWET L-77 mixture solutions.

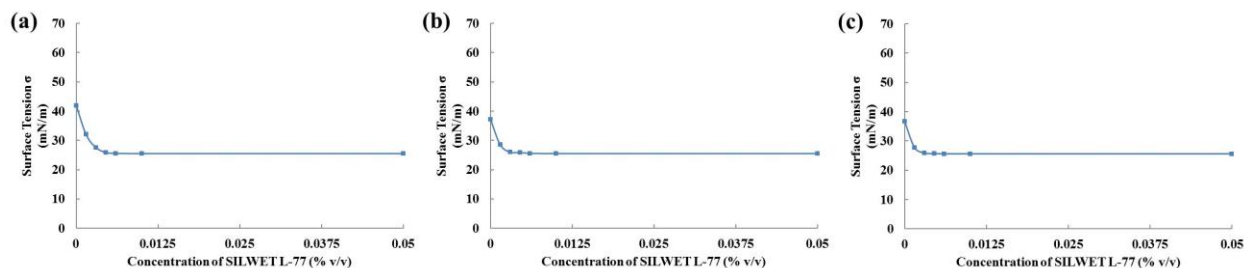


Figure 7.1. Surface tension measured using the Wilhelmy plate technique for mixed solutions of SILWET L-77 and (a) 4 mM of SDS, (b) 8 mM of SDS, and (c) 12 mM of SDS.

7.2.4 Drainage of plane films

The experimental setup (Fig. 7.2a) and method used to study drainage of plane vertical surfactant films is described elsewhere [Sett et al. (2013) and Sett et al. (2014a)]. In brief, a fixed aluminum wire frame (4 cm x 4 cm x 0.087 cm), which supports the film formed, was dipped into 100 ml container containing the surfactant solution of interest. The solution container was raised and lowered using a linear actuator. The experiments were conducted at room temperature of 25° C and relative humidity of 70% and on an optical bench in an isolated dark room. The film on the frame was photographed using a high-speed CCD camera (Phantom Miro 4) and the images were then processed using Matlab. Using this setup, film thicknesses above 30 nm [Sett et al. (2013)] can be measured accurately.

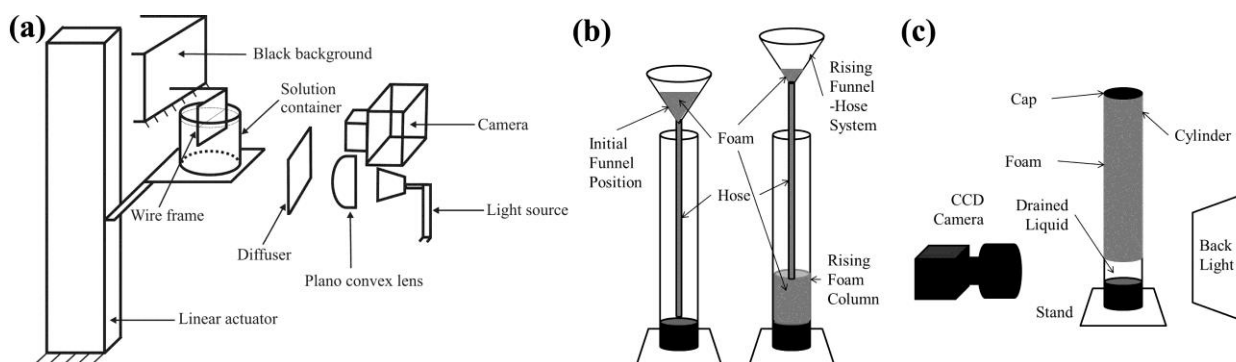


Figure 7.2. (a) Schematic of the experimental setup for drainage of plane vertical films. (b) Filling gravity settler using flexible funnel – hose system, and (c) Drained liquid from the foam recorded using a CCD camera.

The film thickness at the top was measured right below the upper wire at the location 2 cm from the left wire, which allowed us to neglect any effect of side wires on the film thickness. The local film thickness h was determined using the interferometric formula [Sett et al. (2013); Karakashev et al. (2005); Karakashev and Nguyen (2009); Karakashev and Ivanova (2010a); Karakashev et al. (2011) and Karakashev et al. (2008a)].

7.2.5 Gravity settler

A large amount of uniform foam was created by mechanical mixing. Then, 200 ml of the desired solution was placed in a mixing bowl and the solution was stirred for 3 min using a standard household hand mixer. The experimental method was described in detail elsewhere [Jun et al. (2012)]. In brief, the generated foam was then poured into a vertical cylinder (a gravity settler with the inner diameter of 2.58 cm and 104 cm height) using a flexible funnel-hose system. The cylinder (the gravity settler) was filled from the bottom up, as shown in Fig. 7.2b. To ensure that the foam exiting the hose is delivered on top of the existing foam column, the funnel was squeezed and the entire funnel-hose system was raised, simultaneously. The cylinder was capped once the foam was filled up to the top of the cylinder, thus preventing any loss of liquid vapor or gas from the cylinder and isolating the setup from any atmospheric effects during the entire experiment. All experiments were conducted at room temperature of 25° C and relative humidity of 70%. Liquid drained from the foam column was accumulated at the bottom and its height was measured using a CCD camera as shown in Figure 1c.

7.3 Results and discussion

7.3.1 Drainage of plane films

Gravitational drainage of plane vertical soap films for different concentrations of separately anionic surfactant SDS or superspreader SILWET L-77 has been discussed in detail elsewhere [Sett et al. (2013) and Sett et al. (2014a)]. It was found experimentally and theoretically that the thickness of SDS films at a particular location decreases linearly in time during gravitational drainage [Sett et al. (2013)]. Regular ordered horizontal color bands were observed indicating no thickness gradient in the horizontal direction in the film. The characteristic drainage time T and the surface elasticity ε , of such films are determined by an interplay between gravity and the concentrational Marangoni effect. The film thickness at the top of the film decreases linearly in time as [Sett et al. (2013)]

$$h(x, t) = h_0 \left(1 - \frac{t}{T} \right) \quad (7.1)$$

where h_0 is the initial film thickness at the top, and the characteristic time scale T is given by

$$T = \frac{\varepsilon}{\rho (gh_0)^{3/2}} \quad (7.2)$$

with ε being the surface elasticity, ρ being water density, and g being gravity acceleration. The detailed derivation of these formulae can be found in Sett et al. (2013).

The values of T and ε were established using the data for the thickness versus time [Fig. 7.3]. The top part of the film turned black after a certain delay. The black zone descended downwards with time. For the SDS-alone solution S2.0, the black film covered one half of the film length along the wire frame at the instant of bursting. For the SDS solution S4.0, the black film covered almost the entire wire frame length, with traces of the interferometric color bands seen only at the very bottom of the film. On increasing the SDS concentration, the black film

spread to the entire film at the instant of bursting. Also, the black film lasted the longest for the SDS solution S8.0 (which has the concentration equal to the cmc of SDS), followed by S10.0 and S6.0. The results for drainage of films at different concentrations of the SDS-alone plane films are given in Table 7.2.

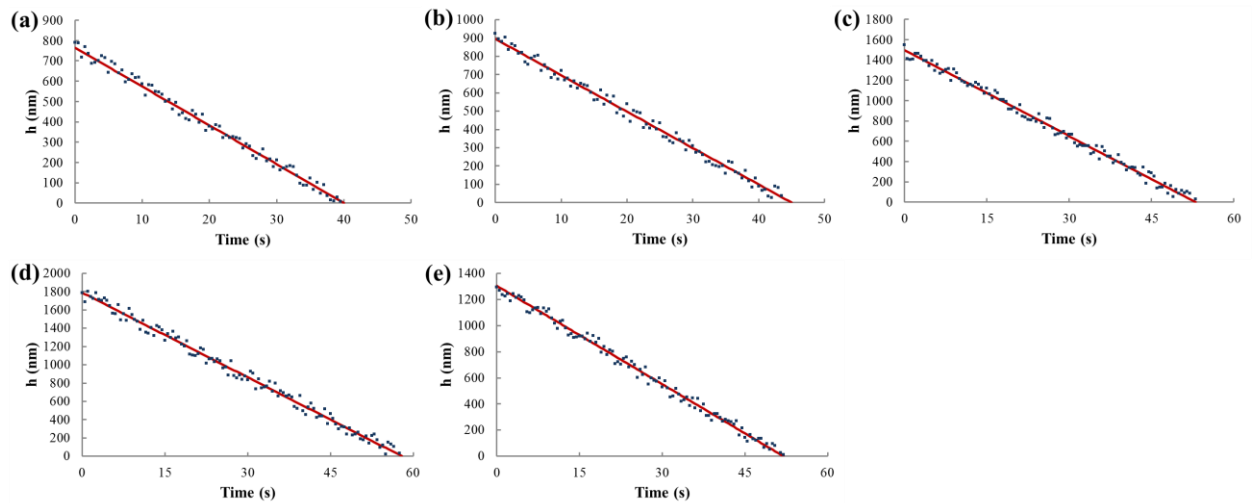


Figure 7.3. Drainage of the SDS-alone solution films: (a) S2.0, (b) S4.0, (c) S6.0, (d) S8.0, and (e) S10.0. The experimental results are shown by symbols. The inclined straight lines correspond to the theoretical prediction of Sett et al. (2013) and Eq. 7.1 in the present work.

Table 7.2. Plane SDS-alone solution films. The film lifetime is denoted by t_ℓ , t_b denotes the time at which black film sets in at the top of the wire frame. The initial film thickness at the top is denoted $h_i=h_0$, and the characteristic drainage time is denoted as T . The values of the surface elasticity ε were found from T using Eq. 7.2.

Sol.	t_ℓ (s)	t_b (s)	$h_i=h_0$ (nm)	T (s)	ε (g/s ²)
S2.0	62	39	765.42	40	0.82
S4.0	77	43	895.13	45	1.17
S6.0	101	52	1497.88	53	2.99
S8.0	118	57	1789.21	58	4.27
S10.0	108	50	1305.12	52	2.38

On the other hand, for plane films formed separately using the superspreader SILWET L-77, very irregular and disordered color bands in the horizontal direction were found, with their intermittency increasing in time [Sett et al. (2014a)]. The lower part of the film became turbid and blurred, and no distinct colors could be observed. Though the interferometric patterns of such films were highly dynamic and “turbulent”-like, they accompanied a remarkable film stabilization at the latter stage of drainage when it was practically arrested [Fig. 7.4]. It was shown that initially the thickness dependence on time was linear in such cases, and the characteristic drainage time T could be found.

The disjoining pressure responsible for the deceleration of the gravitational film drainage is found as [Sett et al. (2014a)]

$$\overline{p_{\text{disj}}}(\bar{h}) = \frac{1}{\bar{h}} \int_{\bar{h}}^1 \frac{[M(\bar{h}) - 1]}{\bar{h}} d\bar{h} \quad (7.3)$$

where $\bar{h}$ is the film thickness normalized by h_0 , $M(\bar{h})$ is a dimensionless function calculated from the deviation of the experimental data for the film thickness from the linear dependence, and the disjoining pressure p_{disj} is normalized by ε/h_0 . The detailed derivation of Eq. (7.3) can be found in Sett et al. (2014a).

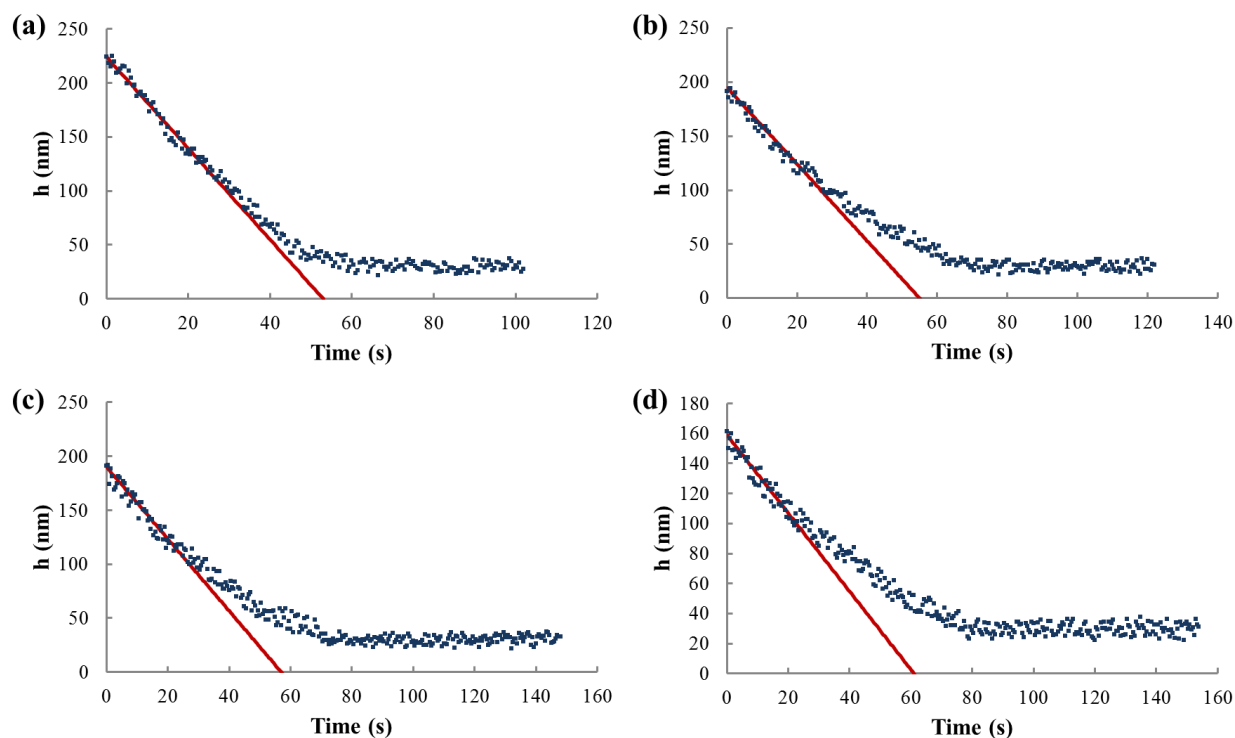


Figure 7.4. Drainage of the superspreader SILWET L-77-alone solution films: (a) L0.1, (b) L0.2, (c) L0.5, and (d) L1.0. The experimental results are shown by symbols. The inclined straight lines correspond to the theoretical prediction of Sett et al. (2013) and Eq. 7.1 in the present work.

However, at the latter stage, the dependence of the film thickness on time had practically saturated, since high disjoining pressure associated with fluffy bilayer aggregates formed by the superspreader practically arrested drainage [Sett et al. (2014a)]. These bilayer aggregates formed by the superspreader [Venzmer (2011); Venzmer and Wilkowski (1998); Ruckenstein (2012) and He et al. (1993)] are hanging from the free surface of the film in distinction from the ordinary surfactant (e.g. SDS) solutions. The latter are capable of forming only much smaller in size spherical micellar aggregates, which do not result in high disjoining pressure, and thus do not arrest drainage. An increase in the SILWET L-77 concentration led to higher values of disjoining

pressure at the later stages, which increased from around 40,000 dyn/cm² for L0.1 to around 50,000 dyn/cm² for L1.0 [Fig. 7.5]. Accordingly, the lifetime of the plane films had increased. The results for drainage of the SILWET L-77-alone plane films at different concentrations are presented in Table 7.3.

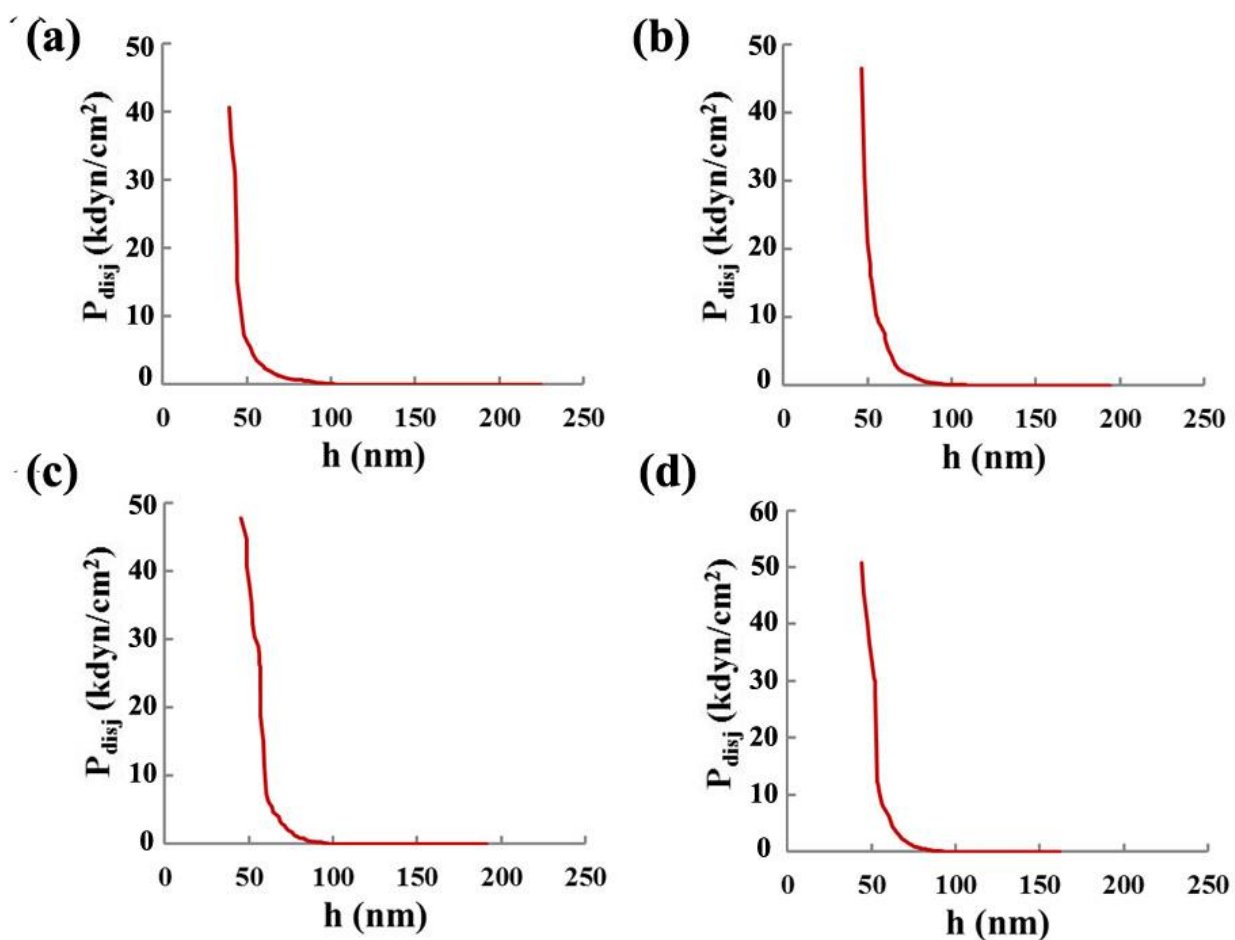


Figure 7.5. Disjoining pressure of the SILWET L-77-alone solution films for (a) L0.1, (b) L0.2, (c) L0.5, and (d) L1.0.

Table 7.3. Superspreader SILWET L-77-alone solution films. The film lifetime is denoted by t_ℓ , t_b denotes the time at which black film sets in at the top of the wire frame. The initial film thickness at the top is denoted $h_i=h_0$; the characteristic drainage time is denoted as T , and the maximum disjoining pressure attained as $p_{\text{disj,max}}$. The values of the surface elasticity ε were found from T using Eq. 7.2. The scaling exponent was obtained from the logarithmic plot of the dimensionless disjoining pressure versus the dimensionless thickness of the film as explained in Sett et al. (2014a). The scaling law for the disjoining pressure $p_{\text{disj}}(h) \sim h^{-m}$ revealed the exponent m values listed in the utmost-right column.

Solution	t_ℓ (s)	t_b (s)	$h_i = h_0$ (nm)	T (s)	ε (g/s ²)	$p_{\text{disj,max}}$ (dyn/cm ²)	Exponent m
L0.1	102	54	225.46	53	0.174	40614	6.34
L0.2	122	67	197.23	55	0.148	46440	10.47
L0.5	148	73	190.78	57	0.146	47677	8.47
L1.0	154	80	166.15	61	0.127	50723	9.22

In the present work solutions of mixtures of SDS and superspreader SILWET L-77 at different concentrations were also used in the plane film drainage experiments. The experiments showed that initially in all such films regular interference color bands were formed (Fig. 7.6). They were similar to the interferometric color bands observed in the plane films of SDS alone [Sett et al. (2013)]. However, at the latter stage the colors mixed with one another, indicating non-uniform film thickness in the horizontal direction. Eventually, the topmost part of the film turned black (after time t_b from the formation of the film, as summarized in Table 7.4) and

remained black for the remaining time until the film burst. Similarly to the interferometric observations with plane films of superspreader SILWET L-77 alone [Sett et al. (2014a)], the black domain was confined at the top part of the film and did not spread downward with time. The color intermittency over the entire film gradually increased until the film burst.

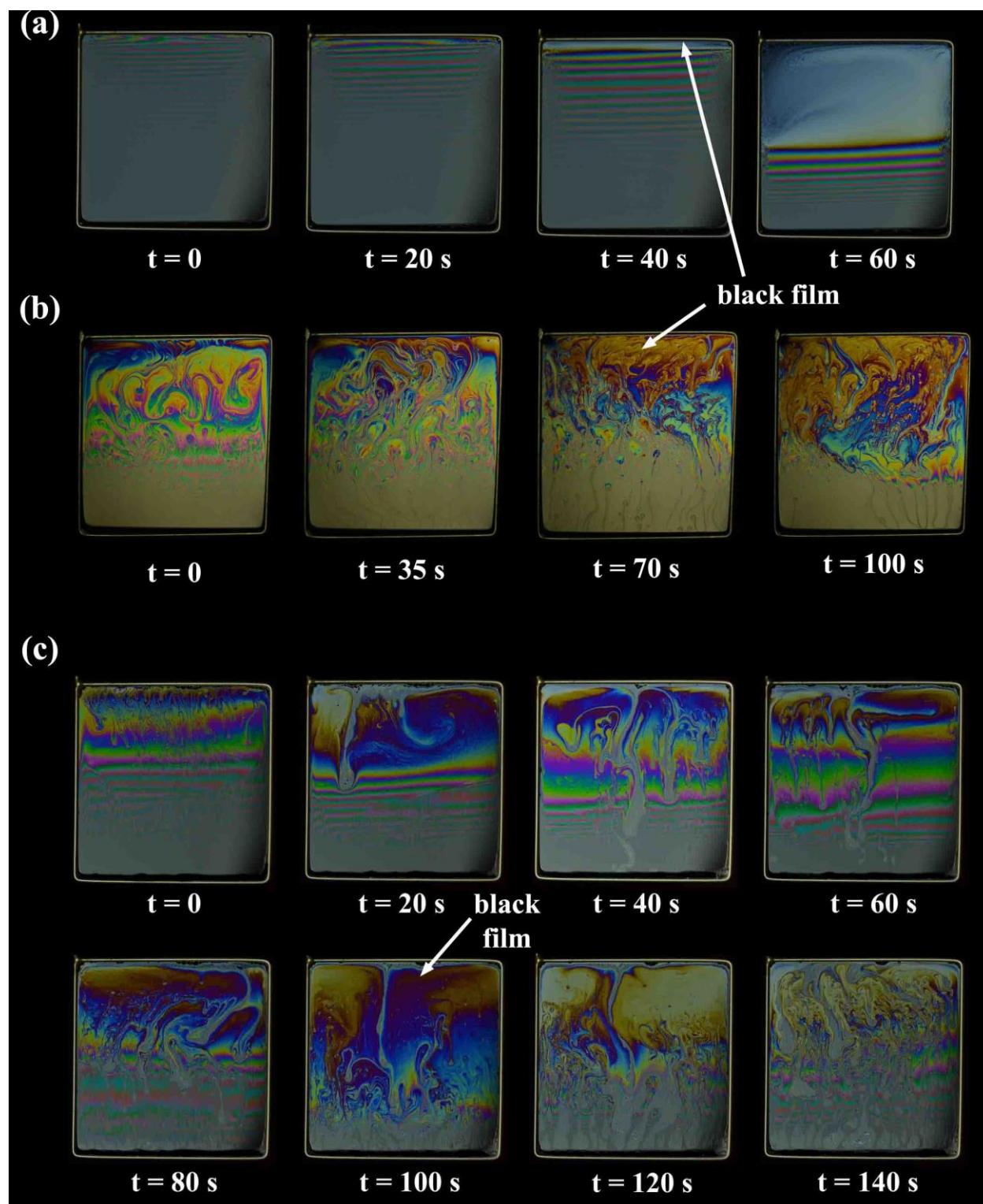


Figure 7.6. Drainage of (a) S2.0, (b) L0.1, and (c) SL12-0.5 plane film.

Table 7.4. SDS and superspreader SILWET L-77 mixture solution films. The film lifetime is denoted by t_ℓ , t_b denotes the time at which black film sets in at the top of the wire frame. The initial film thickness at the top is denoted $h_i=h_0$; the characteristic drainage time is denoted as T and the maximum disjoining pressure attained as $p_{\text{disj, max}}$. The values of the surface elasticity ε were found from T using Eq. 7.2. The scaling exponent was obtained from the logarithmic plot of the dimensionless disjoining pressure versus the dimensionless thickness of the film as explained in Sett et al. (2014a). The scaling law for the disjoining pressure $p_{\text{disj}}(h) \sim h^{-m}$ revealed the values of the exponent m listed in the utmost-right column.

Solution	t_ℓ (s)	t_b (s)	$h_i = h_0$ (nm)	T (s)	ε (g/s ²)	$p_{\text{disj, max}}$ (dyn/cm ²)	Exponent m
SL4-0.5	112	80	613.4	61	0.9	60845	6.78
SL4-1.0	119	84	635.9	62	0.97	80706	6.94
SL4-2.0	124	86	648.9	64	1.03	90426	7.33
SL4-5.0	130	90	652.5	69	1.12	135031	7.18
SL4-10.0	135	91	656.5	72	1.18	140300	7.21
SL8-0.5	126	85	912.6	66	1.79	82337	7.56
SL8-1.0	136	88	915.2	70	1.88	94032	7.43
SL8-2.0	139	90	925.1	72	1.96	124,589	7.81
SL8-5.0	141	94	918.4	75	2.03	145532	7.77
SL8-10.0	145	96	930.1	78	2.15	165418	7.82
SL12-0.5	142	87	1090.0	70	2.45	96859	7.35
SL12-1.0	146	90	1103.1	75	2.67	140094	7.73

SL12-2.0	152	96	1110.7	78	2.78	164924	7.63
SL12-5.0	160	99	1128.1	80	2.82	175742	7.71
SL12-10.0	166	105	1159.82	84	3.22	190062	7.82

In the experiments the linear decay of the film thickness is described by Eq. 7.2, which determines the value of T (cf. the red lines in Fig. 7.7). Then, the values of the surface elasticity ε were found from the values of T using Eq. 7.2. Figure 7.7 also shows that the linear decrease of the film thickness is observed until the film stabilization sets in, when the film thinning becomes much slower and the data deviate from the linear dependence. The disjoining pressure causing the film stabilization is calculated using Eq. 7.3. The results for different concentrations of mixture solutions are summarized in Table 7.4.

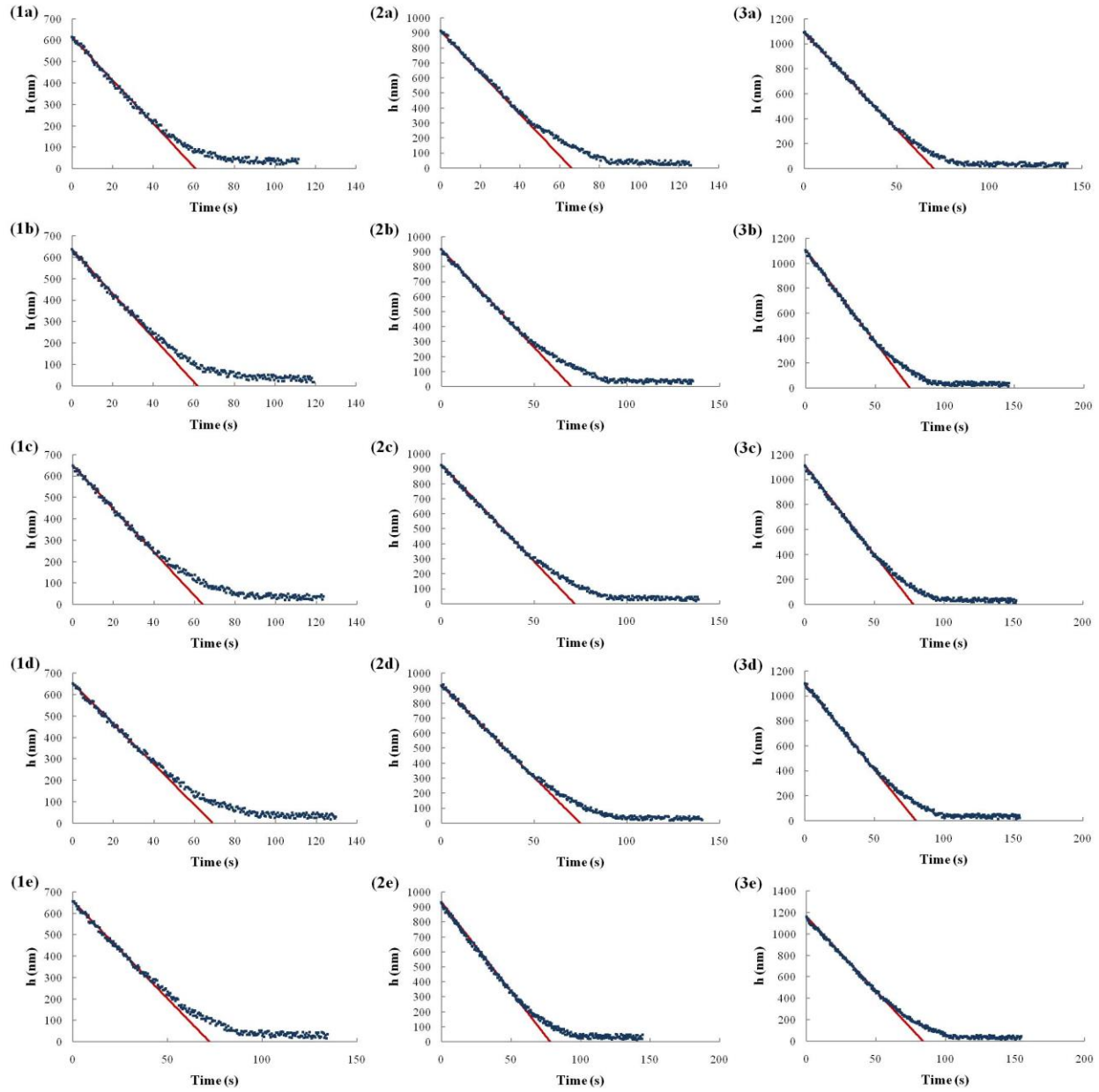


Figure 7.7. Drainage of the plane thin films of SDS/SILWET L-77 mixed solutions for (1) 4 mM SDS solutions: (a) SL4-0.5, (b) SL4-1.0, (c) SL4-2.0, (d) SL4-5.0, and (e) SL4-10.0; (2) 8 mM SDS solutions: (a) SL8-0.5, (b) SL8-1.0, (c) SL8-2.0, (d) SL8-5.0, and (e) SL8-10.0; (3) 12 mM SDS solutions: (a) SL12-0.5, (b) SL12-1.0, (c) SL12-2.0, (d) SL12-5.0, and (e) SL12-10.0. The data correspond to the film top. The experimental results are shown by symbols. The inclined

straight lines correspond to the theoretical prediction of Sett et al. (2013) and Eq. 1 in the present work.

Plane films formed with mix surfactant solutions containing 12 mM of SDS were thicker than the corresponding ones formed with solutions containing 8 mM SDS, which in turn were thicker than the corresponding films formed with solutions containing 4 mM SDS. This trend was similar for plane films formed with SDS alone discussed above and in detail in Sett et al. (2013), where the initial film thickness increased with increasing concentration of the surfactant. Increasing the concentration of the superspreader SILWET L-77 at a fixed concentration of SDS solutions did not change the initial thickness of the film. However, the maximum disjoining pressure attained increased significantly from 40,845 dyn/cm² to 80,706 dyn/cm² for SL4-0.5 to SL4-10.0, from 82,337 dyn/cm² to 165,418 dyn/cm² for SL8-0.5 to SL8-10.0, and from 96,859 dyn/cm² to 190,062 dyn/cm² for SL12-0.5 to SL12-10.0, as shown in Fig. 7.8. It should be emphasized that even though the ratio of SDS to SILWET L-77 is 1:0.5=2:1 for SL4-0.5, SL8-0.5, and SL12-0.5, the absolute concentration of SILWET L-77 is much higher in SL12-0.5 than in SL8-0.5 and SL4-0.5. This increase in the concentration of superspreader SILWET L-77 causes an increase in the disjoining pressure from SL4-0.5 – SL4-10.0 to SL12-0.5 to SL12-10.0.

The disjoining pressures in plane films formed with mixed surfactant solutions were much higher even at sufficiently lower concentration of superspreader SILWET L-77 as compared to that in plane films formed with superspreader SILWET L-77-alone. For example, SL4-0.5 which contains 0.057 %v/v of SILWET L-77 in addition to SDS attained a disjoining pressure of 60,000 dyn/cm², whereas L0.5 or L-77-0.5 of Sett et al. (2014a) (a 0.5 %v/v superspreader SILWET L-77-alone), being 10 times more concentrated attained a disjoining pressure of only

48,000 dyn/cm². The solution SL4-5.0 on the other hand, had SILWET L-77 concentration of 0.573 %v/v, close to that of L0.5 or L-77-0.5 of Sett et al. (2014a), and attained the maximum disjoining pressure of 135,000 dyn/cm². Similarly, solutions SL8-0.5 and SL4-1.0 had SILWET L-77 concentration of about 0.1 %v/v, which was ten times more dilute than that in L1.0 or L-77-1.0 of Sett et al. (2014a), which was 1 %v/v. The corresponding maximum disjoining pressure values measured were 82,000 dyn/cm², 80,000 dyn/cm², and 51,000 dyn/cm², respectively. The solutions SL8-5.0 and SL4-10.0 had the SILWET L-77 concentration of 1.146 %v/v, close to that in L1.0 or L-77-1.0 of Sett et al. (2014a). The disjoining pressures for them were 165,400 dyn/cm² and 140,300 dyn/cm², respectively. It should be emphasized that even though SILWET L-77 concentration might be the same, the mixture solutions contain SDS as an additional surfactant. The individual molecules of the two surfactants (the superspreader and SDS) compete for the same space at the film surface, thereby leaving more of the larger superspreader molecules to remain in the bulk as compared to the comparable superspreader-alone solutions. This creates a larger number of superspreader aggregates in the bulk, which can be self-organized in the fluffy bilayer structures of the superspreader SILWET L-77 hanging from the free surfaces [Sett et al. (2014a)]. Correspondingly, a higher disjoining pressure is achieved compared to the comparable superspreader-alone films.

The deviation of the thickness dependence on time from linearity begins at larger film thicknesses for the mixture (SDS/ SILWET L-77) surfactant solution as compared to the films formed with either SDS alone or superspreader SILWET L-77 alone (Fig. 7.9). The film thickness had no deviation from the linear dependence for the films formed with SDS alone [Sett et al. (2013)]. Also, the deviation from linearity was observed at about $h < 100$ nm for films formed with SILWET L-77 alone [Sett et al. (2014a)]. For comparison, the deviation from

linearity occurred at about $h = 180$ nm for the solutions containing 4 mM SDS with different concentrations of SILWET L-77 (SL4-0.5 – SL4-10.0), at about $h = 300$ nm for the 8 mM solutions (SL8-0.5 – SL8-10.0), and at about $h = 350$ nm for the 12 mM solutions (SL12-0.5 – SL12-10.0). The disjoining pressure in the superspreader solutions is associated with the fluffy film surfaces formed by long superspreader bilayers hanging from the free surfaces [Sett et al. (2014a)]. Since all solutions containing both SDS and SILWET L-77 are above cmc, they contain spherical micelles of SDS along with the fluffy bilayers of SILWET L-77. The hanging bilayers from the free surface interact with these micelles in the film bulk, thereby the effect of the disjoining pressure is felt in a much thicker film formed by a SDS/SILWET L-77 mixture than by SDS or superspreader alone. With an increase in the concentration of SDS from 4 mM to 12 mM, the number of micelles also increases in the bulk, resulting in an earlier onset of the disjoining pressure effects and deviation from linearity.

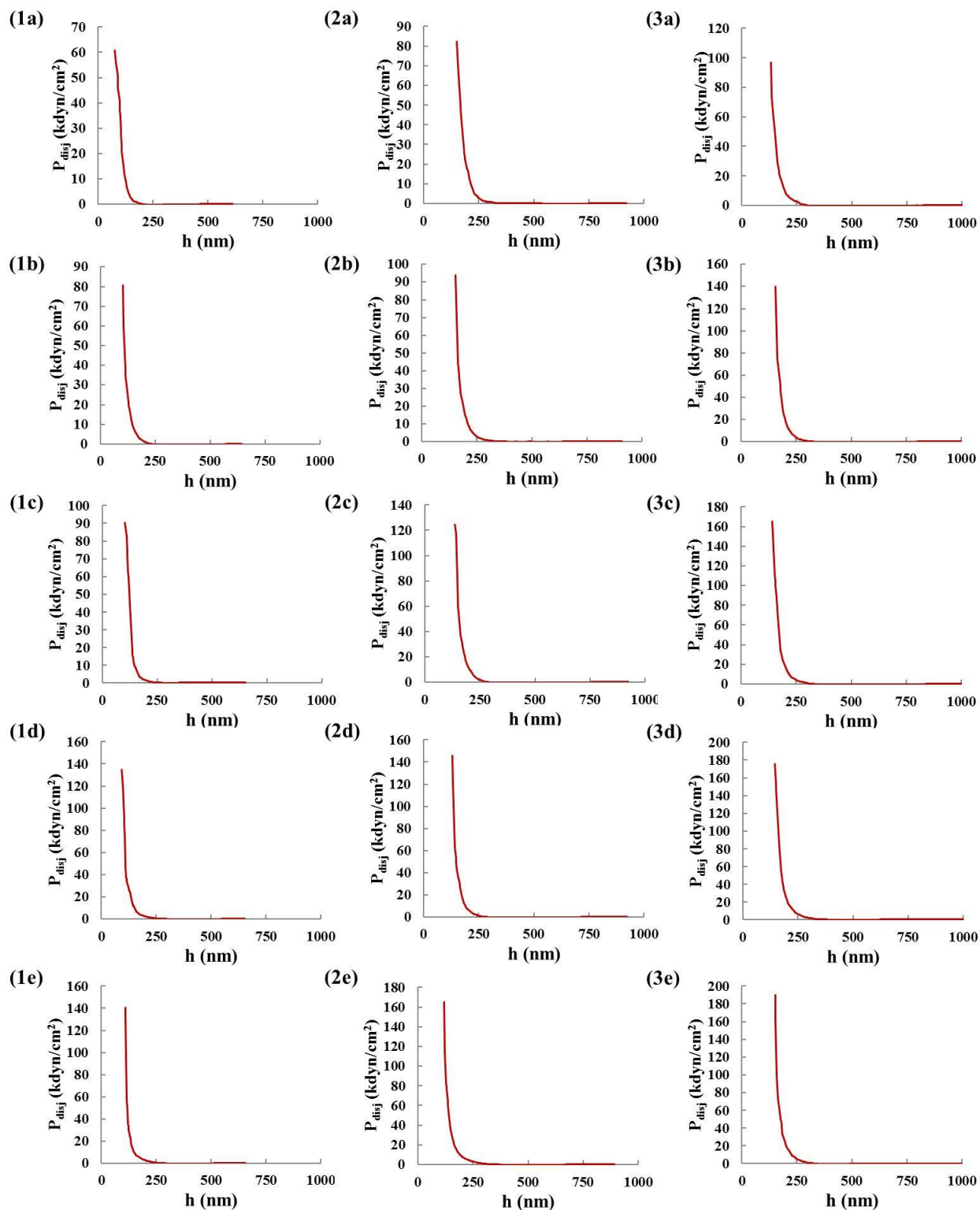


Figure 7.8. Disjoining pressure of the SDS/ SILWET L-77 mixed solutions for (1) 4 mM SDS solutions: (a) SL4_-0.5, (b) SL4-1.0, (c) SL4-2.0, (d) SL4-5.0, and (e) SL4-10.0; (2) 8 mM SDS

solutions: (a) SL8-0.5, (b) SL8-1.0, (c) SL8-2.0, (d) SL8-5.0, and (d) SL8-10.0; (3) 12 mM SDS solutions: (a) SL12-0.5, (b) SL12-1.0, (c) SL12-2.0, (d) SL12-5.0, and (d) SL12-10.0.

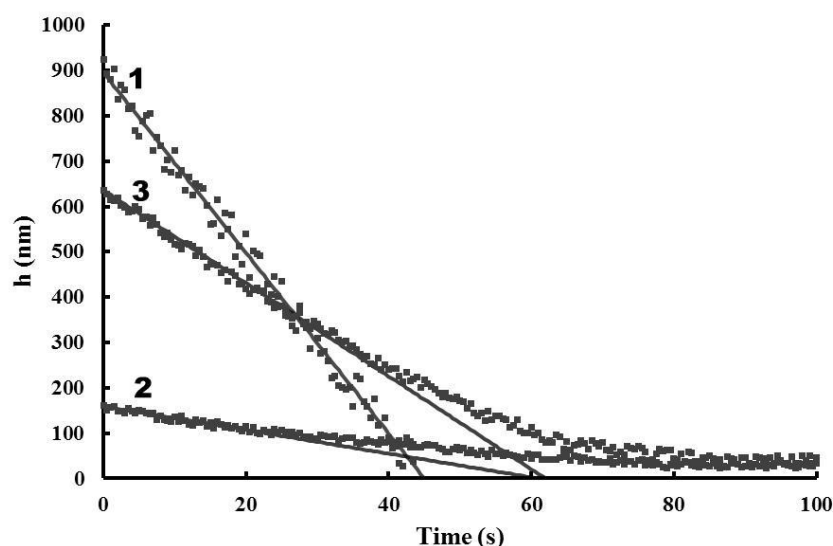


Figure 7.9. Drainage of plane films of S4.0 (line and data 1: SDS alone), L1.0 (line and data 2: SILWET L-77-alone), and SL4-1.0 (line and data 3: SDS/SILWET L-77 mixture). The thickness dependence on time deviates from linearity at higher film thickness for SDS/SILWET L-77 mixture solution films, as it does for the SILWET L-77-alone solution. It is instructive to see that the SDS/SILWET L-77 mixture solution films are stabilized at a slightly larger film thickness than in the SILWET L-77-alone case.

7.3.2 Foam drainage in gravity settler

Different concentrations of the anionic surfactant SDS and superspreader SILWET L-77 were used independently in the foam column experiments. The volume of liquid drained from the foam column was measured from the height of the drained liquid/foam interface at regular intervals of time. The change in the drained volume with time in the films of SDS alone and

superspreader SILWET L-77 alone are shown in Figs. 7.10a and 7.10b, respectively. Foam stability can be characterized by the volume of liquid in the foam rendered dimensionless by the total liquid in the foam at the beginning of the experiment. The latter can be found as the total volume of liquid left in the foam column at the end of the experiment after drainage stops. The foam stability curves for the SDS-alone or superspreader SILWET L-77-alone solutions are shown in Figs. 7.11a and 7.11b, respectively.

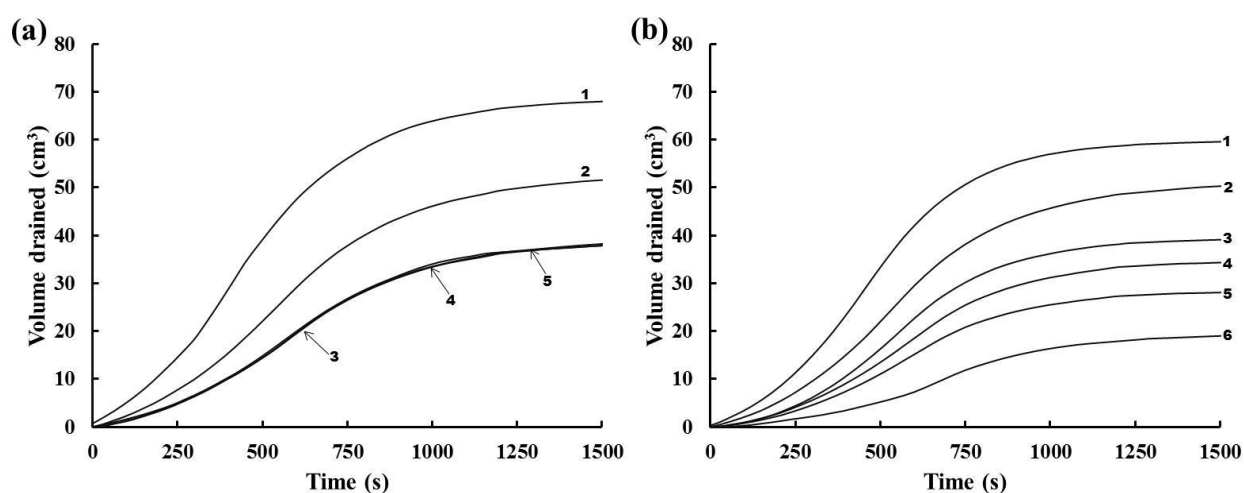


Figure 7.10. Volume of liquid drained for the first 1500 s from the films of (a) the SDS-alone, and (b) superspreader SILWET L-77-alone solutions. The numbers represent different concentrations. For (a) SDS-alone, the results for S4.0, S6.0, S8.0, S10.0, and S12.0 solutions are numbered as 1, 2, 3, 4, and 5, respectively, with curves 3, 4, and 5 overlapping. For (b) SILWET L-77-alone, the results for L0.1, L0.2, L0.5, L1.0, L1.5, and L2.0 solutions are numbered as 1, 2, 3, 4, 5, and 6, respectively.

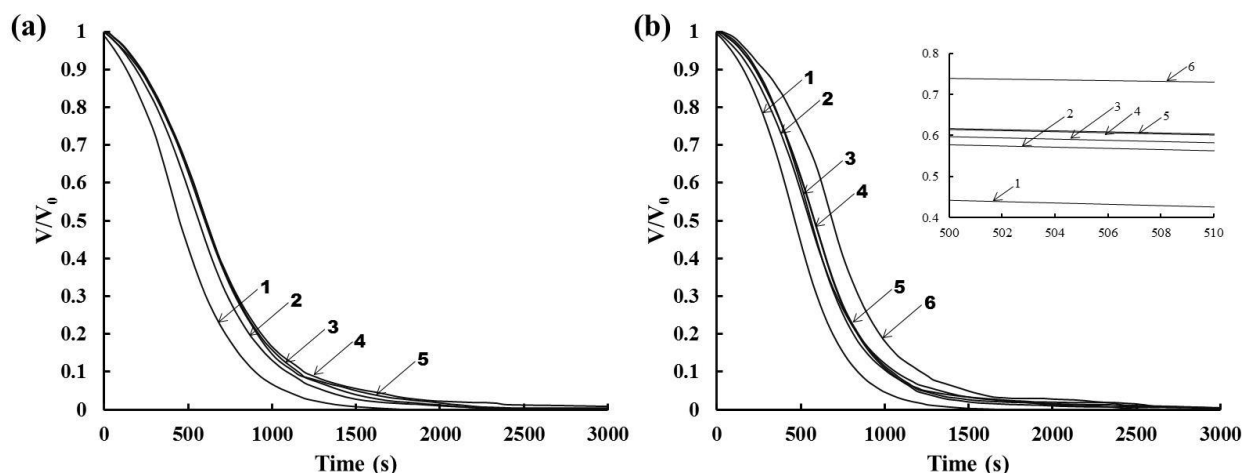


Figure 7.11. Drainage curves for different concentrations of (a) the SDS-alone solutions, and (b) SILWET L-77-alone-solutions. The instantaneous volume of liquid in the foam V is rendered dimensionless by the total volume of the liquid in the foam V_0 . The numbers correspond to different concentrations. The data for (a) the SDS-alone solutions, S4.0, S6.0, S8.0, S10.0, and S12.0 are presented by curves 1, 2, 3, 4, and 5, respectively. For (b) the SILWET L-77-alone solutions L0.1, L0.2, L0.5, L1.0, L1.5, and L2.0 the results are shown by the corresponding curves 1, 2, 3, 4, 5, and 6, respectively. The inset resolves the drainage curves for 10 s, where the mutual locations of different curves are distinctly seen, as compared to the plot in a larger scale.

For both the anionic SDS and the non-ionic superspreader SILWET L-77, the initial liquid content in the foam decreased with the increase in concentration of the surfactant (Fig. 7.10), indicating drier foam and a higher initial gas volume fraction [cf. Table 7.5]. The drainage of the drier foams was slower, indicating more stable foams formed from solutions with higher surfactant concentrations. For SDS solutions, when the concentration increased beyond the critical micelle concentration (cmc) which is 8 mM [Berg et al. (2005) and Mysels (1986)], there was no further decrease in the initial liquid content, and the foam stability remained the same.

All solutions prepared with superspreader SILWET L-77 were above the critical micelle concentration, which is 0.007% (v/v) [Sett et al. (2014a)]. However, the initial liquid content in the foam kept on decreasing [cf. Table 7.5] with the increase in concentration of the superspreader and did not reach any saturation limit, though there was no significant increase in the foam stability, except for the solution L2.0, which showed a remarkably higher foam stability as compared to the other SILWET L-77 solutions (cf. Fig. 7.11b).

Table 7.5. Liquid drainage from the SDS-alone and the superspreader SILWET L-77-alone foams. The initial gas fraction is denoted by Φ ; the time in minutes needed for a foam to drain 10%, 50%, and 90% of the initial liquid volume is denoted as t_{10} , t_{50} , and t_{90} , respectively.

Solution	Φ	t_{10}	t_{50}	t_{90}
S4.0	0.874	2.5	7.5	15.0
S6.0	0.902	3.0	9.5	18.5
S8.0	0.927	3.5	10.0	19.0
S10.0	0.927	3.5	10.0	19.0
S12.0	0.927	3.5	10.0	19.0
L0.1	0.890	2.5	7.5	14.0
L0.2	0.905	3.0	9.0	17.5
L0.5	0.926	3.5	9.0	17.5
L1.0	0.936	4.0	9.5	18.5
L1.5	0.947	4.0	9.5	19.0
L2.0	0.964	4.5	11.5	20.0

One of the most important factors in foaming a liquid is the foam generating power of the liquid, or foamability [Prudhomme (1995)]. The foamability is defined as the total volume of foam generated in a fixed time period beginning from a fixed volume of liquid. For all the experiments, the foam was generated by mixing 200 ml of solution for 3 min. The volume of the foam-filled column was fixed. Therefore, a lower total volume of liquid measured in the gravity settler at the end of experiment would mean that the same volume of foam could be generated from a lower volume of liquid. In other words, a larger volume of foam would be generated from the same initial volume of liquid. Thus, the lesser the volume of liquid in the gravity settler at the end, the higher the foamable is of the surfactant solution. The foamability at different concentrations of the SDS-alone and the superspreader SILWET L-77-alone solutions is shown in Fig. 7.12.

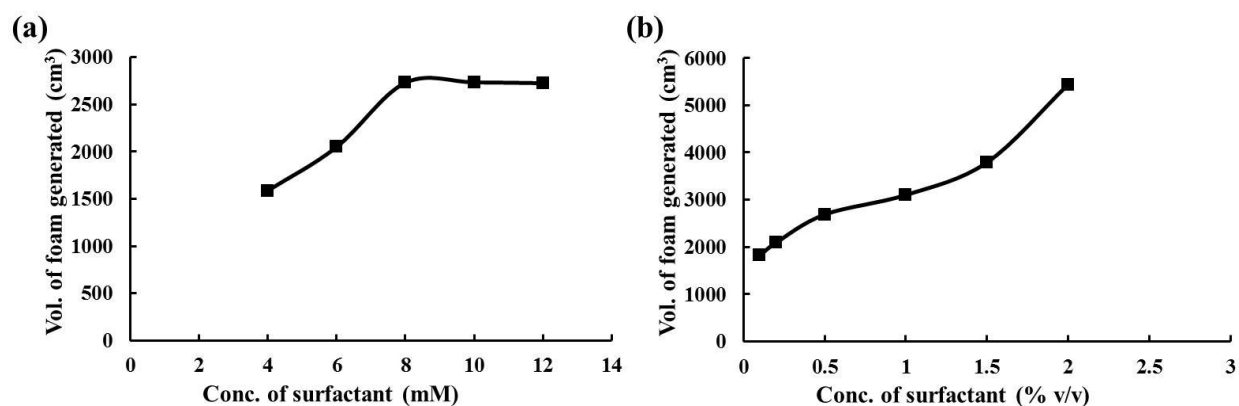


Figure 7.12. Foamability of (a) the SDS-alone, and (b) the SILWET L-77-alone solutions. The symbols represent the experimental data, which are spanned by curves for convenience.

The foamability of SDS increased till the concentration of the surfactant reached the cmc. Beyond that, there was no further increase in the foamability (Fig. 7.12a). The trisiloxane surfactant SILWET L-77 (the superspreader) behaved differently (Fig. 7.12b). Although the concentrations of the superspreader in the solutions were much higher than its cmc, its foamability kept on increasing with an increase in concentration of the superspreader.

Different concentrations of the superspreader SILWET L-77 were added to the 4 mM, 8 mM, and 12 mM SDS solutions. By altering the SILWET L-77 concentration as explained in the experimental section, the mixing ratios used for each of the SDS solutions were 1:0.5, 1:1, 1:2, 1:5, and 1:10. The volume of liquid drained from the foam column and the corresponding foam stability for different mixing ratios for the 4 mM SDS solution are illustrated in Fig. 7.13.

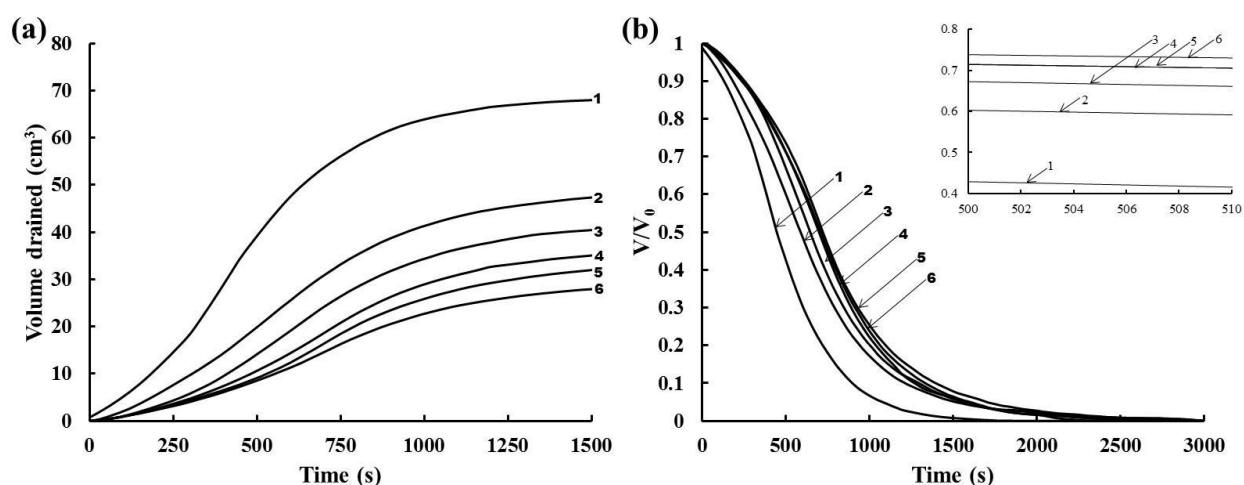


Figure 7.13. (a) Volume of liquid drained for the first 1500 s, and (b) drainage curves for the 4 mM SDS/SILWET L-77 mixture solutions. The S4.0, SL4-0.5, SL4-1.0, SL4-2.0, SL4-5.0, and SL4-10.0 solutions correspond to curves 1, 2, 3, 4, 5, and 6, respectively. The inset resolves the drainage curves for 10 s, where the mutual locations of different curves are distinctly seen, as compared to the plot in a larger scale.

Adding a small amount of SILWET L-77 to 4 mM SDS solution strongly decreased the initial water content in the foam (compare curve 1 for S4.0 with the curve 2 for SL4-0.5 in Fig. 7.13a), thereby increasing the initial gas fraction in the foam. The stability of the foam also increased significantly (Fig. 7.13b) for S4.0 to SL4-2.0, beyond which there was not much change in stability (compare the 4, 5, and 6 curves in Fig. 7.13b for SL4-2.0, SL4-5.0, and SL4-10.0, respectively). Thereafter, increasing the ratio of the superspreader SILWET L-77 in the 4 mM SDS solution, which increased the content of SILWET L-77, further decreased the initial water content in the foam. The decrease in the initial liquid content from SL4-0.5 to SL4-1.0 or from SL4-1.0 to SL4-2.0 and so forth was not as strong as it was from S4.0 to SL4-0.5. The stability of the foam also increased slightly after the initial strong stabilization of the foam seen for SL4-0.5 (Fig. 7.13b). The solution SL4-10.0, which contained the highest concentration of the superspreader SILWET L-77, had the minimum initial water content and maximum gas fraction in the foam [cf. Table 7.6].

Table 7.6. Drainage of liquid from the SDS/SILWET L-77 mixture foams. The initial gas fraction is denoted by Φ ; the time in minutes needed for a foam to drain 10%, 50%, and 90% of the initial liquid volume is denoted as t_{10} , t_{50} , and t_{90} , respectively.

Sol.	Φ	t_{10}	t_{50}	t_{90}
SL4-0.5	0.908	3.0	9.5	20.0
SL4-1.0	0.921	4.0	10.5	21.0
SL4-2.0	0.931	4.0	11.5	22.0
SL4-5.0	0.936	4.0	12.0	23.0
SL4-10.0	0.945	4.0	12.0	23.0
SL8-0.5	0.934	3.5	9.5	18.5
SL8-1.0	0.938	3.5	10.0	20.5
SL8-2.0	0.946	4.0	11.0	21.5
SL8-5.0	0.952	4.0	11.5	22.5
SL8-10.0	0.957	5.0	13.5	23.0
SL12-0.5	0.932	3.0	9.5	18.5
SL12-1.0	0.938	3.5	9.5	18.5
SL12-2.0	0.945	3.5	10.5	21.0
SL12-5.0	0.952	3.5	10.5	21.0
SL12-10.0	0.963	3.5	11.0	21.0

The same mixing ratios of 1:0.5, 1:1, 1:2, 1:5, and 1:10 of SDS and the superspreader SILWET L-77 were used with 8 mM and 12 mM SDS solutions. The volume of liquid drained in the first 1500 s and the foam stability for the SDS solutions with 8 mM and 12 mM at different mixing ratios of SILWET L-77 are shown in Figs. 7.14 and 7.15.

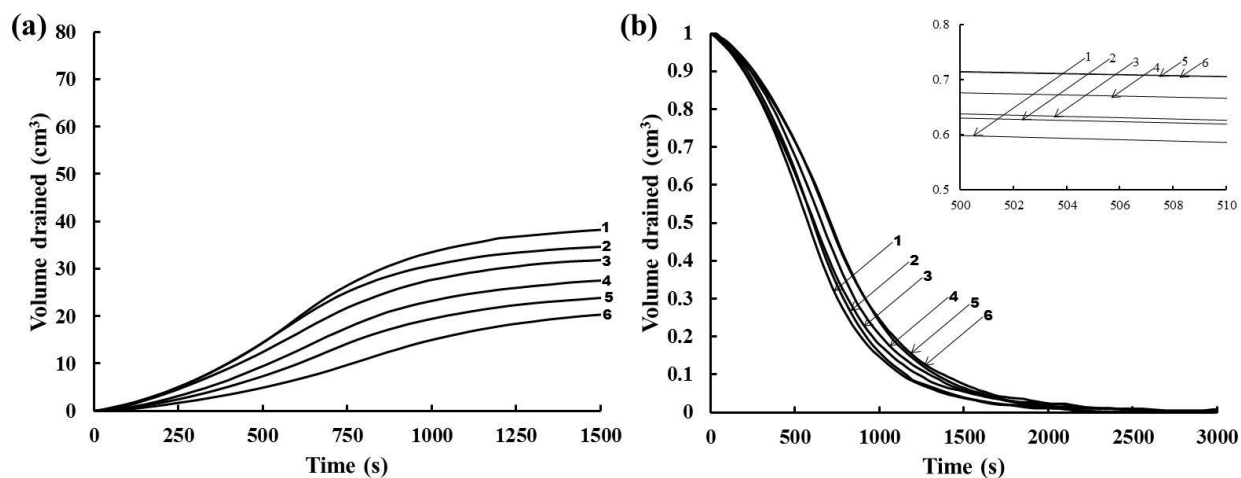


Figure 7.14. (a) Volume of liquid drained for the first 1500 s, and (b) drainage curves for the 8 mM SDS/SILWET L-77 mixture solutions. The solutions S8.0, SL8-0.5, S8L-1.0, S8L-2.0, SL8-5.0, and SL8-10.0 correspond to curves 1, 2, 3, 4, 5, and 6, respectively. The inset resolves the drainage curves for 10 s, where the mutual locations of different curves is distinctly seen, as compared to the plot in a larger scale.

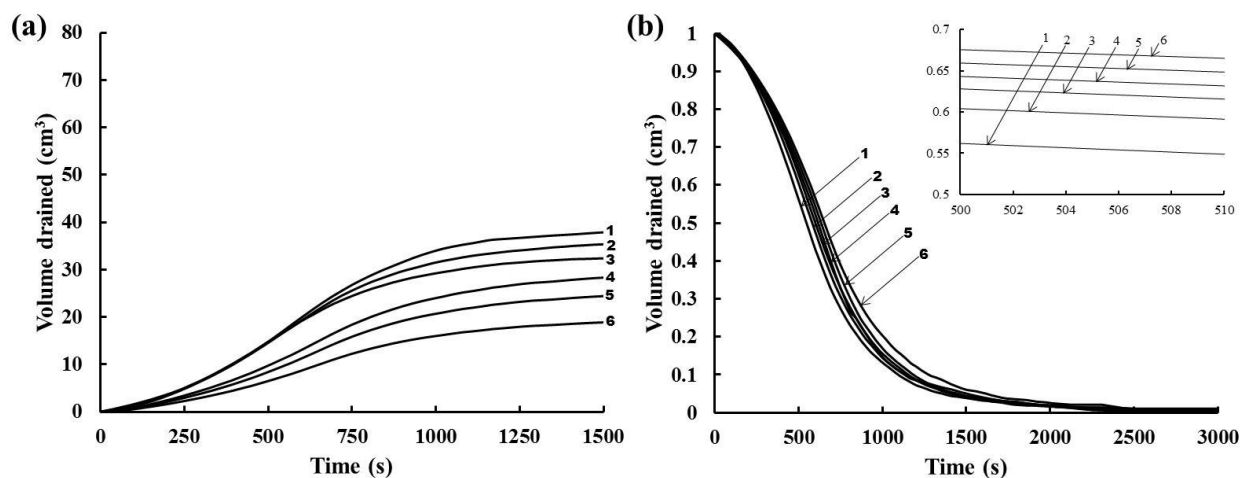


Figure 7.15. (a) Volume of liquid drained for the first 1500 s, and (b) drainage curves for the 12 mM SDS/SILWET L-77 mixture solutions. The S12.0, SL12-0.5, SL12-1.0, SL12-2.0, SL12-5.0, and SL12-10.0 solutions correspond to curves 1, 2, 3, 4, 5, and 6, respectively. The inset resolves the drainage curves for 10 s, where the mutual locations of different curves is distinctly seen, as compared to the plot in a larger scale.

The 8 mM and 12 mM SDS/SILWET L-77 mixture solutions revealed trends similar to the 4 mM SDS/SILWET L-77 mixture solutions. The initial liquid content in the foam decreased with increasing ratios of SILWET L-77. However, the decrease was not as significant from S8.0 to SL8-0.5 or from S12.0 to SL12-0.5, as it was from S4.0 to SL4-0.5 solution. The increase in stability was also very small and gradual with increasing ratios of SILWET L-77 in the 8 mM and 12 mM SDS solutions. The SL8-10.0 and SL12-10.0 solutions had minimum liquid content in the foam among the 8 mM and 12 mM SDS/SILWET L-77 mixture solutions.

The foamability of the 4 mM, 8 mM and 12 mM SDS/SILWET L-77 mixture solutions is illustrated in Fig. 7.16. Note that to maintain the same mixing ratios, at higher concentration of SDS solutions, the corresponding SILWET L-77 concentration was also higher. For example,

SL12-0.5 had a higher concentration of the superspreader SILWET L-77 as compared to SL8-0.5, which in turn had a higher concentration than SL4-0.5.

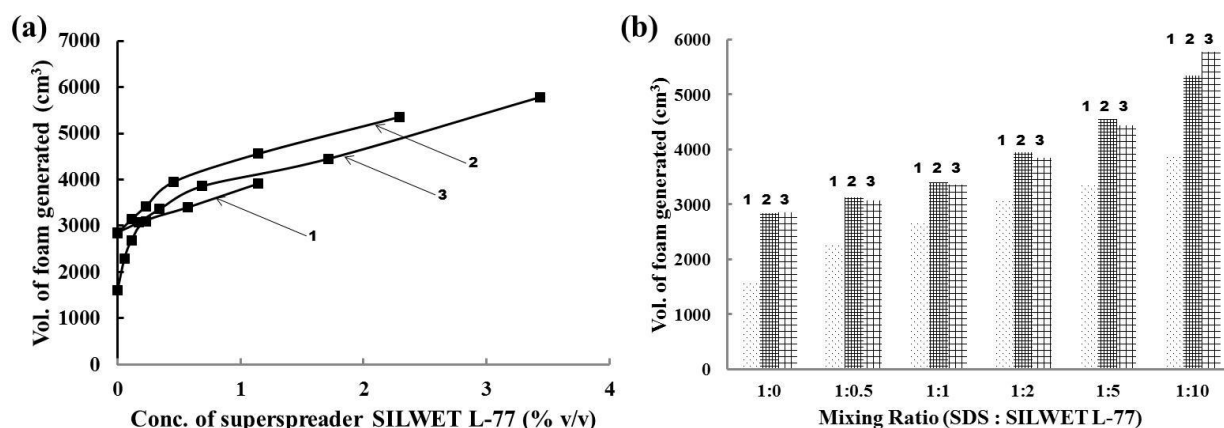


Figure 7.16. Foamability of the SDS/SILWET L-77 mixture solutions in terms of (a) concentration of SILWET L-77, and (b) mixing ratios. Numerals 1, 2, and 3 correspond to the 4 mM, 8 mM, and 12 mM SDS solutions, respectively.

The foamability of the SDS – SILWET L-77 mixture solutions in general increased with increasing mixing ratios. For each of the three concentration of the SDS solutions, their respective 1:10 mixture solutions with superspreader, namely SL4-10.0, SL8-10.0, and SL12-10.0, showed the highest foamability. Adding a small amount of SILWET L-77 to the 4 mM SDS solution enhanced the foamability to a great extent, as is seen in Fig. 7.16a where the range corresponding to the mixed solutions SL4-0.5 and SL4-1.0 creates the initial steep slope of the foamability curve. This can be explained in terms of the total concentration of surfactants in the foam-generating solutions. Since 4 mM of SDS is lower than the SDS cmc, there is an extra space for any other surfactant molecules at the film surface. Fig. 7.12a corroborates this fact, with the foamability of S4.0 being much less than the foamability of S8.0, indicating an extra

space for any extra surfactant molecules at the surface. The extra surfactant molecules, those of SILWET L-77 in the present case, help in stabilizing the lamellae between the bubbles, increasing the foamability of SL4-0.5 and SL4-1.0 solutions significantly.

The foamability of the 8 mM and 12 mM SDS mixture solutions also increased with adding superspreader. This is in contradiction to the generally accepted notion that solution foamabilities do not increase beyond the cmc. In these cases, the concentrations of either of the two surfactants (SDS and superspreader) in the solution were above their individual cmc. Accordingly, the foam column experiments with SDS-only solutions showed no enhancement of foamability beyond its cmc (Fig. 7.12a). At lower mixing ratios, the foamabilities of the 8 mM and 12 mM SDS solutions were almost identical (Fig. 7.16b) and higher than the foamability of the corresponding 4 mM SDS solution. In the other words, SL8-0.5 and SL12-0.5 had the same foamability, which was higher than that of SL4-0.5. At high mixing ratio, the foamability of the 12 mM mixture solution, the foamability of SL12-10.0, was higher than that of the 8 mM mixture solutions, SL8-10.0.

An increase in a solution foamability indicates generation of a large volume of foam beginning from the same initial liquid volume. This means that the total surface area of the liquid lamellae separating the gas bubbles is increased. Since the initial volume of liquid is the same, a higher foamability is possible only when the lamellae are thinner, as compared to a solution with a lower foamability. For sufficiently low surfactant concentrations (S4.0), such thin lamellae are unstable. This is corroborated by the fact that plane films formed from the SDS-alone solution last for a much shorter time [Sett et al. (2013)] than the superspreader SILWET L-77-alone films [Sett et al. (2014a)] and the SDS/SILWET L-77 mixture solution films as discussed in the previous section. Also, the disjoining pressure in the plane films of the mixture solutions was

higher than the disjoining pressure in the films of the superspreader SILWET L-77-alone. The high disjoining pressure attained in the plane films of mixture solutions prevents rupture of thin lamellae between bubbles formed during foam generation. The gas bubbles of these solutions are separated by a very thin but stable lamellae resulting in an enhanced foamability. This effect is also corroborated by the data on solution foamability, where SDS/SILWET L-77 had a higher foamability than that of the corresponding SILWET L-77 solution. It can be concluded that during foam generation, SDS solutions at a higher mixing ratio of SILWET L-77 can form gas bubbles separated by thin but stable lamella. Then, the same initial amount of liquid can result in a larger volume of foam, thus resulting in an increase in foamability.

7.4 Conclusions

The foamability of SDS/SILWET L-77 mixture solutions can be higher than the foamability of either SDS or SILWET L-77 alone, as the comparison of the data in Figs. 7.16 and 7.12 reveals. Only at a very high concentration of the superspreader SILWET L-77-alone in solution (SL12-10.0), the foamability of the mixture solution is the same. This enhanced foamability of the mixture solutions can be directly correlated with the plane film drainage results. We showed that the plane films formed from mixture solutions revealed larger disjoining pressures as compared to the corresponding films of the SDS-alone or SILWET L-77-alone solutions. A higher disjoining pressure stabilizes the thin films of mixture solutions. A higher disjoining pressure in the films of mixed SDS and SILWET L-77 solutions presumably stems from adding the electric and steric components of disjoining pressure in these cases. The electric component of the disjoining pressure is associated with the ionic SDS surfactant, whereas the steric one – with the anionic superspreader SILWET L-77. Due to an enhanced stability of

mixture solutions, a larger volume of foam can be generated with the mixture SDS/ SILWET L-77 solutions, since the gas bubbles are supported by thinner but more stable lamellae. The thinner are the lamellae between two bubbles, the larger is the volume of foam generated from the same initial volume of liquid.

Despite a significant increase in the foamability of the SDS/SILWET L-77 mixture solutions, there is not much of enhancement in the foam stability [cf. Figs. 7.13b, 7.14b and 7.15b], except the case when the initial SDS content in the solution was below its cmc (SL4-0.5 as compared to S4.0). Therefore, a mixture of two surfactants, SDS and SILWET L-77 in the present case can attain foamability, which is much higher than those of these surfactants alone, albeit with almost no increase in the foam stability.

CHAPTER 8

FLUIDITY ENHANCEMENT OF GYPSUM – FOAM SLURRY WITH THE ADDITION OF SUPERSPREADER

8.1 Introduction

The primary aim of this work is to elucidate an enhanced fluidity of gypsum-foam slurry when water contains superspreader SILWET L-77, and to compare the strength, density and solidification rate of drywall boards formed with superspreaders with those produced using ordinary surfactants. Additionally, superspreader was added directly to water in the gypsum slurry without adding foam, and the fluidity, strength and rate of solidification of such slurry was tested.

8.2 Experimental

8.2.1 Materials

Southard stucco, corn starch, accelerator HRA, MCM, liquid dispersant, and retarder were all supplied by USG Corporation. Two kinds of surfactants, USG Stable Soap and USG Unstable Soap were also provided by USG Corporation. SILWET L-77, a trisiloxane surfactant, was obtained from Momentive.

8.2.2 Experimental procedure

Initially 1000 g of stucco was taken, 20 g (2%) of corn starch, 5 g (0.5%) of accelerator HRA and 2.5 g (0.25%) of MCM were added to it. Also, 6.25 g (0.625%) of liquid dispersant and 30 g of 1% concentrated retarder were added to the initial gypsum water before adding

stucco, corn starch, HRA and MCM. The liquid dispersant contained 60% of water. A large mass of stucco was used so that different tests, namely, slump test, temperature profile test and density test, could be done simultaneously. Cubes required for strength tests were made in separate trials for better accuracy. The large mass of stucco also helps in proper mixing and formation of homogeneous gypsum-foam slurry. Water temperature in all the experiments was 24° C. Two different sets of tests were conducted.

8.2.2.1 Addition of superspreader to foam water while keeping the foam volume fixed and reducing the initial amount of water in gypsum

For the first set, the total volume of foam and thus the volume of water added in the gypsum-foam slurry with foam was kept constant as the water-stucco ratio (WSR) was varied from 100 WSR to 70 WSR. The water-stucco ratio was varied in these samples by varying the initial amount of water added to the dry mixture. The experiments were conducted at water-stucco ratios of 100 WSR, 90 WSR, 85 WSR, 80 WSR, 75 WSR and 70 WSR at foam density of 0.07 g/cm³ (4.37 lb/ft³). The foam density was kept constant by keeping the air flow rate of the foam generator fixed at 3.5 LPM and the soap solution flow rate at 0.26 kg/h. This fixed the total amount of water added with foam for any WSR. Also, two different surfactant mixture compositions were used for generating foam. For the first set of experiments, 0.25% of USG Stable Soap and 0.25% of USG Unstable Soap were mixed in the foam water using the foam generator (Samples A – F). For the second set of experiments, 0.1% of superspreader SILWET L-77 was added to the above mixture of surfactants (Samples SA – SF). The composition and concentration of the materials used is listed in Table 8.1. The entire mixture was initially mixed for 10 s using the Hobart mixer. Foam was added for the next 15 s under continuous mixing (i.e.

from 11 to 25 s). After completion of adding foam, the entire gypsum-foam slurry was further mixed for another 20 s to achieve uniform distribution of the components. So the total mixing time was 45 s. At the end of mixing, the gypsum-foam slurry was first poured into the slump test cylinder, followed by thermocouple-containing container. The temperature change was recorded using TRS (Temperature Rate Set) software. The experiment was repeated, and gypsum-foam slurry was poured into the mold to form cubes for compression tests. The labels of the samples is given in Table 8.2. To achieve a better accuracy, three trials were done for each sample.

Table 8.1 Composition and concentration of different materials at different WSR

Weight of stucco (g)	1000	1000	1000	1000	1000	1000
Corn Starch (%)	2.00	2.00	2.00	2.00	2.00	2.00
Weight of Starch (g)	20.00	20.00	20.00	20.00	20.00	20.00
Accelerator (%)	0.50	0.50	0.50	0.50	0.50	0.50
Weight of Accelerator (g)	5.0	5.0	5.0	5.0	5.0	5.0
MCM (%)	0.25	0.25	0.25	0.25	0.25	0.25
Weight of MCM (g)	2.5	2.5	2.5	2.5	2.5	2.5
Liquid Dispersant (%)	0.625	0.625	0.625	0.625	0.625	0.625
Wt. of Liq. Dispersant (g)	6.25	6.25	6.25	6.25	6.25	6.25
Water from Dispersant (g)	3.75	3.75	3.75	3.75	3.75	3.75
WSR	100.00	90.00	85.00	80.00	75.00	70.00
Total Water (g)	1000.0	900.0	850.00	800.00	750.0	700.00
Foam density (g/cm ³)	0.07	0.07	0.07	0.07	0.07	0.07
Soap Sol flow rate (kg/min)	0.26	0.26	0.26	0.26	0.26	0.26
Air Sol flow rate (LPM)	3.50	3.50	3.50	3.50	3.50	3.50
Foam vol. flow rate (cm ³ /s)	62.72	62.72	62.72	62.72	62.72	62.72
Time of Foam addition (s)	15.00	15.00	15.00	15.00	15.00	15.00
Total water from foam (g)	65.86	65.86	65.86	65.86	65.86	65.86
Total Stucco water (g)	934.14	834.14	784.14	734.14	684.14	634.14
Retarder Added (g)	30.00	30.00	30.00	30.00	30.00	30.00
Pure water added to stucco (g)	904.14	804.14	754.14	704.14	654.14	604.14
Tot. Vol. of foam added (cm ³)	940.86	940.86	940.86	940.86	940.86	940.86

Table 8.2 Labeling of different samples used for the gypsum-foam slurry tests where the total volume of foam added was kept constant.

WSR	Foam water containing 0.25% of USG Unstable Soap and 0.25 % of USG Stable Soap	Foam water containing 0.25% of USG Unstable Soap, 0.25 % of USG Stable Soap, and 0.1% of SILWET L-77
100	Sample A	Sample SA
90	Sample B	Sample SB
85	Sample C	Sample SC
80	Sample D	Sample SD
75	Sample E	Sample SE
70	Sample F	Sample SF

8.2.2.2 Addition of superspreader to gypsum water

The second set of tests was conducted without adding foam. Different concentrations of superspreader in the range 0 – 0.4% of total water was added to the gypsum water directly along with the liquid dispersant and retarder prior to the addition of the solid mixture of stucco, corn starch, HRA and MCM. These set of tests were conducted at a fixed water-stucco ratio of 100 WSR. The mixing time was 45 s and the rest of the experimental procedure was the same as in the previous set. The labeling of the samples is given in Table 8.3.

Table 8.3 Labeling of different samples used for the gypsum slurry tests without addition of foam.

WSR	Conc. of superspreader in gypsum water (%)	Foam water containing 0.25% of USG Unstable Soap, 0.25 % of USG Stable Soap and 0.1% of SILWET L-77
100	0	Sample G
100	0.05	Sample H
100	0.1	Sample I
100	0.2	Sample J
100	0.3	Sample K
100	0.4	Sample L

8.2.2.3 Addition of superspreader to foam water while keeping initial amount of water in gypsum slurry fixed, and reducing foam water in gypsum slurry by reducing foam density

For the third set of tests, the initial water added to gypsum slurry was kept constant and the total water in the gypsum-foam slurry was reduced by reducing the foam water. The control was chosen at 110 WSR, 10% of this water being foam water. So 990 g of water was initially added to the dry mixture (which included 30 g of retarder). For all the samples, this amount was fixed as the initial water was added to the dry powder. The water-stucco ratio was varied in these samples by varying the water added through foam. The foam density was varied by initially keeping the air flow rate of the foam generator fixed at 3.5 LPM and varying the soap solution

flow rate from 0.33 kg/min to 0.13 kg/min, the latter being the minimum flow rate that could be reached with the foam generator. Then, to attain an even lower foam density, the soap solution flow rate was fixed at 0.13 kg/min and the air flow rate was increased from 3.5 LPM to 5.0 LPM. It should be emphasized that the total volume of air pumped into the gypsum slurry was the same for all samples. This was maintained by varying the total time of foam addition to gypsum slurry. Also, two different surfactant mixture compositions were used for generating foam. For the first set of experiments, 0.25% of USG Stable Soap and 0.25% of USG Unstable Soap were mixed in the foam water using the foam generator (Samples M – P). For the second set of experiments, 0.1% of superspreader SILWET L-77 was added to the above mixture of surfactants (Samples SM – SP). The different foam densities and the corresponding WSR values for the samples are listed in Table 8.4. The entire mixture was initially mixed for 10 s using the Hobart mixer. Foam was added for the next 20 s under continuous mixing (i.e. from 11 to 30 s). After completion of adding foam, the entire gypsum-foam slurry was further mixed for another 15 s to achieve uniform distribution of the components. So the total mixing time was 45 s. At the end of mixing, the gypsum-foam slurry was first poured into the slump test cylinder, followed by thermocouple-containing container. The temperature change was recorded using TRS (Temperature Rate Set) software. The experiment was repeated, and gypsum-foam slurry was poured into the mold to form cubes for compression tests. The labels of the samples are given in Table 8.5. To achieve a better accuracy, three trials were done for each sample.

Table 8.4 Composition and concentration of different materials at different WSR

Total Stucco Water (g)	990	990	990	990
Retarder Added (g)	30	30	30	30
Pure water added to stucco (g)	960	960	960	960
Soap sol. flow rate (kg/min)	0.33	0.23	0.13	0.13
Air flow rate (LPM)	3.50	3.50	3.50	5.0
Foam vol. flow rate (cm ³ /s)	63.83	62.17	60.50	85.50
Foam density (g/cm ³)	0.086	0.062	0.036	0.025
Time of foam addition (s)	20.00	20.00	20.00	14.00
Total air from foam (cm ³)	1166.67	1166.67	1166.67	1166.67
Total water from foam (g)	110	76.67	43.33	30.33
WSR	110	106.67	103.33	102.03

Table 8.5 Labeling of different samples used for the gypsum-foam slurry tests where the initial water added to gypsum slurry was kept constant

Soap sol flow rate (kg/min)	Air flow rate (LPM)	Foam density (g/cm ³)	Foam water containing 0.25% of USG Unstable Soap and 0.25 % of USG Stable Soap	Foam water containing 0.25% of USG Unstable Soap, 0.25 % of USG Stable Soap, and 0.1% of SILWET L-77
0.33	3.5	0.086	Sample M	Sample SM
0.23	3.5	0.062	Sample N	Sample SN
0.13	3.5	0.036	Sample O	Sample SO
0.13	5.0	0.025	Sample P	Sample SP

8.3 Results and discussion

8.3.1 Addition of superspreader to foam water while keeping volume of foam fixed and reducing the initial amount of water in gypsum slurry

Figure 8.1 shows the comparison of the slump diameter with and without superspreader in the foam water. The fluidity of the gypsum-foam slurry increased on addition of 0.1% superspreader SILWET L-77 to foam water.

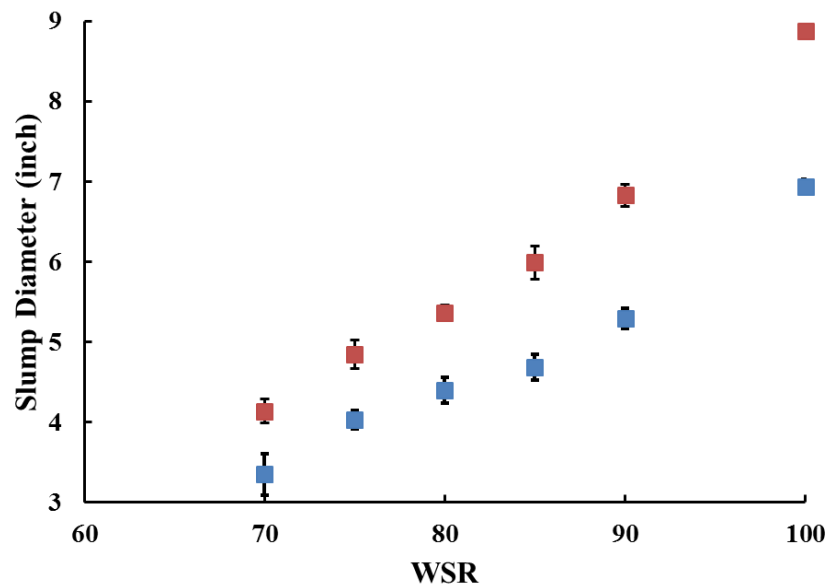


Figure 8.1. Slump tests of gypsum-foam slurry for the samples with and without superspreader in foam water. Red symbols correspond to the results with adding 0.1 % of superspreader SILWET L-77, the blue ones show the results without superspreader.

The slump test results show that addition of superspreader to foam water greatly enhances the fluidity of gypsum-foam slurry. With samples without superspreader in foam water (Samples A – E), the slump diameter was lesser by more than 0.75 inch at 70 WSR, 75 WSR, 80

WSR and more than by 1 inch at 85 WSR, 90 WSR and 100 WSR as compared to samples with 0.1% superspreader SILWET L-77 in foam water (Samples SA – SF). In fact, the slump diameter of sample SB is greater than that of samples B, C and D. In the other words, the fluidity of 75 WSR sample with 0.1% superspreader SILWET L-77 in foam water is greater than even that of 85 WSR sample without superspreader. So, on adding only 0.1% superspreader SILWET L-77 to foam water, the same fluidity can be obtained with 12% less water (75 WSR as compared to 85 WSR).

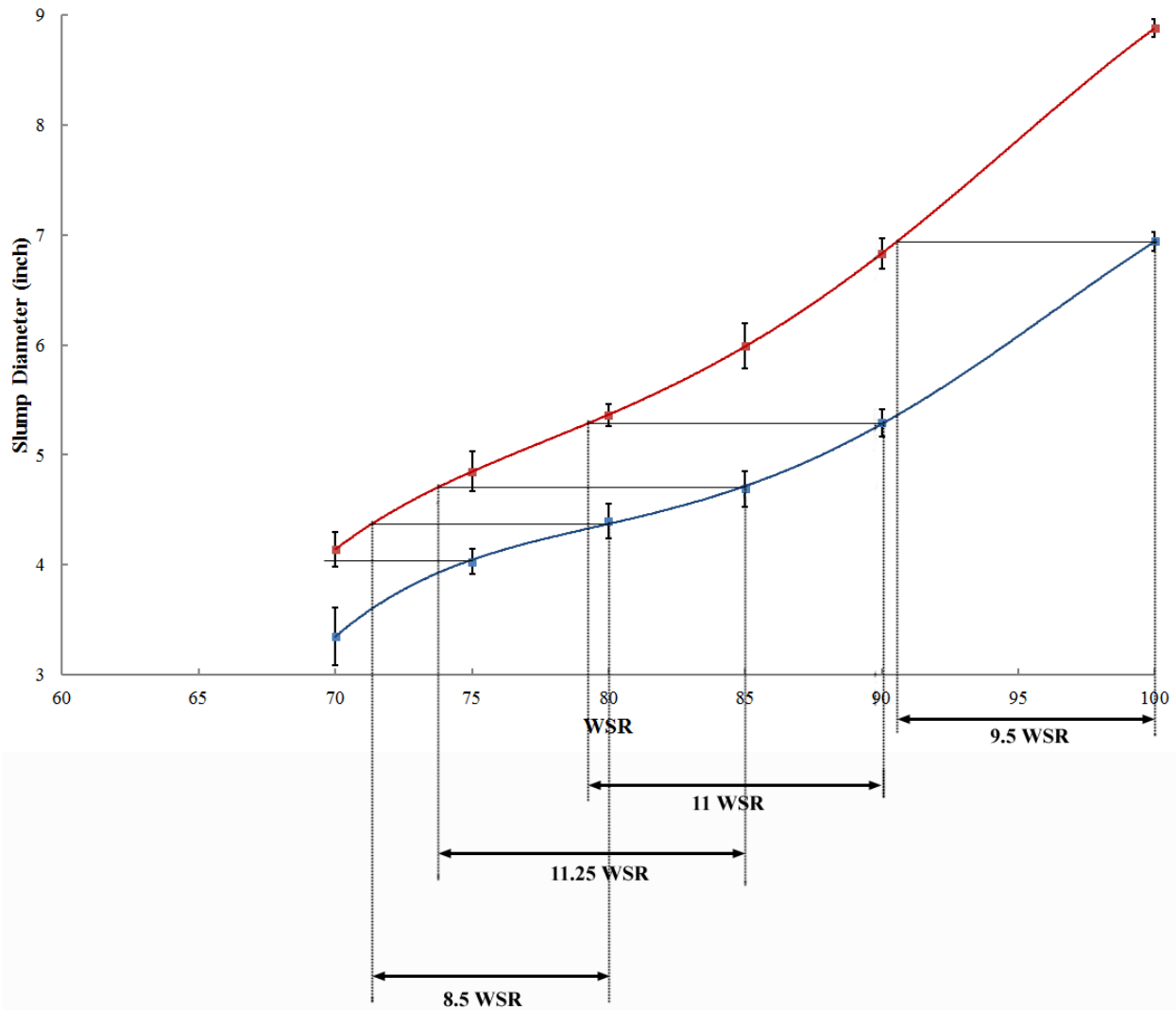


Figure 8.2. Gain in WSR on addition of 0.1 % superspreader to foam water to obtain the same slump diameter. The red line correspond to the results with adding 0.1 % of superspreader SILWET L-77, the blue one shows the results without superspreader.

Using a fourth order polynomial approximation, the slump diameter data in Fig. 8.1 can be fitted, for both cases with and without superspreader in foam water. The polynomial used for approximating the fitting line for slump diameter of samples without superspreader in foam water (Samples A - E) was

$-0.00001W^4+0.0044W^3-0.5763W^2+33.251W-712.53$ where W is for WSR.

The polynomial used for approximating the fitting line for slump diameter of samples with superspreader in foam water (Samples SA – SF) was

$-0.00001W^4+0.0038W^3-0.4865W^2+27.578W-580.63$ where W is for WSR.

Figure 8.2 shows the gain in WSR on addition of superspreader to foam water. The gain is maximum for samples B and C, where the same fluidity of the gypsum-foam slurry can be achieved by reducing water by 11 WSR and 11.25 WSR, respectively, with foam water containing 0.1 % superspreader SILWET L-77.

Figure 8.3 shows the TRS curves for samples with and without 0.1% superspreader SILWET L-77 in foam water. For samples without superspreader in foam water (Samples A – F), the reaction rate increased with decrease in water from 90 WSR to 70 WSR (Fig. 8.3a). Also, the maximum temperature reached increased. For samples with 0.1% superspreader SILWET L-77 in foam water (Samples SA – SF), a similar trend was observed (Fig. 8.3b) with no significant difference among the different samples at different stucco-water ratio with and without 0.1 % superspreader SILWET L-77 in foam water. This shows that the reaction rate is approximately the same irrespective of whether the foam water contained superspreader or not. Figure 8.3c shows the comparison between the reaction rates for samples with and without 0.1% superspreader SILWET L-77 in foam water at different WSRs, namely 100 WSR, 90 WSR, 80 WSR, 75 WSR, and 70 WSR and the two curves overlap in all cases.

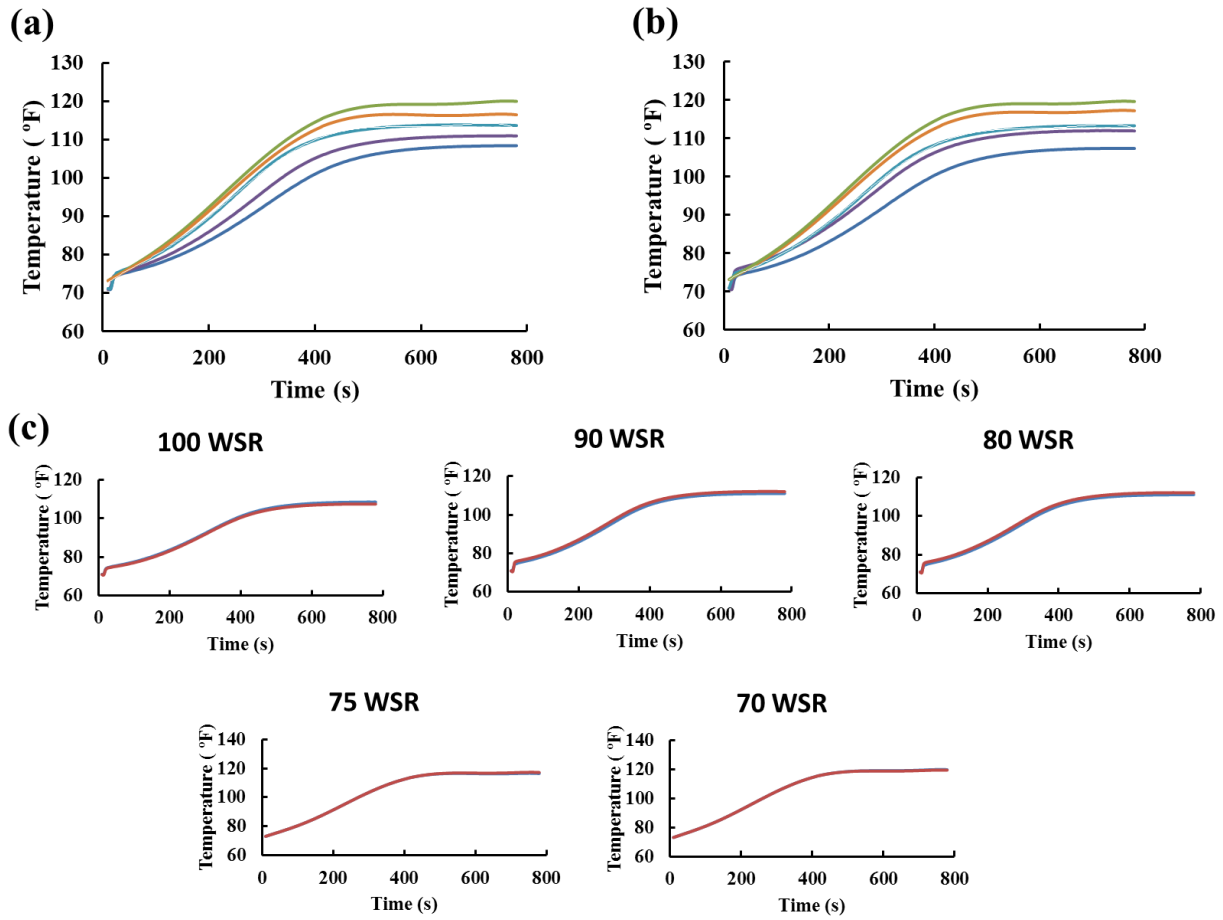


Figure 8.3. Temperature curves during setting of the gypsum-foam slurry for samples (a) without and (b) with 0.1% superspreader SILWET L-77 in foam water. Different colors indicate different water-stucco ratio with blue, purple, cyan, orange, and green representing 100 WSR, 90 WSR, 80 WSR, 75 WSR, and 70 WSR, respectively. The comparison in temperature curve for two different surfactant compositions used to generate foam at different water-stucco ratios is shown in (c) where red and blue curves represent the cases with and without superspreader in foam water, respectively. The comparison in (c) shows practically no difference in the setting curve in the cases with and without superspreader in foam water.

The strength tests were conducted by crushing cubes of different samples. The results of the strength tests are shown in Fig. 8.4. As can be seen in the figure, the strength of the cubes did not decrease on addition of 0.1% superspreader SILWET L-77 to foam water. In fact, for stucco-water ratio of 100 WSR, 90 WSR, 85 WSR, 80 WSR and 75 WSR, the strength increased on addition of the superspreader to foam water. Table 8.6 shows the percentage increase in strength on addition of the superspreader to foam water. At 70 WSR, there was hardly any air in samples without superspreader (Sample E). This caused the dramatic increase in its strength.

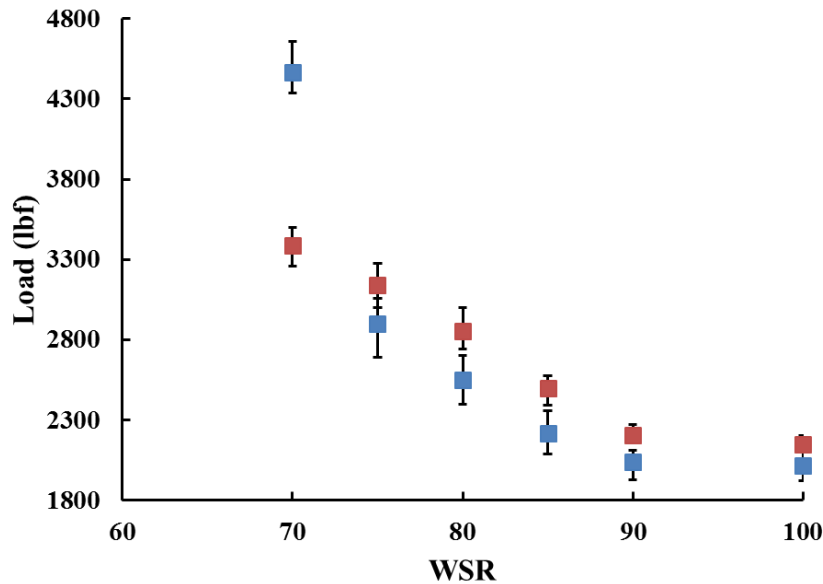


Figure 8.4. Crushing test results for samples without and with 0.1% superspreader SILWET L-77. Red symbols correspond to the samples containing 0.1% superspreader SILWET L-77 in foam water. Blue symbols correspond to the samples without superspreader in foam water.

Table 8.6 Percentage increase in strength of gypsum-foam cubes for samples containing 0.1% superspreader in foam water.

Sample	% increase in strength
SA	6.73
SB	8.28
SC	12.71
SD	12.16
SE	8.37
SF	-24.12

Figure 8.5 shows the comparison of dry densities of different samples. The addition of superspreader to foam water increases the dry density of the samples. However, the increase is not significant. At 70 WSR, samples without superspreader in foam water hardly entrapped any air causing the density to increase significantly. Such an effect is not seen with foam water containing 0.1% superspreader SILWET L-77 at 70 WSR.

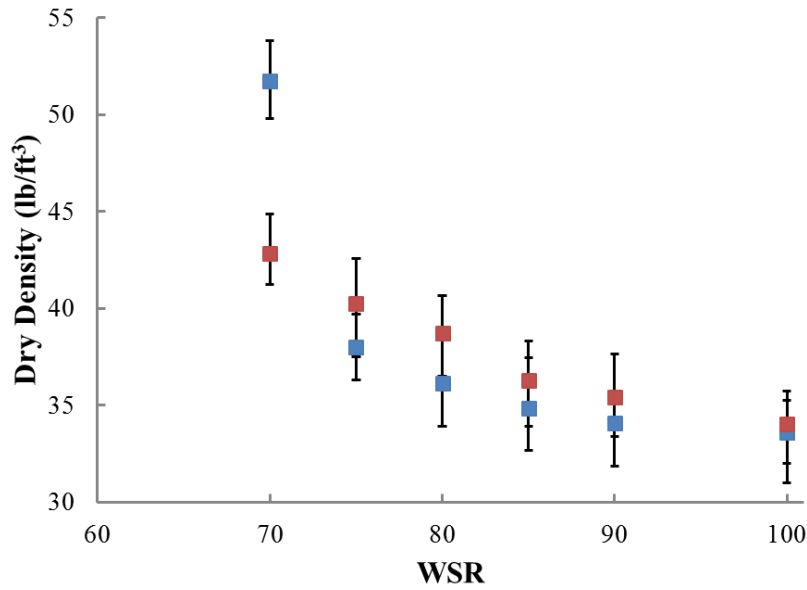


Figure 8.5. Dry densities of samples with and without superspreader in foam water. The red symbols correspond to the samples containing 0.1% superspreader in foam water. The blue symbols correspond to the samples without any superspreader in foam water.

Figure 8.6 shows the normalized strength of the samples with 0.1% superspreader SILWET L-77 in foam water according to the definition

$$L_n = L_m \frac{\rho_{ns}^3}{\rho_m^3} \quad (8.1)$$

where L_n is the normalized load in lb, L_m is the measured strength of the cube containing 0.1% superspreader in foam water in lb, ρ_{ns} is the dry density of the sample without superspreader and ρ_m is the measured dry density of the sample containing 0.1% superspreader in foam water. It shows that at 100 WSR, 90 WSR, 85 WSR, 80 WSR and 75 WSR, the normalized strengths of samples SA – SE are identical to the measured strengths of samples A – E. There was barely any

air entrapped in the sample F, and so its density and strength were much higher than those for the other samples.

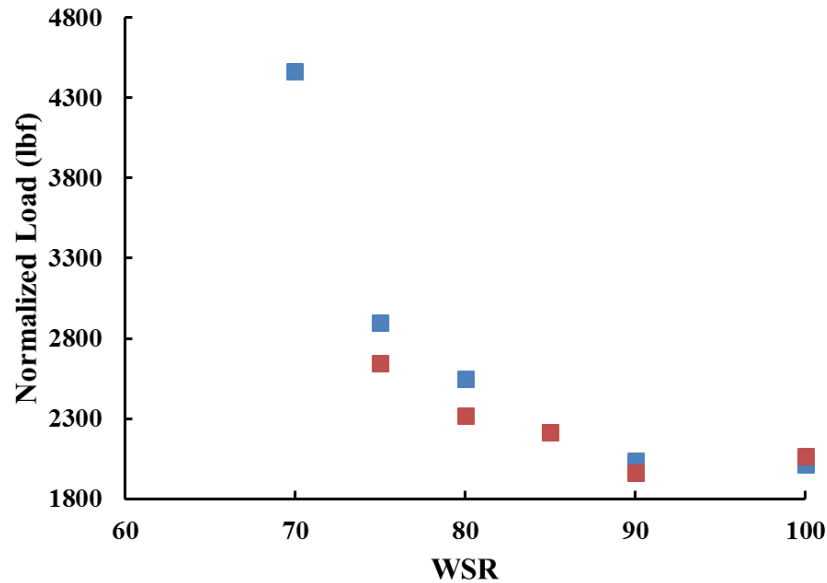


Figure 8.6. Normalized strength test results. The red symbols correspond to the normalized load for samples containing 0.1% superspreader in foam water. The blue symbols correspond to the actual loads of samples without superspreader in foam water.

The higher densities of gypsum-foam slurry formed with foam water containing superspreader indicate lesser air volume entrapped in the slurry. The slurry with superspreader formed larger bubbles, but lesser in number as compared to the corresponding slurry without superspreader. So, the volume fraction of air in the samples (samples SA – SF) is lower compared to the corresponding samples without superspreader in foam water (samples A – E).

In general, air is entrapped inside the gypsum-foam slurry in the form of bubbles originating from foam. The spherical air bubbles can be considered as air emulsion in the slurry matrix. The Einstein-Taylor relation between the relative viscosity and volume concentration of emulsions of air bubbles is given by

$$\mu_r = 1 + \phi \quad (8.2)$$

where μ_r is the relative viscosity and ϕ is the volume fraction.

Since gypsum-foam slurry formed with foam water containing superspreader has a lower air volume fraction, from Eq. (8.2) it can be concluded that such a slurry has lower viscosity. This lower viscosity facilitates spreading and provides the higher fluidity of the gypsum-foam slurry with superspreader in the foam water.

8.3.2 Addition of superspreader to gypsum water

The addition of 0.1% superspreader to foam water as discussed in the previous section could have an effect on the gypsum slurry as a whole along with its effect on the foam. To investigate whether the enhancement in fluidity of the gypsum – foam slurry on addition of superspreader was caused only due to the superspreader effect on the stable foam, or whether the initial slurry is also affected, tests were conducted with directly adding superspreader to gypsum slurry. All tests were conducted at a fixed stucco-water ratio of 100 WSR and no foam was added to the gypsum slurry.

Figure 8.7 shows the slump diameters at increasing concentrations of superspreader SILWET L-77 at 100 WSR. The fluidity of the gypsum slurry increased slightly on increasing the concentration superspreader SILWET L-77 from 0.05 %v/v to 0.4 %v/v.

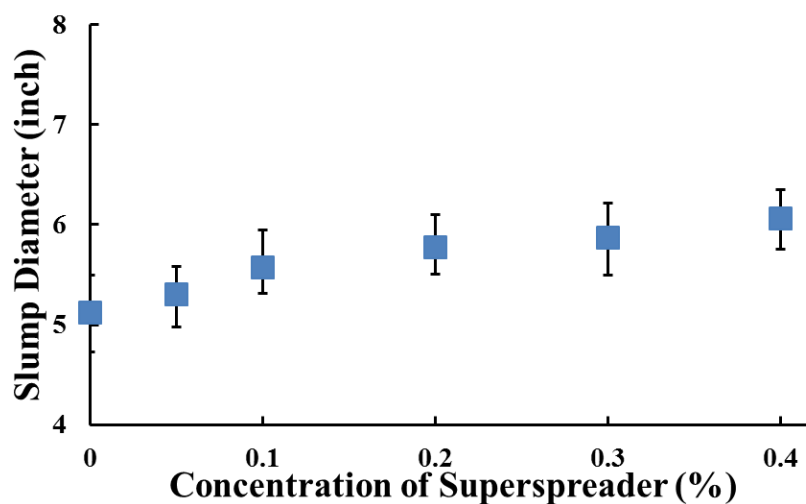


Figure 8.7. Slump tests of gypsum slurry samples with increasing concentration of superspreader SILWET L-77.

The slump test results show that addition of superspreader SILWET L-77 to gypsum water has practically no effect on the fluidity of gypsum slurry, especially at the concentrations in the range 0.05 %v/v to 0.1 %v/v.

Figure 8.8 shows the TRS curves for samples with increasing concentration of superspreader SILWET L-77 in gypsum slurry. There was not much change in the reaction rate with the addition of superspreader to gypsum water. Figure 8.9 shows the TRS curves for the same concentration of superspreader SILWET L-77 for different trials, which reveals good repeatability of the results.

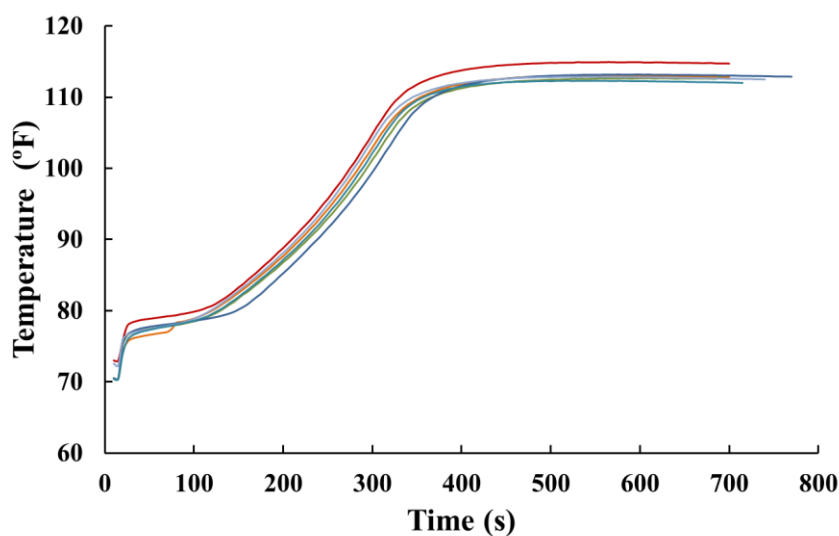


Figure 8.8. Temperature curves during setting of the gypsum slurry for samples with increasing concentration of superspreader SILWET L-77. Different colors correspond to different concentrations: red, orange, green, blue, sky blue and cyan colors representing 0, 0.05%, 0.1%, 0.2%, 0.3%, and 0.4% concentration of superspreader SILWET L-77.

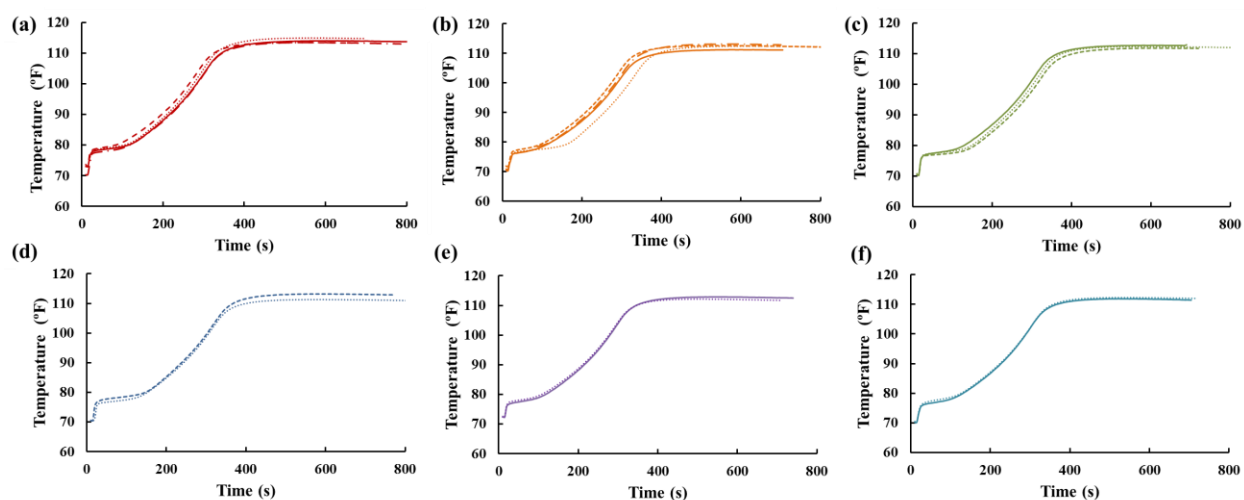


Figure 8.9. TRS curves for different trials of gypsum slurries at (a) 0, (b) 0.05 %v/v, (c) 0.1 %v/v, (d) 0.2 %v/v, (e) 0.3 %v/v, and (f) 0.4 %v/v concentration of superspreader SILWET L-77 in gypsum water.

The strength tests were conducted by crushing cubes of different samples. The results of the strength tests are shown in Figure 10. As can be seen in the figure, the strength of the samples decreased with increasing concentration of superspreader in gypsum water.

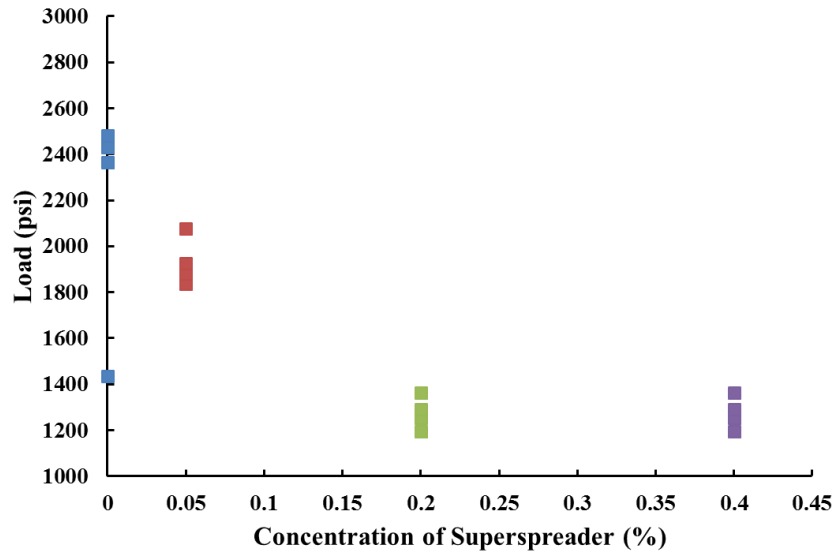


Figure 8.10. Crushing test results for samples with increasing concentration of SILWET L-77 in gypsum water.

Figure 8.11 shows the comparison of dry densities of different samples. The addition of superspreader to gypsum water decreases the dry density of the samples.

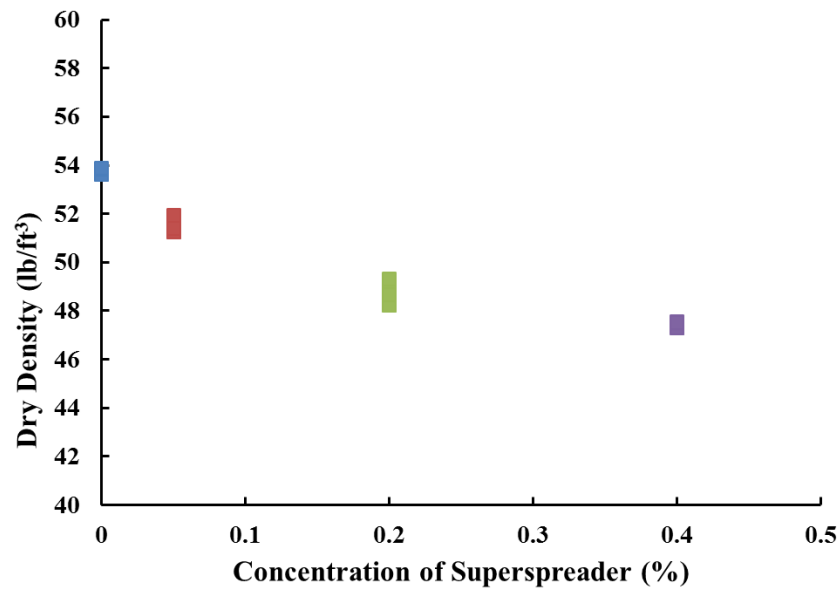


Figure 8.11. Dry densities of samples with increasing concentration of superspreader in gypsum water.

8.3.3 Addition of superspreader to foam water while keeping the initial amount of water in gypsum slurry fixed, and reducing foam water in gypsum slurry by reducing foam density

Figure 8.12 shows the comparison of the slump diameter with and without superspreader in the foam water. The fluidity of the gypsum-foam slurry increased on addition of 0.1% superspreader SILWET L-77 to foam water.

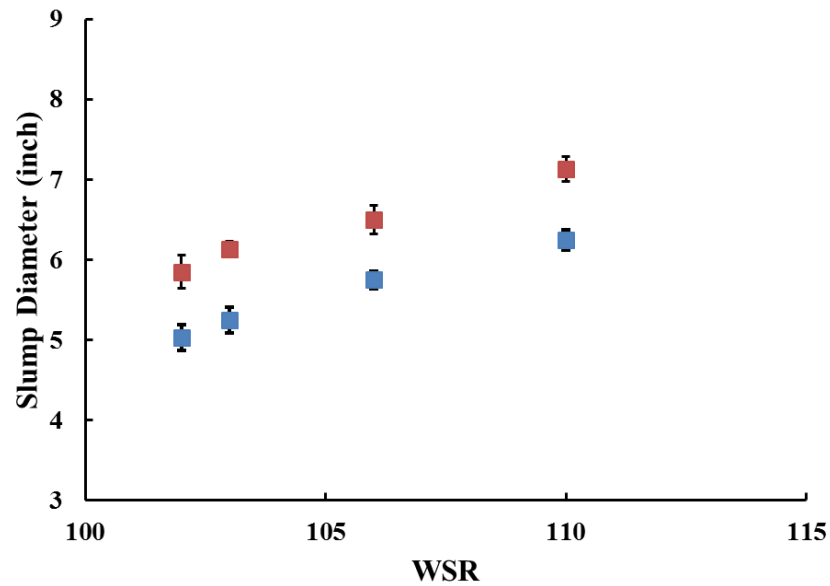


Figure 8.12. Slump tests of gypsum-foam slurry for the samples with and without superspreader in foam water. Red symbols correspond to the results with adding 0.1 % of superspreader SILWET L-77, the blue ones show the results without superspreader.

The slump test results show that addition of superspreader to foam water enhances the fluidity of gypsum-foam slurry. For the samples without superspreader in foam water (Samples M – P), the slump diameter was smaller by over 0.85 inch at 110 WSR and over 0.75 inch at 106 WSR, 103 WSR, and 102 WSR, as compared to the samples with 0.1% superspreader SILWET L-77 in foam water (Samples SM – SP).

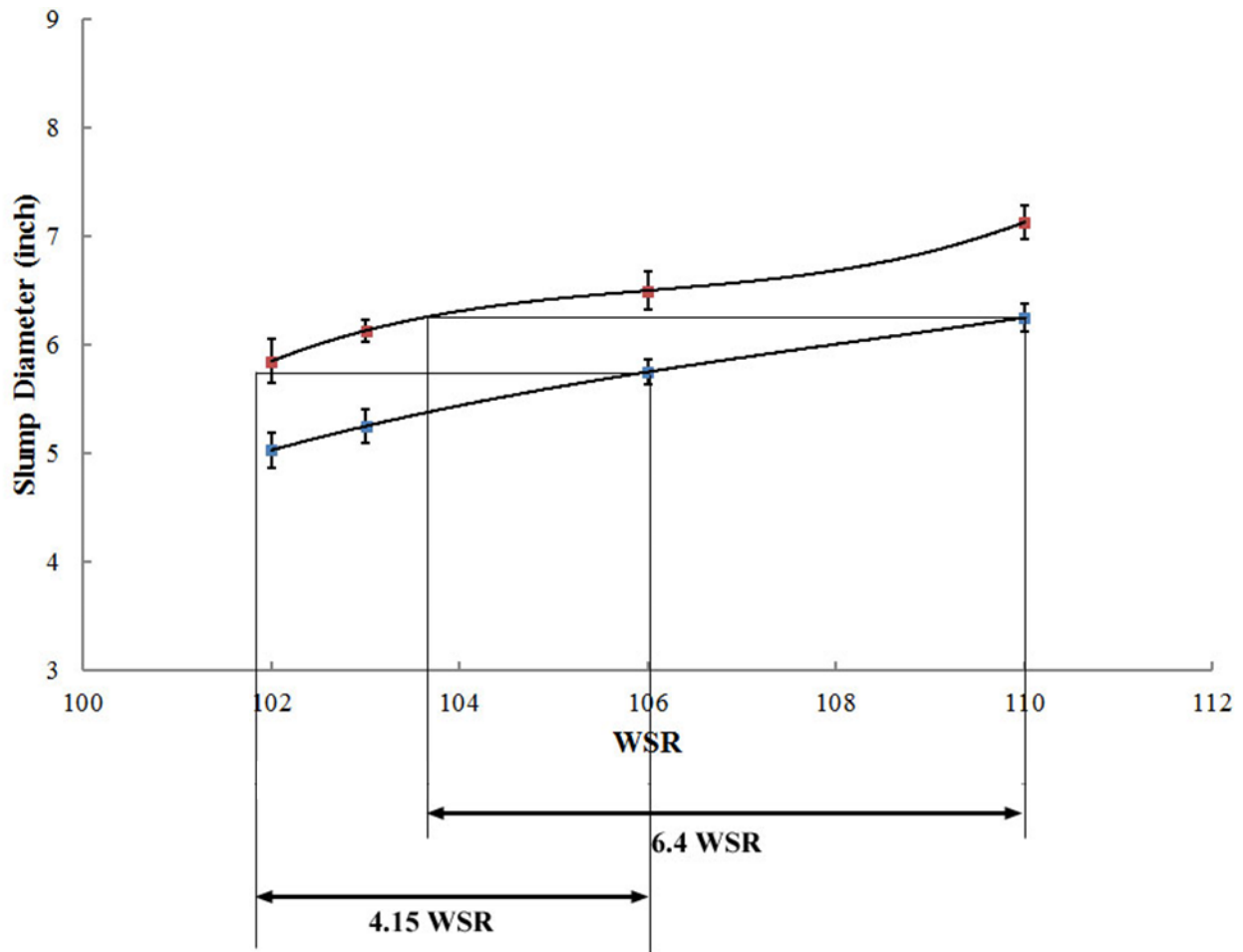


Figure 8.13. Gain in WSR on addition of 0.1 % superspreader to foam water to obtain same slump diameter. The red symbols correspond to the results with adding 0.1 % of superspreader SILWET L-77, the blue ones show the results without superspreader.

Using a third order polynomial approximation, the slump diameter data in Fig. 8.12 can be fitted, for both cases with and without superspreader in foam water. The polynomial used for approximating the fitting line for slump diameter of samples without superspreader in foam water (Samples M - P) was

$0.0009W^3 - 0.3003W^2 + 32.695W - 1185$ where W is for WSR.

The polynomial used for approximating the fitting line for slump diameter of samples with superspreader in foam water (Samples SM – SP) was

$0.0055W^3 - 1.7515W^2 + 185.8W - 6565.8$ where W is for WSR.

Figure 8.13 shows the gain in WSR on addition of superspreader to foam water. The gain is maximal for sample M, where the same fluidity of the gypsum-foam slurry can be achieved by reducing water by 6.4 WSR with foam water containing 0.1 % superspreader SILWET L-77.

Figure 8.14 shows the TRS curves for samples with and without 0.1% superspreader SILWET L-77 in foam water. For samples without superspreader in foam water (Samples M – P), the reaction rate increased with decrease in water from 110 WSR to 102.03 WSR (Fig. 8.14a). Also, the maximum temperature reached increased. For samples with 0.1% superspreader SILWET L-77 in foam water (Samples SM – SP), a similar trend was observed (Fig. 8.14b) with no significant difference among the different samples at different stucco-water ratios with and without 0.1 % superspreader SILWET L-77 in foam water. This shows that the reaction rate is approximately the same irrespective of whether the foam water contained superspreader or not. Figure 8.14c shows the comparison between the reaction rates for samples with and without 0.1% superspreader SILWET L-77 in foam water at different WSRs, namely 110 WSR, 106.67 WSR, 103.33 WSR, and 102.03 WSR and the two curves overlap in all cases.

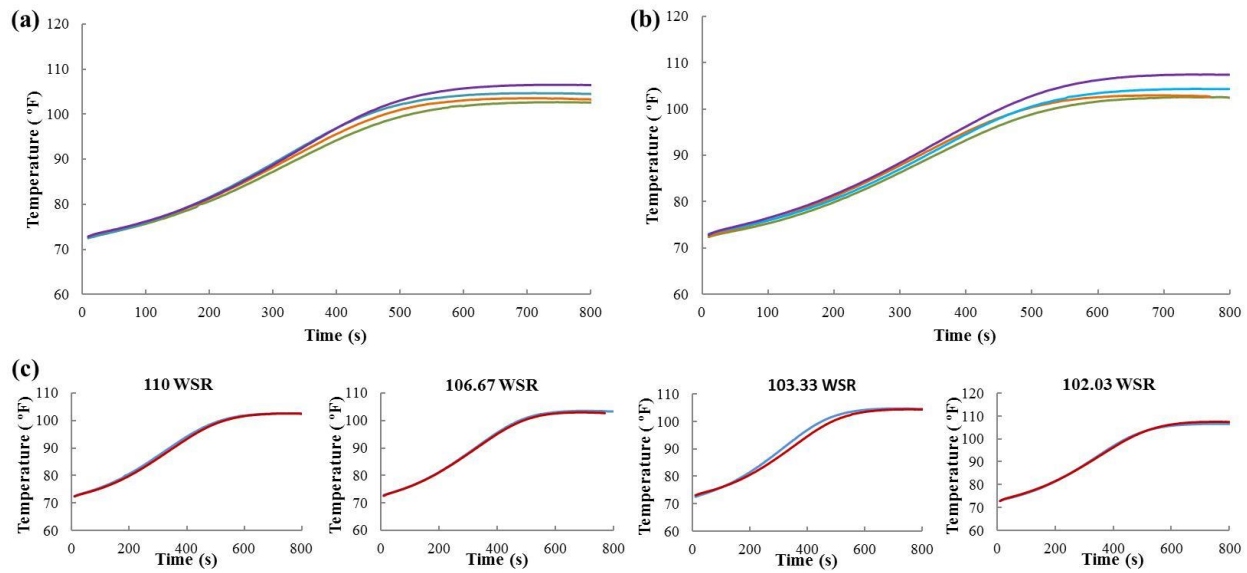


Figure 8.14. Temperature curves during setting of the gypsum-foam slurry for samples (a) without and (b) with 0.1% superspreader SILWET L-77 in foam water. Different colors indicate different water-stucco ratios, with green, orange, cyan, and purple representing 110 WSR, 106.67 WSR, 103.33 WSR, and 102.03 WSR, respectively. The comparison in temperature curve for two different surfactant compositions used to generate foam at different foam generator settings leading to different WSR is shown in (c), where red and blue curves represent the cases with and without superspreader in foam water, respectively. The comparison in (c) shows practically no difference in the setting curve in the cases with and without superspreader in foam water.

The strength tests were conducted by crushing cubes of different samples. The results of the strength tests are shown in Fig. 8.15. The strength of the cubes decreases for samples with 0.1 % superspreader SILWET L77 in foam water. Figure 8.15 shows that the decrease in strength for samples with 0.1 % superspreader SILWET L77 is more pronounced at lower WSR, implying that lower foam densities lead to a greater reduction in strength for samples containing 0.1 % superspreader SILWET L77 in foam water.

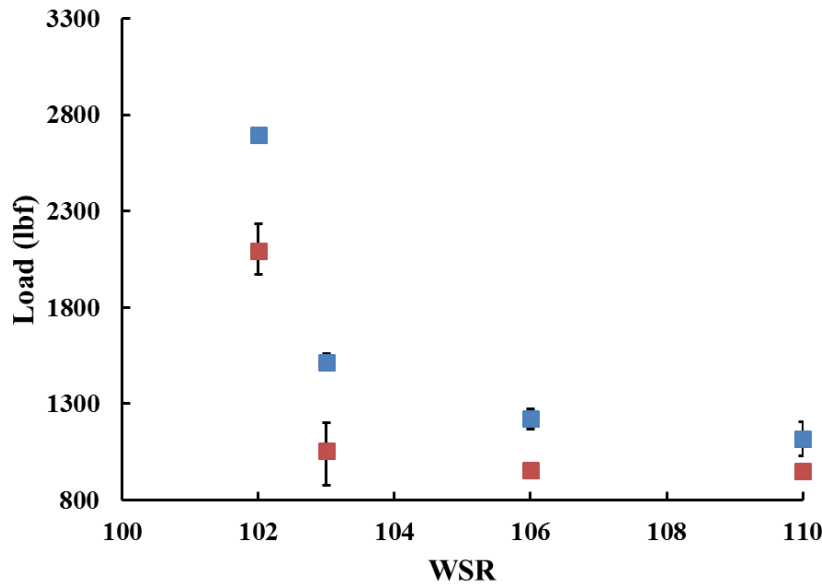


Figure 8.15. Crushing test results for samples without and with 0.1% superspreader SILWET L-77. Red symbols correspond to the samples containing 0.1% superspreader SILWET L-77 in foam water. Blue symbols correspond to the samples without superspreader in foam water.

Figure 8.16 shows the comparison of dry densities of different samples. At foam density 0.086 g/cm^3 the dry densities of the samples with (Sample SM) and without superspreader (Sample M) in foam water are the same. However, at lower foam densities of 0.062 g/cm^3 , 0.036 g/cm^3 and 0.025 g/cm^3 , the dry densities for samples with 0.1 % superspreader in foam water (Samples SN, SO, and SP, respectively) are lower than those without superspreader in foam water (Samples N, O, and P, respectively), represented by lower WSR values in Fig. 8.16. The percentage of decrease also increases with reducing foam density. This can be explained as follows. At lower foam densities, foam without superspreader is highly unstable and a very small volume of air is entrapped in the gypsum slurry from foam. This causes the sharp increase in dry densities for these samples and Sample P (foam density 0.025 g/cm^3 , 102 WSR) has the highest

dry density. Such an effect is not seen with foam water containing 0.1% superspreader SILWET L-77, indicating stable foam even at low foam densities.

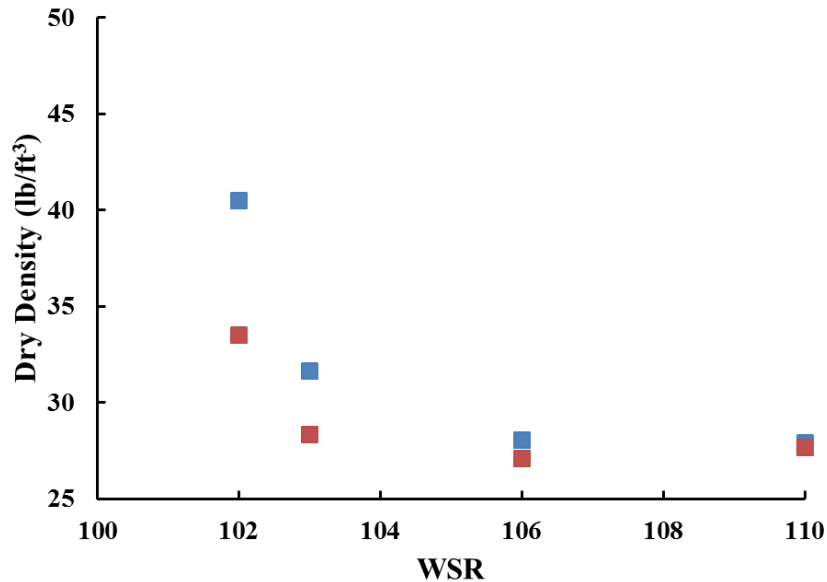


Figure 8.16. Dry densities of samples with and without superspreader in foam water. The red symbols correspond to the samples containing 0.1% superspreader in foam water. The blue symbols correspond to the samples without any superspreader in foam water.

Figure 8.17 shows the normalized strength of the samples with 0.1% superspreader SILWET L-77 in foam water according to Eq. (8.1). It shows that the normalized strengths of samples SM – SO are almost identical to the measured strengths of Samples M – O. At 102 WSR and foam density of 0.025 g/cm^3 , the normalized strength of Sample SP is much higher than the measured strength of Sample P due to the exceptionally high density of Sample P.

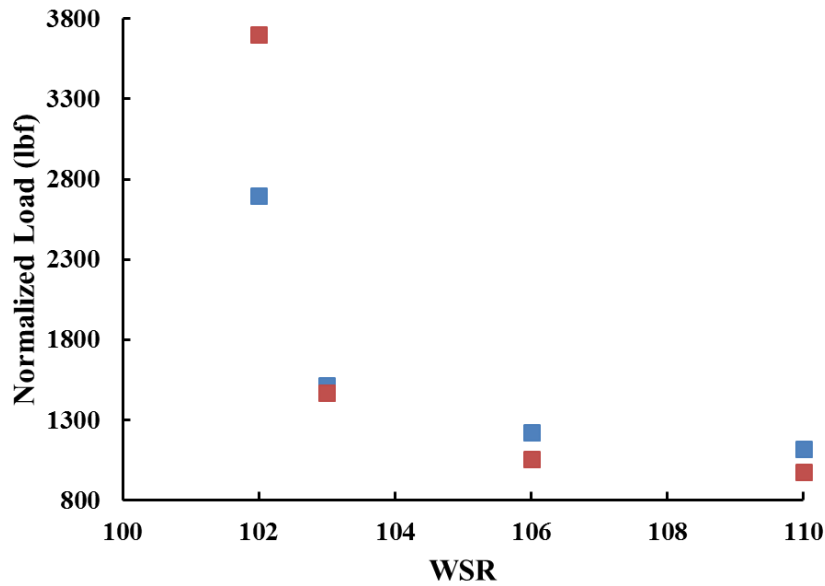


Figure 8.17. Normalized strength test results. The red symbols correspond to the normalized load for samples containing 0.1% superspreader in foam water. The blue symbols correspond to the actual loads of samples without superspreader in foam water.

8.4 Conclusions

Using only 0.1% of superspreader SILWET L-77 along with the regular concentrations of USG Soaps in foam water, a higher fluidity of gypsum-foam slurry was achieved. The enhancement in fluidity was solely due to the higher foamability and stability of the foam on addition of the superspreader, since adding the superspreader directly to gypsum water without the addition of foam did not have a significant effect on the fluidity. In the samples with only 0.1% of superspreader in foam water, which is roughly 0.01% of the total water, the same fluidity can be achieved at 11 WSR lower water-stucco ratio as compared to samples without superspreader in foam water by reducing the initial stucco water. The rates of solidification of the samples were identical and the strength of the cubes was also not compromised on the

addition of the superspreader to foam water. On the contrary, the strengths increased. The dry densities of gypsum-foam slurries containing the superspreader in foam water were slightly higher than those of the corresponding samples without superspreader.

Operating at such lower water-stucco ratio might cause problems in flow of the gypsum slurry uphill, i.e. before the addition of foam. By keeping the initial water added to gypsum slurry fixed and reducing the foam water by decreasing foam density, the samples with only 0.1% of superspreader in foam water attain the same fluidity at 6.4 WSR lower water-stucco ratio as compared to samples without superspreader in foam water. In this case too, the rates of solidification of the samples were identical and the strength of the cubes was also not compromised on the addition of the superspreader to foam water.

The high fluidity achieved on addition of the superspreader SILWET L-77 to foam water allows reduction in the overall water-stucco ratio, hence reducing the total water required in the process.

CHAPTER 9

ION-SPECIFIC EFFECTS IN FOAMS

This chapter has been previously published in Sett et al. (2015).

9.1 Introduction

In this work, various ion-specific effects on the stability of foams have been studied. The relevance of the ion-specific salt effects on the stability of emulsions, stabilized by ionic surfactants is discussed along with new unexpected findings of critical concentrations of added salts which causes destabilization of sodium dodecyl sulfate (SDS) foams.

Ion-specific effects on the stability of foams and foam films stabilized by sodium dodecylsulfate (SDS) and added salt

9.2 Experimental

9.2.1 Materials

Sodium dodecyl sulfate (SDS), an anionic surfactant, lithium chloride (LiCl), sodium chloride (NaCl), and potassium chloride (KCl) were purchased from Sigma Aldrich. Initially, 0.5 g of SDS was added to 300 ml of ethanol. The solution was kept on a hot plate at 80 °C and stirred until SDS dissolved completely. Then, 0.5 g of SDS was added to the same solution and stirred until the SDS dissolved completely. The addition of SDS was repeated until no further SDS dissolved in ethanol. It was found that the maximum amount of SDS that could be dissolved in this process was 3 g (1 g/100 ml ethanol). This solution was then cooled and placed in a refrigerator for 2 h which resulted in crystallization of SDS. After that, ethanol was drained out and the solution container was again kept on the hot plate at 80 °C.

Fresh ethanol was added to SDS crystals until the entire SDS dissolved. This was repeated three times to remove any traces of dodecanol in SDS.

9.2.2 Solution preparation

SDS salt mixture solutions were prepared as follows. Initially, using SDS, 0.5 mM aqueous solution was prepared by adding 0.014 g of SDS in 100 ml of deionized water. Then, 0.047 g, 0.106 g, 0.148 g, and 0.191 g of LiCl were added to four separate 0.5 mM aqueous SDS solutions to have LiCl concentrations of 11 mM, 25 mM, 35 mM, and 45 mM, respectively. Similarly, NaCl and KCl, were added to different 0.5 mM SDS aqueous solutions forming salt solutions with different concentrations – 11 mM, 25 mM, 35 mM and 45 mM, etc.

9.2.3 Experimental setups and methods

9.2.3.1 Vertical foam film.

The experimental setup and method used to study drainage of vertical planar films are described in Sett et al. (2013): A fixed aluminum wire frame (4 cm x 4 cm x 0.087 cm) (see Fig. 9.1), which supports the film was dipped into a 200 ml container with a solution.

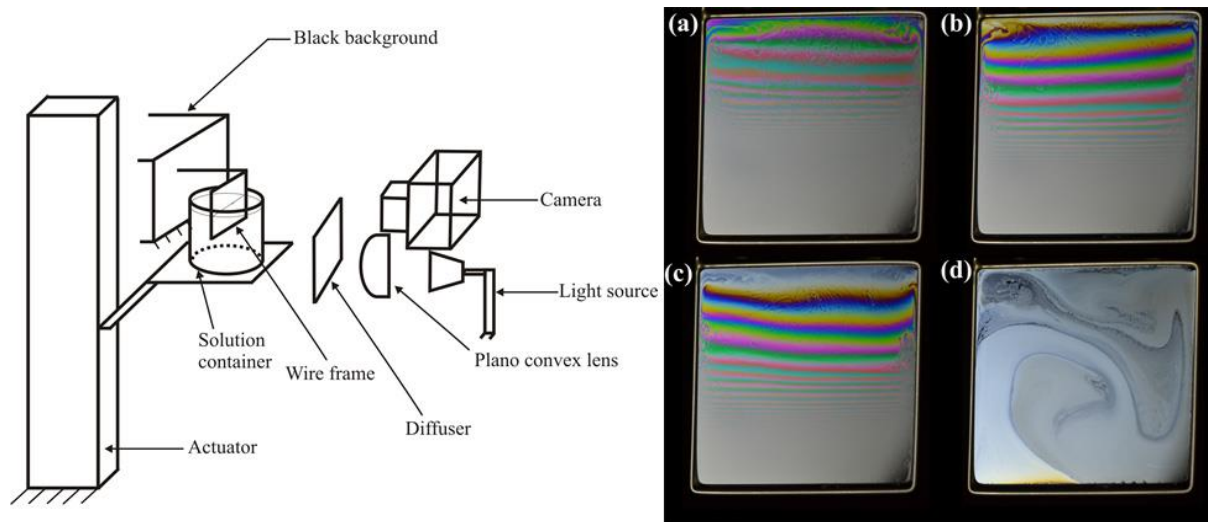


Figure 9.1. (Left) Schematic of the experimental setup with drainage from plane films [Sett et al (2013)]. (Right) Images of the time evolution of a vertical foam film stabilized by 0.5 mM SDS + 25 mM KCl (a) $t = 0$ s, (b) $t = 18$ s, (c) $t = 36$ s, and (d) $t = 54$ s.

The solution container was raised and lowered using a linear stage. The film was illuminated perpendicularly with coherent polychromatic light. The latter was reflected by the two surfaces of the film, thus resulting in an interference pattern (see Fig. 9.1, right), whose time evolution was captured by a CCD camera (Phantom Miro-4) and stored in computer for further off-line processing. The interference pattern obtained from a certain spot of the film (right below the top wire and 2 cm from the left wire) was processed for obtaining the local film thickness at the very spot versus time. In all of the cases we have established linear dependence of the film thickness on time until the formation of black film, which does not thin anymore, but endure for a certain time until rupturing. The corresponding values of the surface elasticity ε can be calculated using the equation [Sett et al. (2013)]

$$T = \frac{\varepsilon}{\rho(gh_0)^{3/2}} \quad (9.1)$$

where T is characteristic time of film drainage until film rupture, ρ is density of the water, g is acceleration due to gravity, h_0 is the film thickness at the very instant of film formation

($t = 0$). The drainage of the film depends linearly on the time, as it was shown in Sett et al. (2013) and is seen in Fig. 9.2 for 12 mM salt solutions.

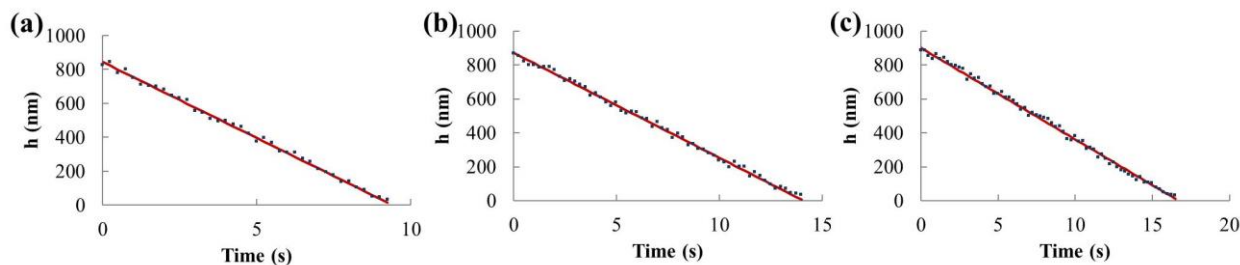


Figure 9.2. Drainage of plane films of SDS – salt solutions: (a) 11 mM LiCl, (b) 11 mM NaCl, and (c) 11 mM KCl. The data correspond to the film top. The experimental results are shown by symbols. The inclined straight line corresponds to the theoretical prediction of Sett et al. (2013).

The characteristic time of film drainage was calculated by asymptotical continuation of the experimental drainage curve from the onset of black film until zero nanometer film thickness. Hence, we determined the lifetime of the film and of the black film after its formation, the characteristic time for reaching of zero nanometer thickness, the rate of foam film drainage, and the elastic moduli of the foam films.

9.2.3.2 Foam column experiments

A large amount of uniform foam was created by mechanical mixing. 200 ml of a desired solution was placed in a mixing bowl and the solution was stirred for 3 min using a standard household hand mixer. The experimental method is described in detail elsewhere [Jun et al. (2012)] The generated foam was then poured into a cylinder (inner diameter of 2.58 cm and 104 cm tall) using a funnel-hose system and was filled from the bottom up. The funnel-hose system was raised as the level of foam increased, so that the foam exiting the

hose would be on top. The cylinder was capped once the foam was filled to the top of the cylinder, which prevented loss of liquid vapor or air from the cylinder during the entire experiment. The drained liquid height was measured using a CCD camera from which the drainage velocity was calculated.

9.2.3.3 Surface tension measurements

Surface tension measurements accredited to Dr. Stoyan Karakashev.

The surface tension isotherms of 0.5 mM Sodium dodecylsulfate with different concentrations of LiCl, NaCl, and KCl were measured by means of profile analysis tensiometry (tensiometer K10ST of Kruss, GmbH, Germany). The whole instrument stands on a stable (vibration-proof) table in a clean dark room with a controlled temperature. The temperature of the test fluid in the cuvette was kept constant at $(20 \pm 0.1) ^\circ\text{C}$ during the experiment using the water bath. The bubble formation and its volume were controlled by the syringe pump using the software. Once formed, the bubble shape was illuminated, equilibrated and its image was captured by the CCD video camera, stored, and processed by the computer software. The edge (the interface profile) of the bubble was digitally detected with sub-pixel resolution and was fitted with the numerical solution of the Young–Laplace equation, allowing the determination of surface tension, volume and area of the bubble. The accuracy in surface tension was in the ± 0.2 mN/m range.

9.3 Results and discussion

9.3.1 Thin film experiments and analysis

Figure 9.3 shows the drainage of planar films of SDS – salt solutions for different concentrations of salts, while the lifetime of the foam lamella containing 0.5 mM SDS at different concentrations of the added salts in the concentration range of 11 mM – 45 mM is

shown in Figure 9.4. One can see regularity in the cases of LiCl and NaCl. In the whole concentration range NaCl stabilizes the foam lamella better than LiCl. On the contrary, the case with KCl is different. It stabilizes the foam lamella better than the other salts only at 11 mM added salt. However, at larger concentrations, it becomes the worst foam lamella stabilizer. Moreover, at a certain critical concentration (45 mM) KCl acts as strong destabilizer.

Figure 9.5 depicts the dependence of the lifetime of the foam lamella, stabilized by 0.5 mM SDS, versus the specific energy of adsorption [Slavchov et al. (2014)] of Li^+ , Na^+ , and K^+ (see Table 9.1) ions on air/water interface in the concentration range of 11 mM – 45 mM of added salt.

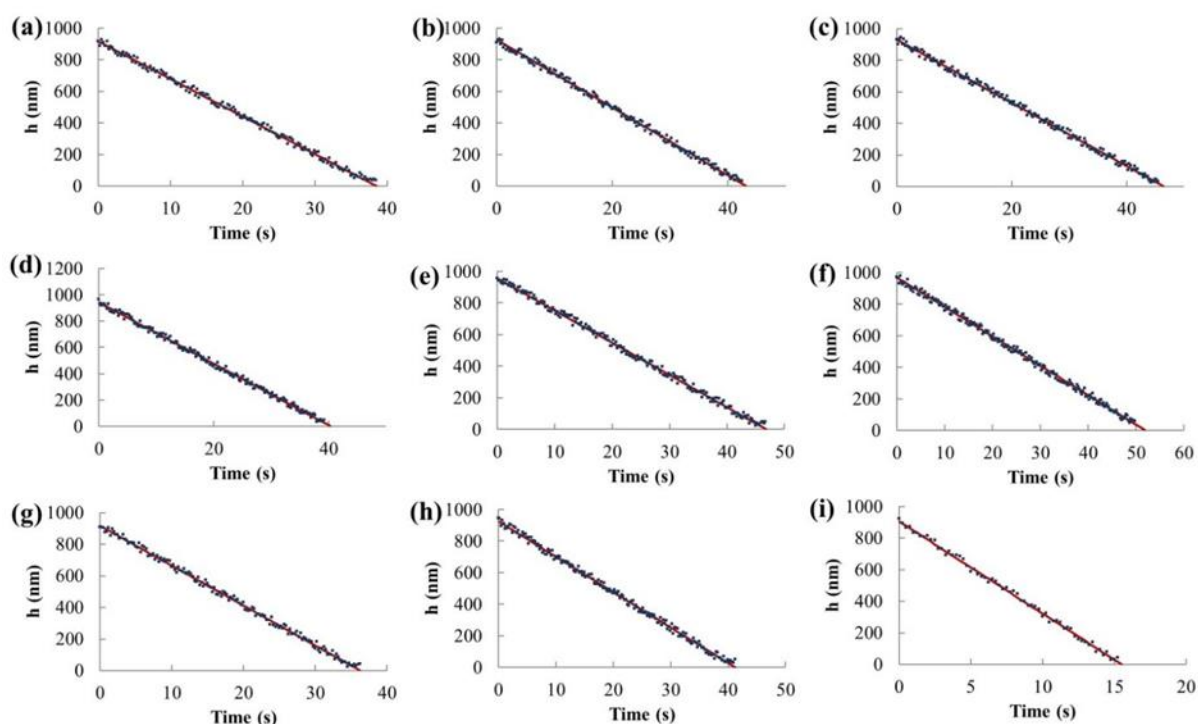


Figure 9.3. Drainage of plane films of SDS – salt solutions: (a) 25 mM LiCl, (b) 35 mM LiCl, (c) 45 mM LiCl, (d) 25 mM NaCl, (e) 35 mM NaCl, (f) 45 mM NaCl, (g) 25 mM KCl, (h) 35 mM KCl, and (i) 45 mM KCl. The data correspond to the film top. The experimental results are shown by symbols. The inclined straight line corresponds to the theoretical prediction of Sett et al. (2013).

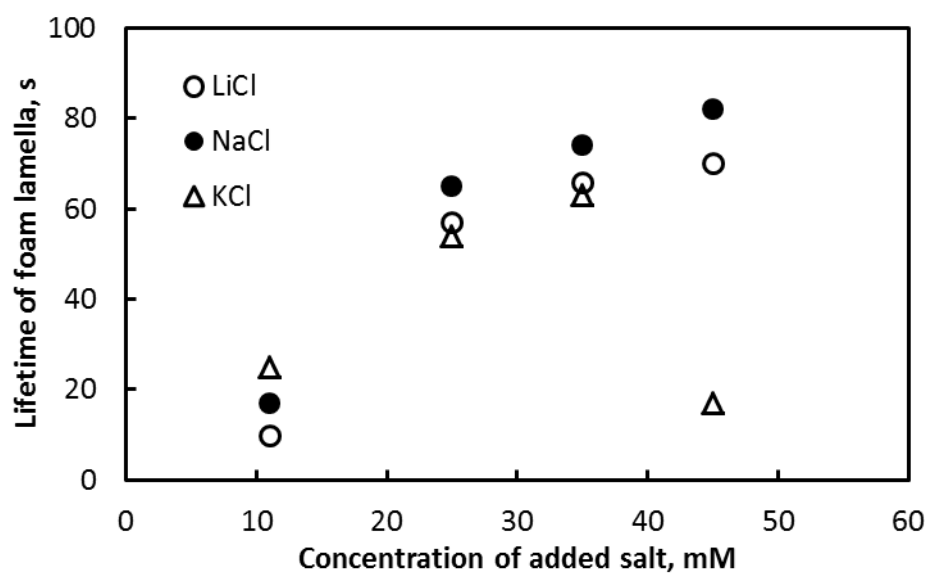


Figure 9.4. The dependence of the lifetime of the foam lamella on the concentration of the added salt in the presence of 0.5 mM SDS.

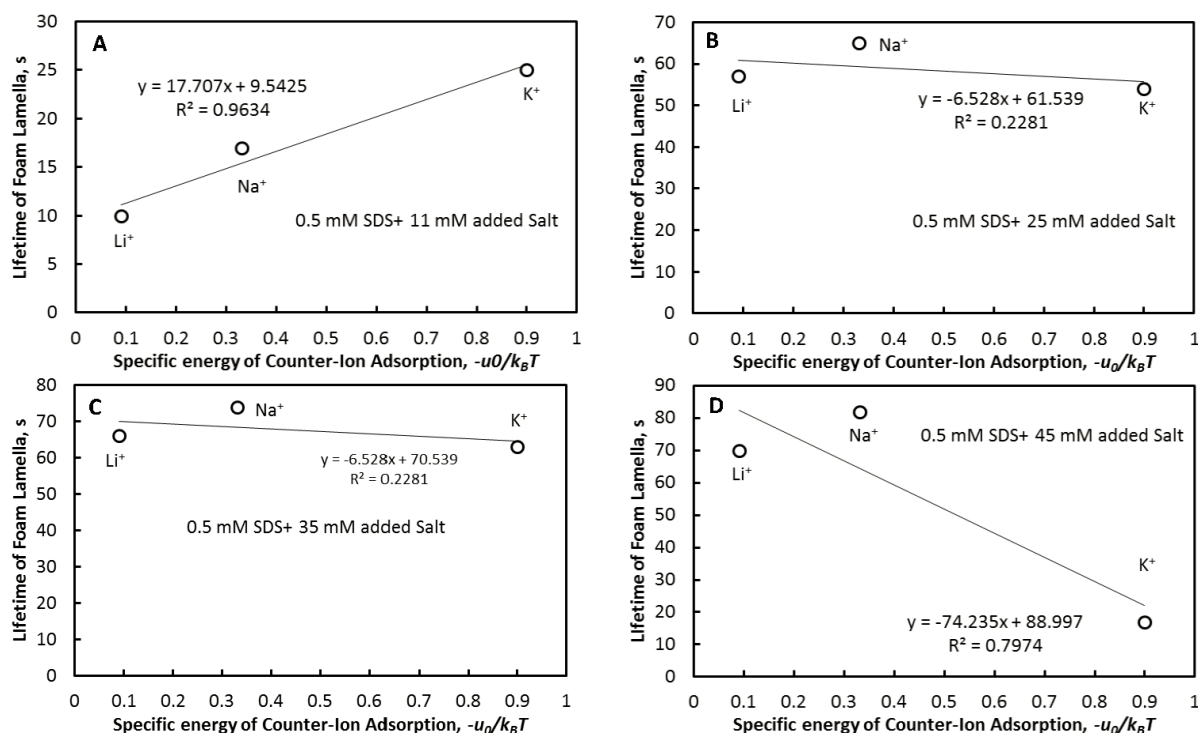


Figure 9.5. The lifetime of the foam lamella versus the specific energy of counter-ion adsorption for films stabilized by: (A) 0.5 mM SDS + 11 mM MCl (M=Li, Na, K); (B) 0.5 mM SDS + 25 mM MCl (M=Li, Na, K); (C) 0.5 mM SDS + 35 mM MCl (M=Li, Na, K); (D) 0.5 mM SDS + 45 mM MCl (M=Li, Na, K).

At 11 mM added salt (Fig. 9.5A), one can see a linear dependence between the lifetime of the foam film and the specific energy of counter-ion adsorption on air/water interface, in line with the results reported in Ivanov et al. (2011). Figure 9.5A shows that larger the value of the specific energy of counter-ion adsorption, longer is the life of the foam film, as the counter-ions promote higher adsorption of surfactant on the oil/water interface to cause better stabilization.

At larger salt concentrations, however, though the lifetime of the foam films increase, the above-mentioned linear dependence is violated (see Figs. 9.5B and 9.5C). At 45 mM added salt, the K⁺ counter-ion suddenly shows a destabilizing effect - the lifetime of the films fall almost to the level observed without any salt added (~15s). (see Fig. 9.5D). Beyond this

critical concentration of 45 mM for KCl, higher KCl concentrations do not shorten the lifetime of the foam films any further.

To understand the mechanism of the novel behavior in the presence of 45 mM KCl, we analyzed the surfactant adsorption at the air/water interface using experimental surface tension isotherms of 0.5 mM sodium dodecyl sulfate (SDS) in the presence of added in significant excess LiCl, NaCl, and KCl [Ivanov et al. (2011) and Slavchov et al. (2014)] (see Table 9.1 and Fig. 9.6). Table 9.1 presents the lifetime of the foam lamellas, black films, their initial foam film thicknesses, the characteristic time of foam film drainage, the speed of thinning of the foam films, the experimental elasticity and the Gibbs elasticity (for more details see the supplementary material) of foam films, stabilized by 0.5 mM SDS, in the concentration range of 11 mM – 45 mM of added salt.

The surface elasticity of the vertical foam films correlates with the lifetime of the films, the lifetime of the black films, the characteristic time of foam film drainage, and the speed of thinning of the foam films. At 45 mM KCl all the parameters of the vertical foam film correspond to unstable film – short lifetime, shorter characteristic time, fast drainage and small values of the elasticity. At this stage of our investigation we did not observe such anomalies with the addition of LiCl and NaCl. For this reason, we assumed the effect of KCl as extraordinary. Yet, we hypothesized that LiCl and NaCl should have the same effect at proper concentrations of added salt. One can see a substantial difference between the experimental and the Gibbs elasticity of the foam films. This difference is expectable as the Gibbs elasticity and the visco-elastic moduli of the foam films are different.

Table 9.1. The lifetime (see experimental methods) of the foam lamellas, black films, their initial foam film thickness, the characteristic time of foam film drainage, the experimental and Gibbs elasticities in the presence of 0.5 mM SDS and 11 mM, 25 mM, 35 mM, and 45 mM added MCl (MCl, M=Li, Na, K) of added salt.

Added salt	Lifetime of the film (s)	Lifetime of black films (s)	h_0 (nm)	T (s)	U (nm/s)	ε (mN/m)	Gibbs elasticity (mN/m)
11 mM LiCl	10	9	843.7	9.4	89.8	0.22	31.4
25 mM LiCl	57	38	916.2	38.5	23.8	1.04	38.36
35 mM LiCl	66	43	926.6	43.1	21.5	1.18	41.38
45 mM LiCl	70	46	929.5	46.5	20.0	1.28	43.66
11 mM NaCl	17	14	871.7	14.4	60.5	0.35	37.86
25 mM NaCl	65	40	943.1	40.4	23.3	1.14	45.81
35 mM NaCl	74	46	955.4	46.8	20.4	1.343	49.15
45 mM NaCl	82	51	967.8	51.9	18.7	1.518	51.64
11 mM KCl	25	16	900.6	16.7	53.9	0.439	50.31
25 mM KCl	54	36	917.6	36.3	25.3	0.98	58.72
35 mM KCl	63	41	924.1	41.2	22.4	1.125	61.99
45 mM KCl	17	15	905.3	15.5	58.4	0.41	64.32

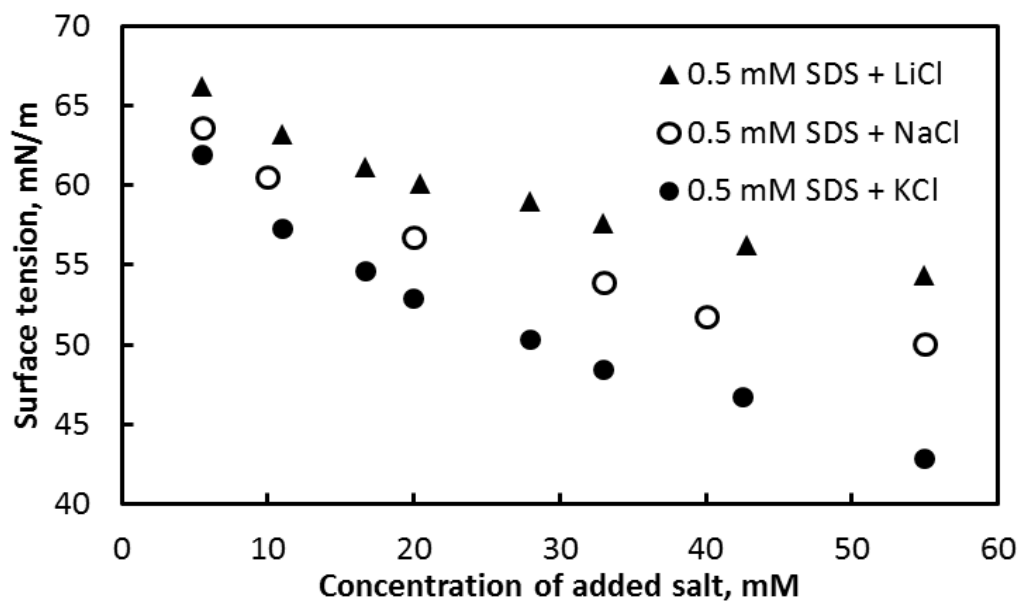


Figure 9.6. Surface tension isotherms of 0.5 mM SDS + added salts; The relative experimental error is ± 0.2 mN/m.

One can see that the surface activity of dodecyl sulfate ions (DS^-) increases in the order of Li^+ , Na^+ , K^+ of the added counter-ions, and at 45 mM KCl (the first vertical line in Fig. 9.7 and critical concentration for KCl) the adsorption of DS^- ions at the air/water interface is $4.4 \times 10^{-6} \text{ mol/m}^2$.

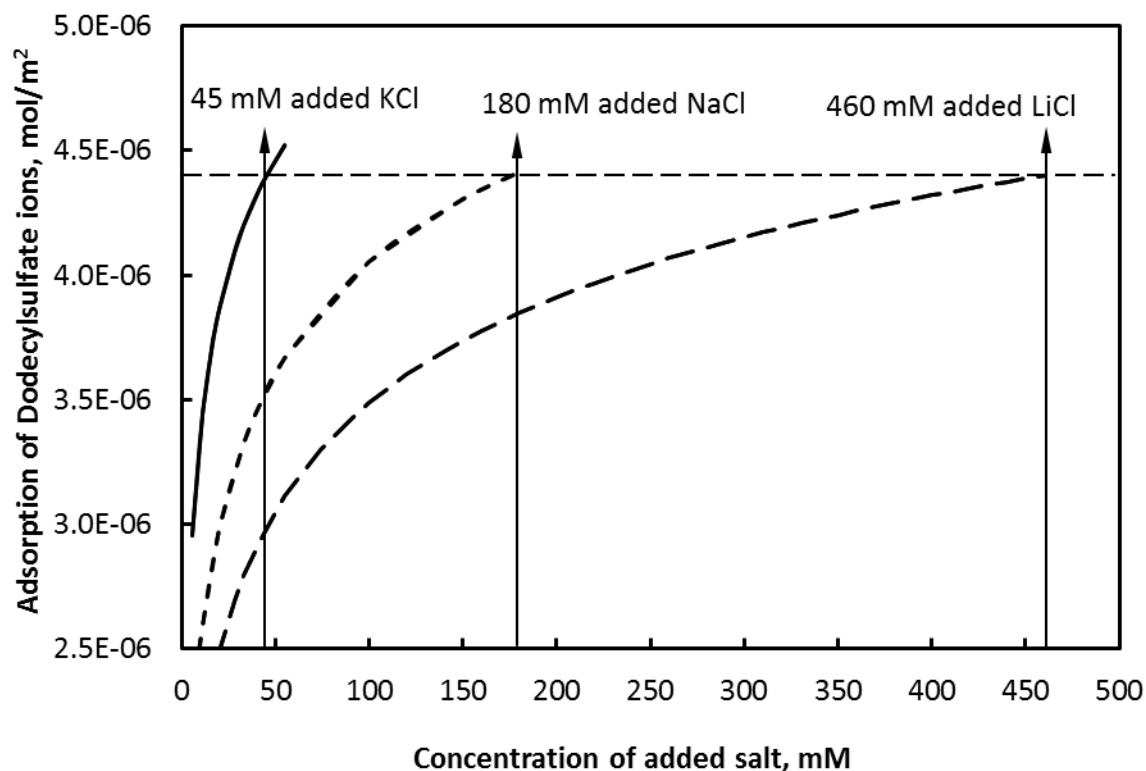


Figure 9.7. Adsorption of DS^- ions on the air/water interface of 0.5 mM SDS as a function of the concentration of added salt (MCl , $M=Li, Na, K$) – prediction of level of adsorption at the critical point of foam film de-stabilization; the average error calculation of the adsorption is about 1.5% (for more information about the modeling of surface coverage see Ivanov et al. (2006) and Slavchov et al. (2014)).

We hypothesized that at similar adsorption of DS^- ions for the other salts, the foam films may become unstable as well. From Fig. 9.7, based on the modified model of Ivanov et al. [Slavchov et al. (2014) and Karakashev (2014)] we predicted the same adsorption of DS^- ions would be achieved at 180 mM NaCl and 460 mM LiCl and we might expect to observe corresponding film destabilization for those salts. Indeed, the destabilization occurred exactly at the predicted values, as the results are shown in Table 9.2.

Table 9.2. Added salt and corresponding lifetimes of the foam lammelaes, black films, their initial foam film thickness, specific time of foam film drainage, and experimental and Gibbs elasticities for the cases of 450 mM and 460 mM LiCl and correspondingly 175 mM and 180 mM NaCl.

Added Salt	Lifetime of film(s)	Lifetime of black films (s)	h_0 (nm)	T (s)	U (nm/s)	ε (mN/m)	Gibbs elasticity (mN/m)
450 mM LiCl	95	55	971.6	55.2	17.6	1.624	64.16
460 mM LiCl	14	13	892.1	13.3	67.1	0.344	64.35
175 mM NaCl	103	59	992.4	59.3	16.7	1.801	64.26
180 mM NaCl	16	14	908.6	14.5	62.7	0.386	64.50

A hypothesis for the mechanism of this surprising, but now predictable, sudden destabilization is that salt addition (via screening interactions) serves to pack more DS^- ions at the interface up to the critical adsorption ($\Gamma = 4.4 \times 10^{-6} \text{ mol/m}^2$). Upon further addition, the salt causes some precipitation or structuring of the SDS, the surfactant coverage of the interface is suddenly reduced, increasing the surface tension, and resulting in faster drainage. The decrease is not necessarily equilibrium, as for newly formed films, the equilibration of SDS molecules from the new structures may be slower than the drainage of the films, and thus the limiting factor. Once thinned out, the resulting black films (about 30 nm thickness) have no volume from which to form full layers, thus have significantly shorter lifetimes due to the sparser adsorption layer coverage.

The suddenly faster film drainage was consistent with our hypothesis for dynamic, non-equilibrium cause of the shorter lifetimes of the films, if equilibrium concentrations

could not be reached. We used a plot of the experimentally determined surface tension and drainage velocities to try and infer the effective surface tension during the faster drainage of the films, and from the adsorption theory of Ivanov et al.(2006), the effective equilibrium surfactant coverage of air/water interface (Fig. 9.8).

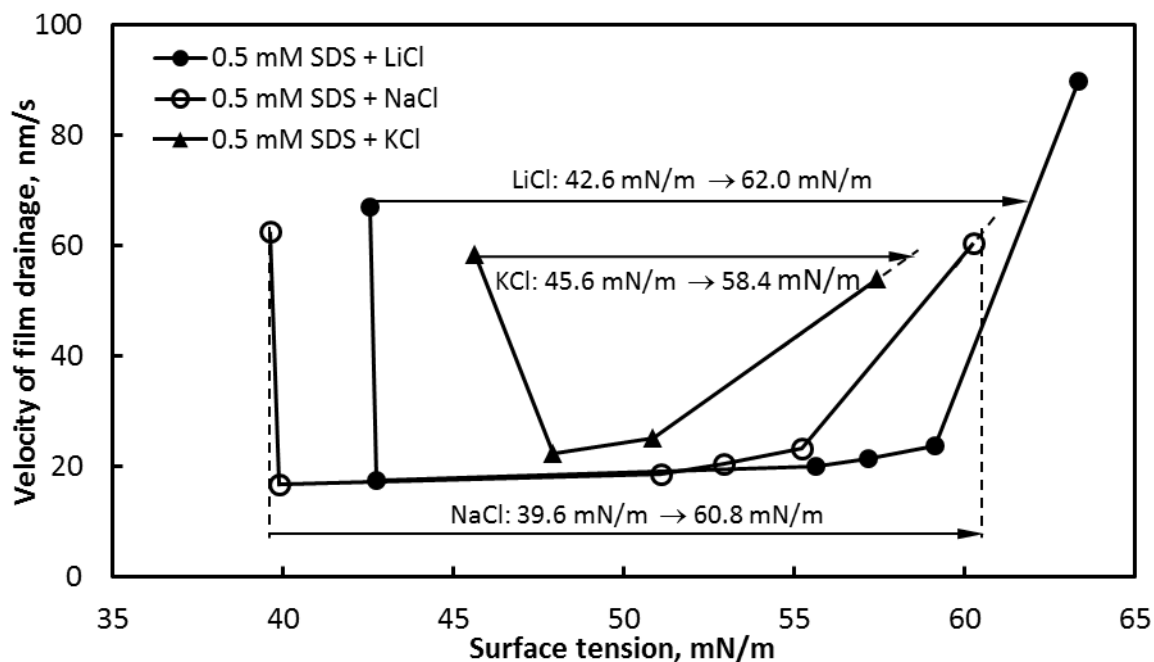


Figure 9.8. Velocity of film drainage versus surface tension of air/water interface for the three particular cases – 0.5 mM SDS + LiCl, 0.5 mM SDS + NaCl, and 0.5 mM SDS + KCl.

This unexpected increase of the speed of film drainage, in our opinion, corresponds to the increased value of the surface tension related to the decrease of adsorption of DS^- ions on the film's surfaces. The transitions from lower equilibrium to the higher dynamic values of the surface tension are indicated in Fig. 9.8 with horizontal arrows. One can see that in all cases after the transition, the new values of surface tension are in the region of strong dependence of the rate of film drainage on the surface tension. Another possible way to determine the surface tension at the very critical point of destabilization of the foam film is

by means of its experimental elasticity. However, this could be possible only if the experimental elasticity coincides with the Gibbs elasticity. It is evident from Tables 9.1 and 9.2 the significant difference between the values of the Gibbs and the experimental elasticities.

9.3.2. Foam experiments and analysis

The method of foam generation plays an important role in this process as well. For this reason a deviation between the critical concentrations in the film and in the foam could be expected. The difference in the critical salt concentrations between foam films and foam could be due to foam fractionation. The large number (and corresponding surface area) of soap bubbles in the foam extracts the surfactant from the bulk solution. For this reason foam usually has a higher concentration of the surfactant than that of the surfactant solution. Various salt concentrations of LiCl, NaCl, and KCl were used with 0.5 mM SDS for the foam column experiments. The volume of liquid drained from the foam column was measured from the height of the drained liquid/foam interface at regular intervals of time. Foam stability can be characterized by the volume of liquid in the foam rendered dimensionless by the total liquid in the foam at the start of the experiment, which is found by measuring the total volume of liquid left in the foam column at the end of the experiment after drainage stops. We established that the foam stability correlates very well with the rate of foam drainage. Unstable foam usually drains faster. Figure 9.9 presents the volume of liquid drained (Fig. 9.9A) and the drainage curve (Fig. 9.9B) of foam prepared from 0.5 mM SDS and added KCl in the concentration range of 10 mM – 45 mM added salt. One can see that the rate of foam drainage decreases (foam stability enhances) upon the increase of the concentration of KCl until 45 mM, at which the rate of foam drainage is increased substantially. The latter corresponds to low foam stability.

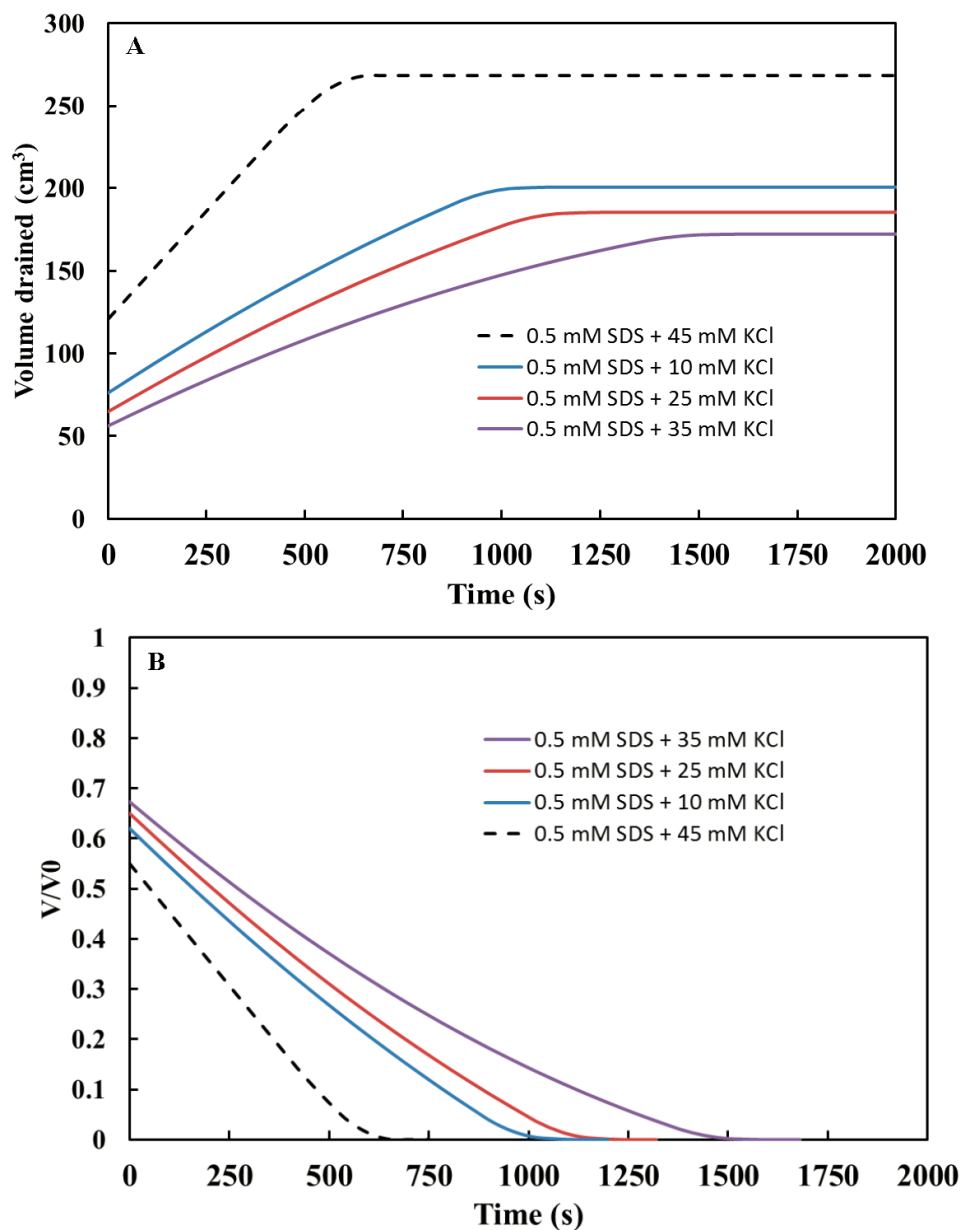


Figure 9.9. (A) Volume of liquid drained for the first 2000 s and (B) drainage curves for 0.5 mM SDS + 10 mM KCl, 25mM KCl, 35 mM KCl and 45 mM KCl.

One can see that the critical concentration of KCl, at which the foam stability decreases significantly, coincides with this one for foam films (45 mM KCl). For LiCl and NaCl the same trends were observed (Figs. 9.10 and 9.11) but the critical concentrations at which destabilization was observed were twice as high as for the single film experiments.

Since the foam geometry depends more significantly on the preparation method, the single film experimental results allow the best analysis for interpretation and prediction. Though not as quantitatively understood, we provide the results of the foam experiments as a reminder of more complex effects due to surfactant fractionation and a practical guide to expectations in foam formulation experiments.

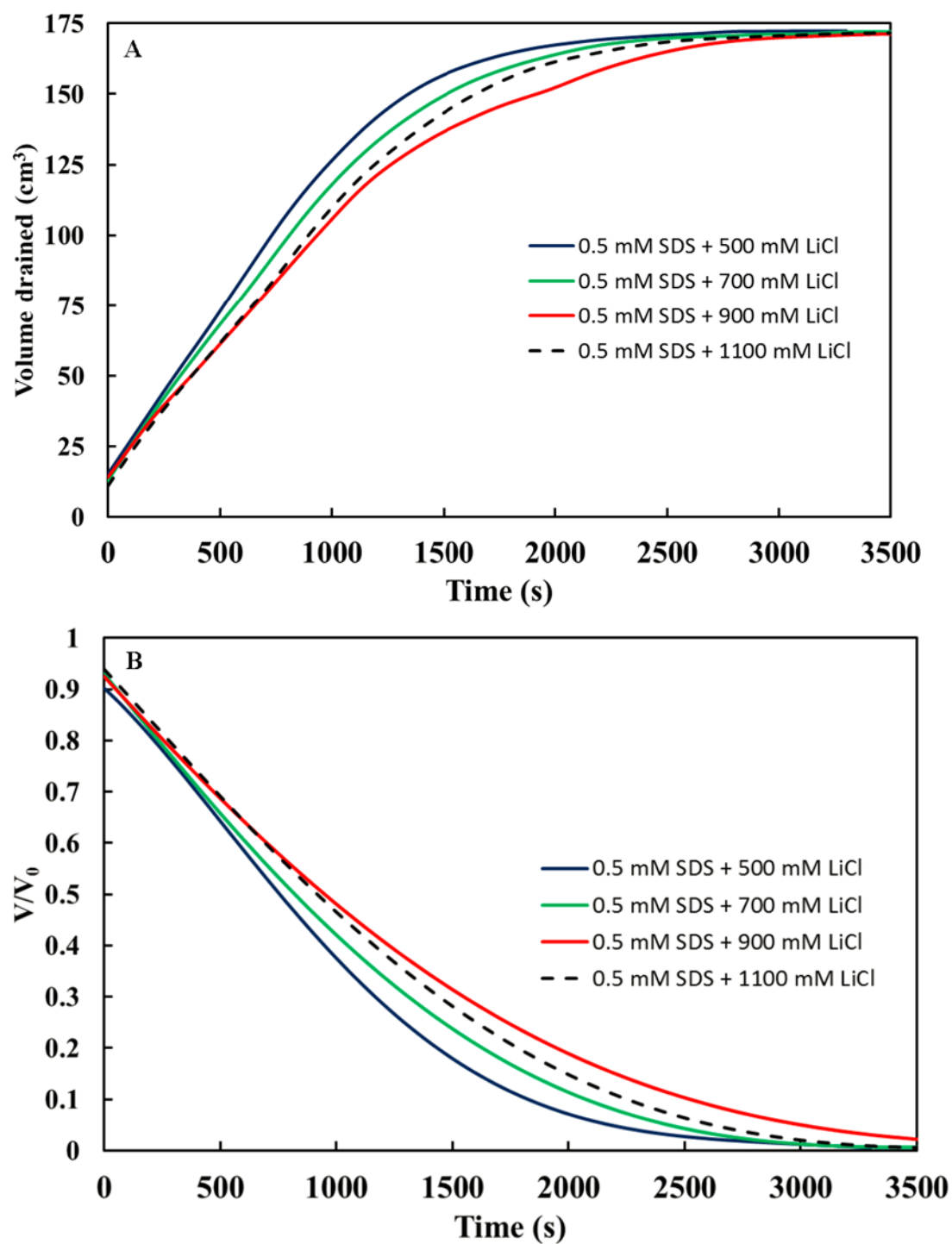


Figure 9.10. (A) Volume of liquid drained for the first 3500 s and (B) drainage curves for 0.5 mM SDS + 500 mM LiCl, 700 mM LiCl, 900 mM LiCl and 1100 mM LiCl.

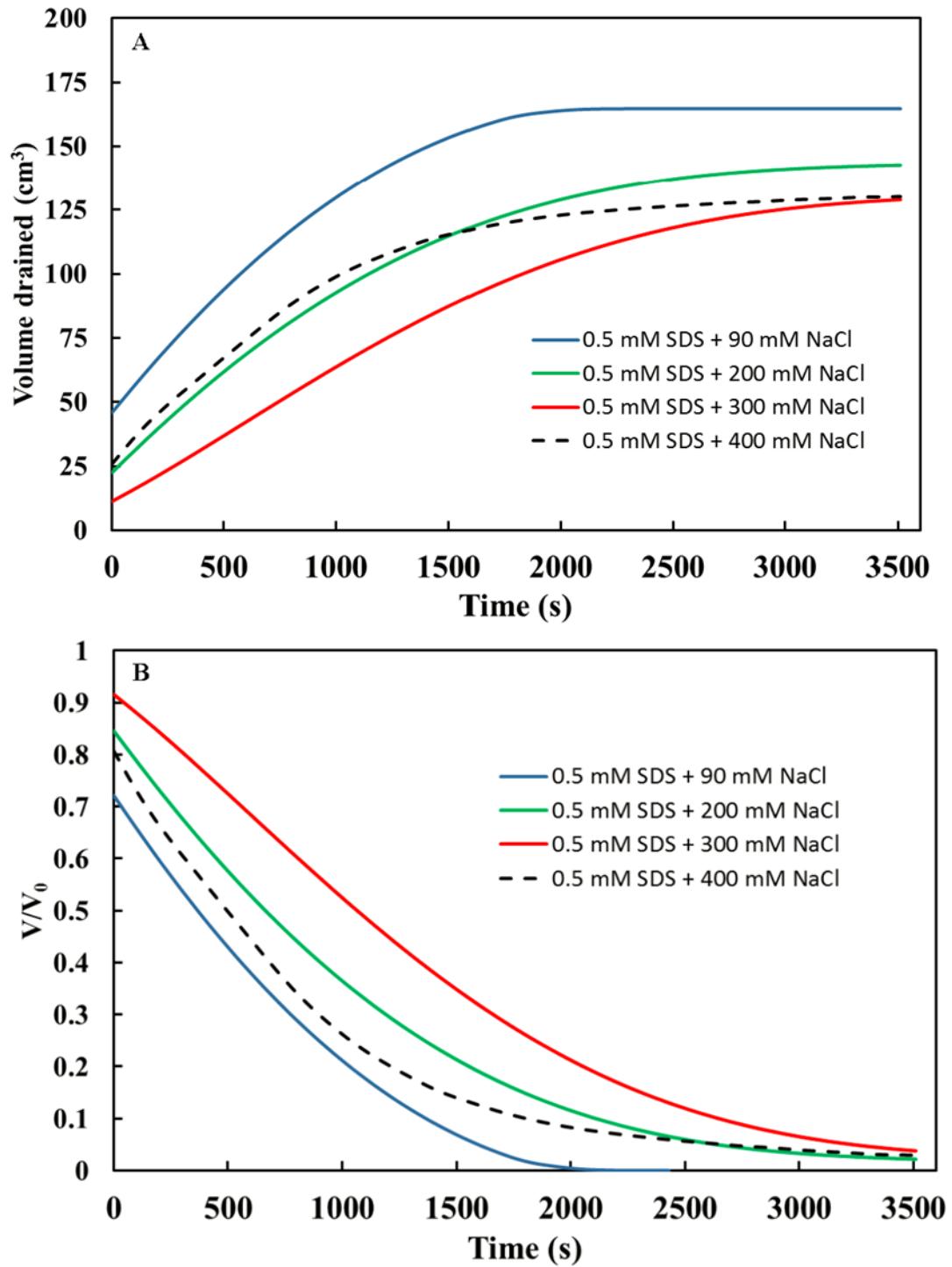


Figure 9.11. (A) Volume of liquid drained for the first 3500 s and (B) drainage curves for 0.5 mM SDS + 90 mM NaCl, 200 mM NaCl, 300 mM NaCl and 400 mM NaCl.

9.4 Conclusion

This work has the following basic observations:

1. The stability of foams and foam films increases with small amounts of added salt, and the increase can be quantified by the specific energy of counter-ion adsorption at the air/water interface.

2. There is a critical concentration for each salt, above which the salt acts as a defoamer. This can be explained by a reduced solubility (and/or formation of pre-micellar structures) of the surfactant at the critical salt concentration. The critical point of transition to unstable foam films appears at a certain critical value of the adsorption of dodecyl sulfate ions ($4.4 \times 10^{-6} \text{ mol/m}^2$), which does not depend on the type of the salt. The level of this instability, however, depends on the type of the salt.

CHAPTER 10

EXPERIMENTAL INVESTIGATION OF ELECTROKINETIC STABILIZATION OF GRAVITATIONAL DRAINAGE OF IONIC SURFACTANTS FILMS

This chapter has been previously published in Sett et al. (2016).

10.1 Introduction

The present work explores free liquid surfaces with the embedded charges left as a charged hydrophobic tails of the ionic surfactants when their hydrophilic cations or anions have been solubilized. Here this situation arises in plane liquid films of the ionic surfactant solutions supported on a vertical rectangular frame. In the recent work [Sett et al. (2013)] marginal regeneration was practically absent in the gravitational drainage of the vertical plane films because the gravity-driven flow dominated the capillary suction to the horizontal wires in the frame supporting the film. This allows one to uncover the other basic phenomena characteristic of gravitational drainage of the vertical plane films of surfactant solutions. Therefore, an intriguing opportunity is opened by subjecting vertical films of solutions of ionic surfactants to the electric field in the vertical direction, which revealed the electroosmotic flows directed against gravity and resulting in the film thickening [Bonhomme et al. (2013)].

In the present work we demonstrate experimentally a new aspect of the electroosmotic phenomena in vertical films of the ionic surfactants [below and above the critical micelle concentration (cmc)] subjected to the electric field in the vertical direction, which elucidates several new elements characteristic of gravitational drainage of such films.

10.2 Experimental section

10.2.1. Experimental setup

The experimental setup is sketched in Fig. 10.1. An aluminum wire frame (4 cm x 4 cm x 0.087 cm), is dipped into a container with surfactant solution. After that, the container is lowered, and a vertical surfactant film stays supported on the frame. The vertical sides of the frame have symmetric dielectric central insets which allow using the upper and lower parts of the frames as electrodes when voltage is applied to them. The film on the frame is photographed using a high-speed CCD camera (Phantom Miro 4) and the images are processed using Matlab. The intensity of each pixel in the color image is split into three wavelengths corresponding to red, blue, and green light. For each wavelength, the thickness of the film is calculated using the following interferometric formula [Sett et al. (2013) and Sett et al. (2014a)]

$$h = \frac{\lambda_0}{2\pi n_w} \left[M\pi \pm \arcsin \sqrt{\frac{\Delta(1+r^2)^2}{(1-r^2)^2 + 4r^2\Delta}} \right] \quad (10.1)$$

In Eq. (10.1) $\Delta = (I_0 - I_{\min,0}) / (I_{\max,0} - I_{\min,0})$; I_0 is the instantaneous intensity corresponding to the wavelength λ_0 , and $I_{\min,0}$ and $I_{\max,0}$ are the minimum and maximum intensities, respectively; r is the Fresnel's reflection coefficient, which is defined as $r = (n_w - 1) / (n_w + 1)$ for the normal incident light, with $n_w = 1.333$ being the refractive index of water, M is the order of interference, $M = 0, 1, 2, \dots$. To find the order of interference the following method was used. The film first bursts at the top. At the burst moment the film thickness at the top $h = 0$. This implies minimum light intensity in that area, i.e. $\Delta = 0$. From Eq. (10.1) in the present work (as well as of Sett et al. (2013)), it can be seen that the order of interference, $M = 0$ corresponds to the top of the film. Tracing back in time the measured light intensity from the moment of film bursting, M is

increased by 1 and the plus sign changed to minus sign in Eq. (10.1) each time the arcsine term becomes equal to $\pi/2$.

Using this micro-interferometric technique, one can determine the local film thicknesses h above 30 nm [Sett et al. (2013) and Sett et al. (2014a)]. In the present work we concentrate on the film thickness at the top, namely right below the upper wire at the distance of 2 cm from the left wire, where any hydrodynamic effects of the side wires on the film thickness can be safely neglected (the electric field effects of the side wires are discussed below). A white light source, Magicshine Light MJ-808U-4M, kept at the focal length of a plano convex lens ($f = 12.5$ cm), was used to produce parallel beam of light. Lumiquest diffuser was used to obtain uniformity of white light. A variable dc voltage source (Mastech DC power supply HY6003D) was used to create an electric field across the two metal halves of a wire frame separated by dielectric insets. One of the vertical sides of the frame of each of the two metal halves was extended outward starting from a frame corner to facilitate wire connections to the voltage source. The location of these two appendices ensured that connections to the DC source do not disturb the film in the frame. An analog DC micro-ammeter in the range 0-20 μA was used to measure the current. Throughout the drainage experiment, the ammeter was continuously photographed using Dino Lite digital microscope to record the measured current variation in time.

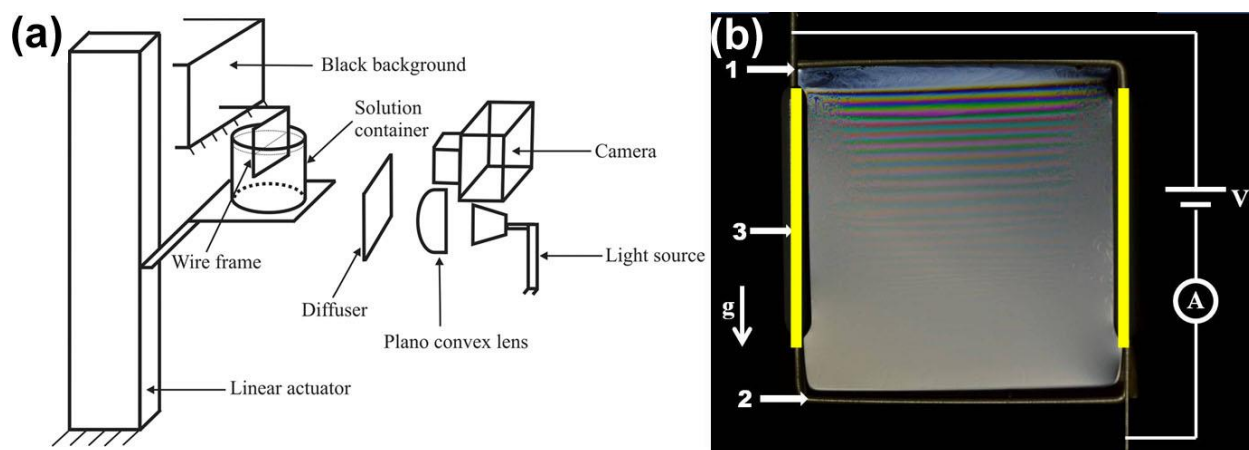


Figure 10.1. (a) Schematic of the experimental setup for gravitational drainage of plane vertical films. (b) The photograph of the film-supporting frame with the interferometric pattern seen on the film, with 1 being the upper electrode, 2 being the lower electrode, 3 being the dielectric insets in the side wires and $\mathbf{g}$ being the gravity acceleration vector.

10.2.2. Preparation of solutions

Several different aqueous surfactant solutions were used: Sodium Dodecyl Sulfate (SDS) with molecular weight $M_w = 288.38$ Da - an anionic surfactant at concentrations in the range 4-16 mM, i.e. below and above the critical micelle concentration (cmc) of 8 mM; Dodecyltrimethylammonium Bromide, DTAB, with molecular weight $M_w = 308.34$ Da - a cationic surfactant at concentrations in the 5 – 30 mM range, i.e. below and above the critical micelle concentration of 15 mM; (both obtained from Sigma Aldrich); as a reference, we employed the non-ionic surfactant tetraethylene glycol monoethyl ether (C_8E_4), with molecular weight $M_w = 306.44$ Da at concentrations in the 5 – 15 mM range, i.e. below and above the critical micelle concentration of 7.5 mM, also obtained from Sigma Aldrich.

10.3. Results and discussion

As expected, gravitational drainage of the reference solution of the non-ionic surfactant C_8E_4 was practically not affected by the electric field applied (Fig. 10.2).

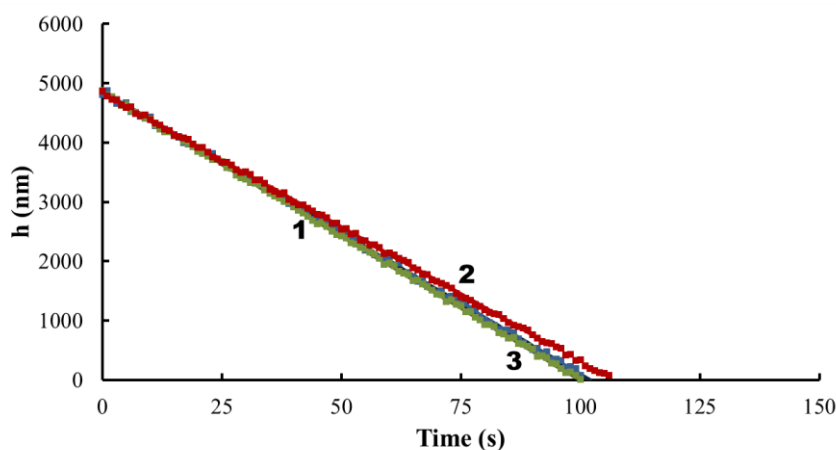


Figure 10.2. Film thickness near the top versus time for the 0.5 mM non-ionic surfactant C_8E_4 , where all three cases practically overlap, which reveals no effect of the electric field applied. Line 1-no voltage applied (the film lifetime $\tau = 102$ s), 2-top electrode is cathode at voltage of 40 V ($\tau = 107$ s), 3-top electrode is anode at voltage of 40 V ($\tau = 100$ s).

However, the gravitational drainage of the anionic surfactant was affected by the applied field, and sometimes in a very counter-intuitive way (Fig. 10.3). Indeed, when the top electrode was cathode, the film thickness increased and its lifetime was significantly longer (doubled) than without the electric field, as the comparison of lines 2 and 1 in Fig. 10.3 shows. This can be explained by the electroosmotic pumping fluid up due to the electroosmotic flow in the diffuse layers near the free surfaces [Bonhomme et al. (2013)], where the excessive charge is positive (due to the dominance of sodium cations in the case of SDS). However, with the reversed

polarity, with the top electrode being anode, this explanation would imply the electroosmotic pumping fluid down, resulting in the film thinning and shortening of its lifetime, while the experiment shows that the film still thickens (albeit less) and still lasts longer than in the case with no field applied (line 3 in Fig. 10.3). This counter-intuitive effect shows that the physical background of this fascinating simple experiment is more involved than the picture drawn in [Bonhomme et al. (2013)]. It should be emphasized that the gravitational drainage of the cationic surfactant DTAB reveals a similar anomaly, but obviously at the reverse polarity as shown in Fig. 10.4. Namely, when the top electrode is cathode and the electroosmotic flow in the predominantly negative diffuse layers near the free surfaces would be directed downward, DTAB films are still thicker and last longer than without voltage being applied.

Before discussing the implications of the unexpected behavior revealed by line 3 in Fig. 10.3 for SDS, and similar anomalous result for DTAB, we use the electric current measurements to elucidate the nature of the micellar counter-ions in these solutions. Figure 10.5 shows that on increasing the applied voltage from 15 V to 40 V, the electric current across the film increases for all concentrations of anionic surfactant SDS. Also, the decrease of current with time was slower when the top electrode was cathode for all concentrations of SDS. Similarly for cationic surfactant DTAB, the measured electric current increased with increasing applied voltage and the decrease of the current with time was slower when the top electrode was anode.

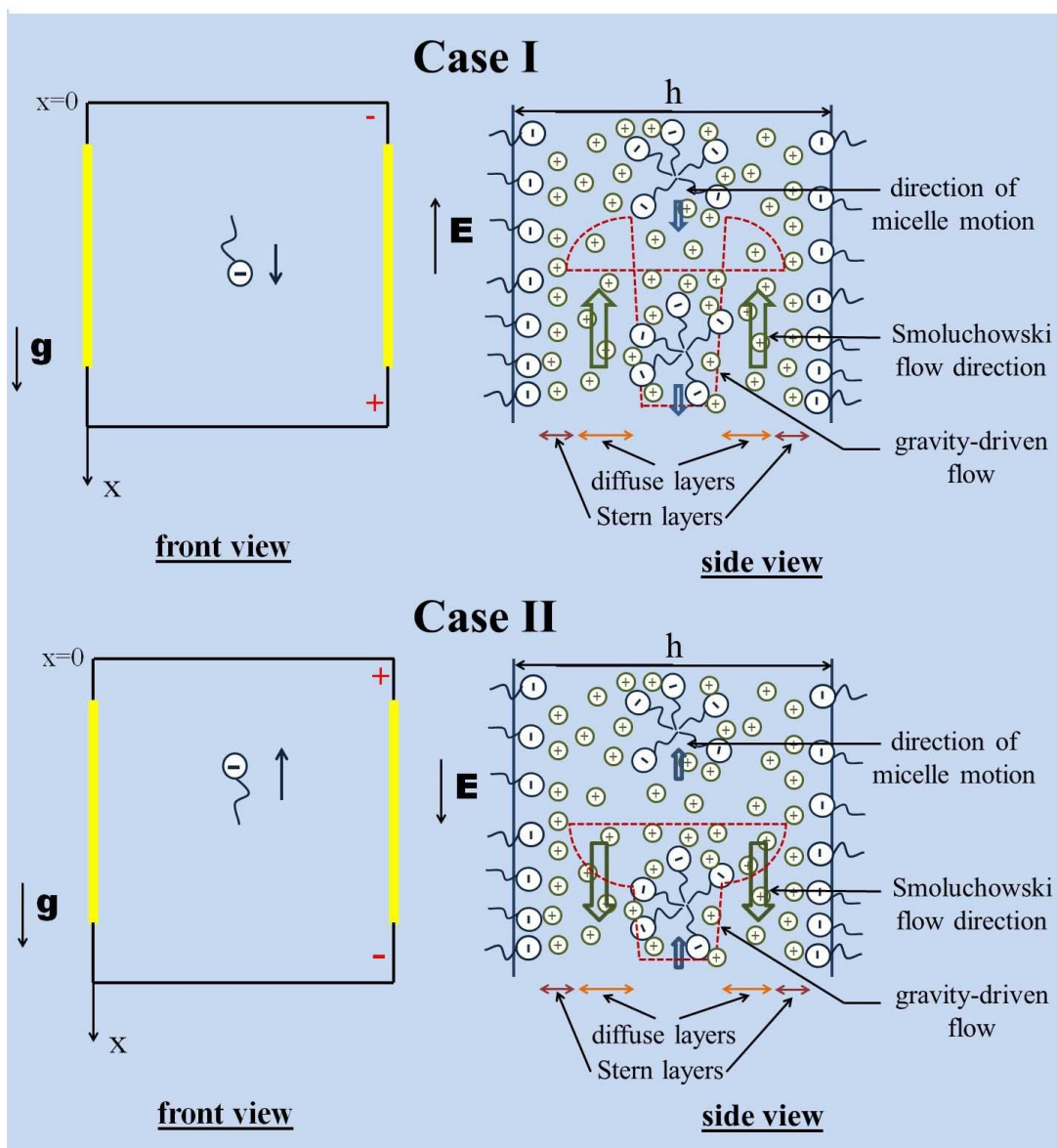
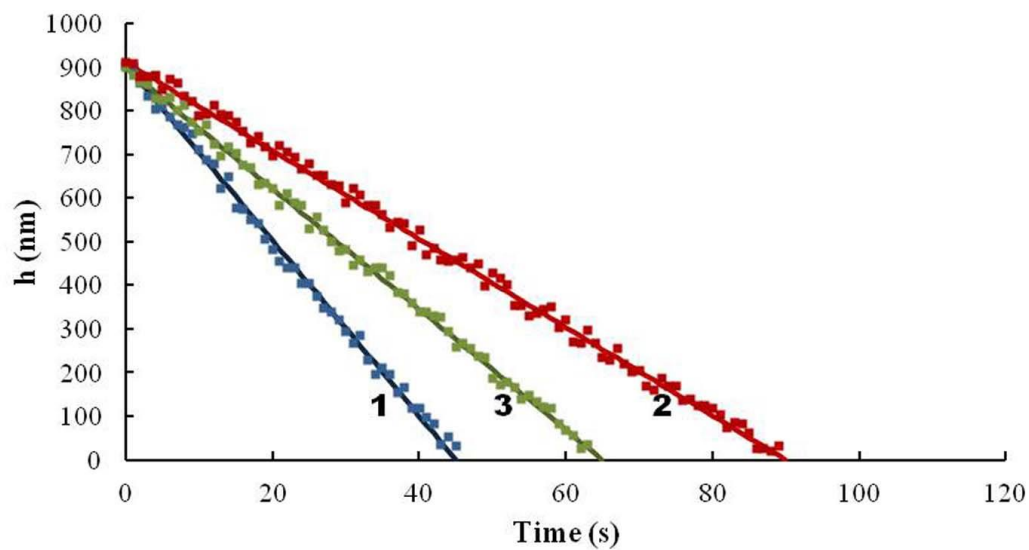


Figure 10.3. Film thickness near the top versus time for the 16 mM anionic SDS films. Line 1- no voltage applied ($\tau = 43$ s), 2-top electrode is cathode at voltage of 40 V (Case I-middle, $\tau = 87$ s), 3-top electrode is anode at voltage of 40 V (Case II-bottom, $\tau = 61$ s). In each case, to the right from the corresponding front view, a significantly enlarged side view is shown. The side views sketch the surfactant layers at the film surfaces, the Stern layers, the electroosmotic flows in the diffuse layers, and micelles surrounded with counter-ions. Also, the velocity profiles are shown by dashed lines.

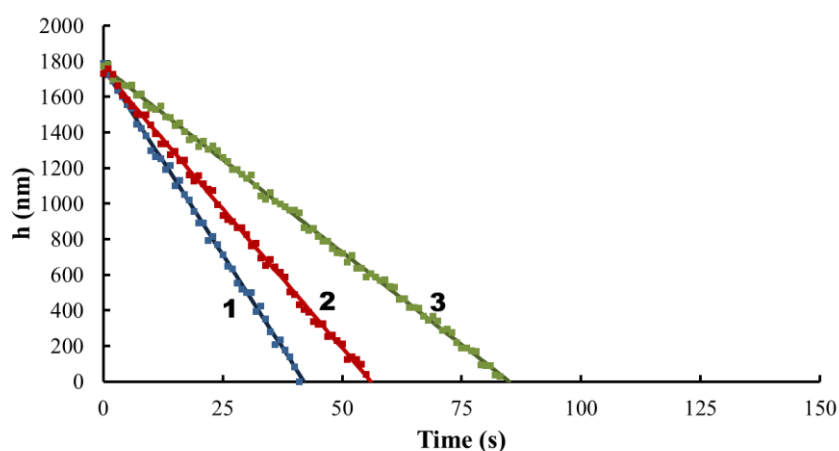


Figure 10.4. Film thickness near the top versus time for the for the 30 mM cationic DTAB films. Line 1-no voltage applied ($\tau = 42$ s), 2-top electrode is cathode at voltage of 40 V ($\tau = 56$ s), 3-top electrode is anode at voltage 40 V ($\tau = 85$ s).

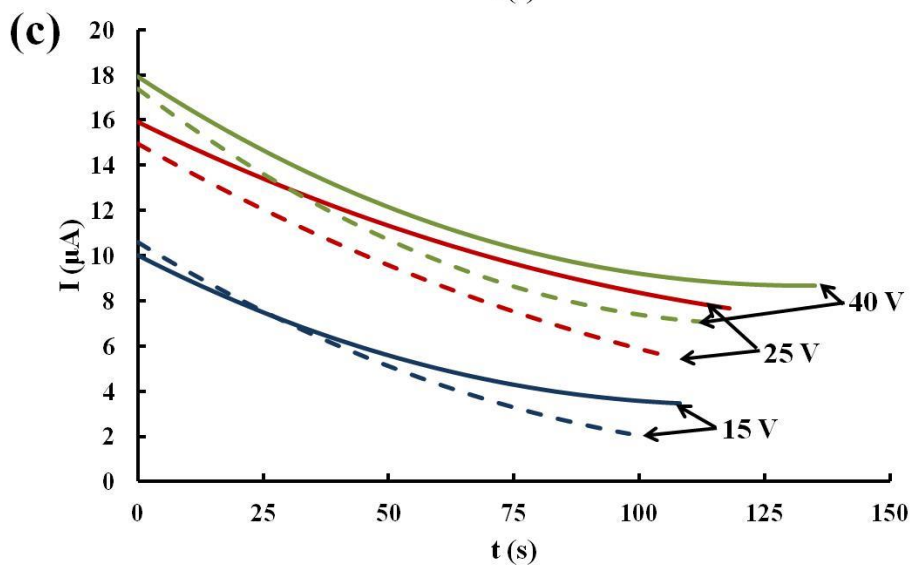
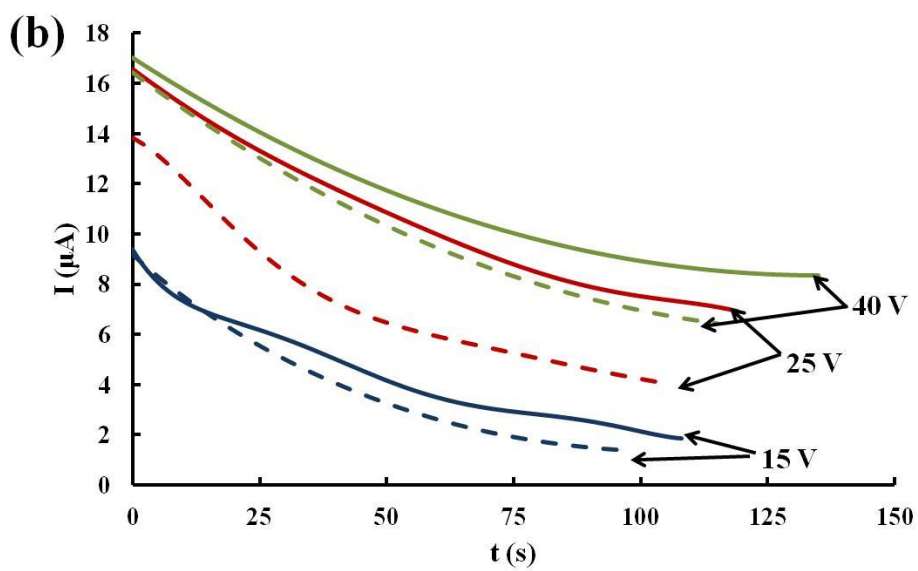
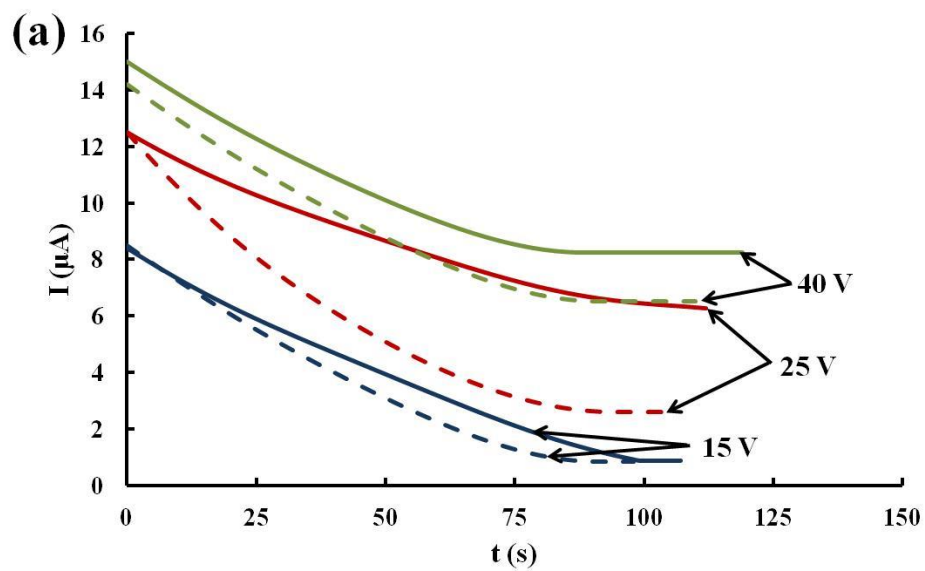


Figure 10.5. Measured electric current versus time for plane films of (a) 6 mM, (b) 10 mM, and (c) 16 mM SDS solutions. In the panels, the results for different applied voltages of 15 V, 25 V, and 40 V are denoted by the blue, red, and green colors, respectively. The current in the film when the top electrode was cathode (Case I) is presented by solid lines, while the dashed lines show the case with the top electrode being anode (Case II).

Using the measured current as a function of time t , $I(t)$, and Ohm's law, the specific conductance $\sigma(t)$ is evaluated as $\sigma(t) = I(t)L_{\text{ver}} / [h(t)L_{\text{hor}}2U]$, where L_{hor} and L_{ver} denote the horizontal and vertical sides of the frame (in the experiments $L_{\text{hor}} = L_{\text{ver}} = 4$ cm), $h(t)$ is the measured film thickness, and $2U$ is the applied voltage. The dependence of the specific conductance on time in planar SDS films for different concentrations and different applied voltages are shown in Fig. 10.6. For all cases, close to the moment when the films became black and disappeared (in the range $50 \text{ nm} < h < 100 \text{ nm}$), there was a sharp increase in the specific conductance, which is discussed in detail below. Under comparable conditions, for the anionic surfactant SDS films, the final values of the specific conductance are higher when the top wire frame was cathode (compare the solid lines with the corresponding dashed lines in Fig. 10.6). With an increase in voltage, the specific conductance also increases, albeit insignificantly. Similar results were obtained with cationic surfactant DTAB, i.e. the specific conductance increased sharply when the film was sufficiently thin and its magnitude increased with the applied voltage. Under comparable conditions in DTAB solution films, the final value of specific conductance was higher when the top wire frame was anode.

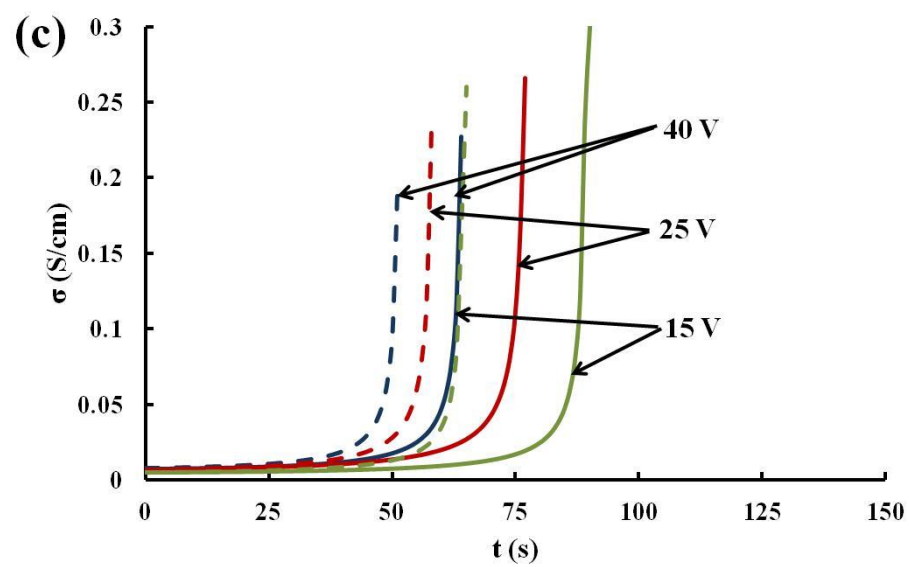
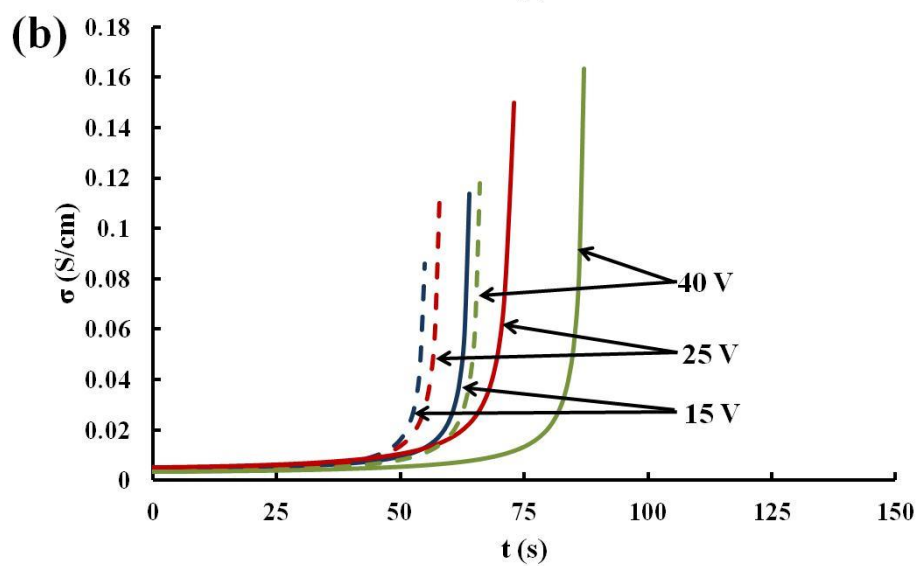
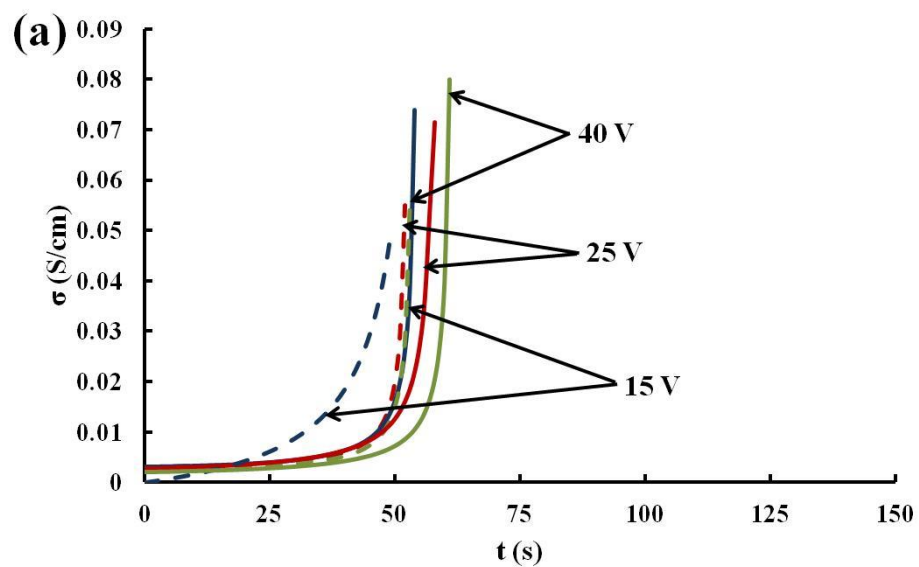


Figure 10.6. Specific conductance versus time t for (a) 6 mM, (b) 10 mM, and (c) 16 mM SDS solution films. In the panels, the results for different applied voltages of 15 V, 25 V, and 40 V are denoted by the blue, red, and green colors, respectively. The current in the film when top electrode is cathode (Case I) is presented by solid lines, while the dashed lines show the case with top electrode being anode (Case II).

The change of the specific conductance with concentration can be used to calculate the aggregation number, n of surfactant molecules in a micelle above the critical micelle concentration (cmc), and the number of counter-ions bound to such a micelle, m [Evans (1956); Shah et al. (1999) and Shah et al. (2001)]. The aggregation number n was calculated as $n = (4\pi/3)l^3N_A d_m / (10^{24}M_w)$, with l being the length of the hydrocarbon chain in surfactant, N_A being Avogadro's number, and d_m being the micellar density [Evans (1956) and Shah et al. (2001)]. The length l was found as $l = (1.5 + 1.265n_c)$ in Å, where n_c is the number of carbon atoms in the hydrocarbon chain [Shah et al. (1999) and Shah et al. (2001)]. The degree of counter-ion binding, β , is found as the ratio of the slopes of the dependences of the specific conductances in the micellar and pre-micellar regimes. The maximum values of the specific conductances in each case were measured at $t=0$, the moment of film formation (cf. Fig. 10.6). These values for SDS in Case I are shown in Fig. 10.7; cf. Evans (1956) and Shah et al. (2001). Then, the number of bound counter-ions, m is found as $m = \beta n$ [Shah et al. (2001); Shah et al. (1999); Tanford (1980); Shanks and Franses (1992)]. Table 10.1 lists the values of n and m for different concentrations and different voltages for the anionic surfactant SDS and cationic surfactant DTAB found in the present experiments. The degree of counter-ion binding, β ,

decreases when voltage increases for both anionic SDS and cationic DTAB. This means that as voltage increases, the number of bound counter-ions surrounding the micelles decreases.

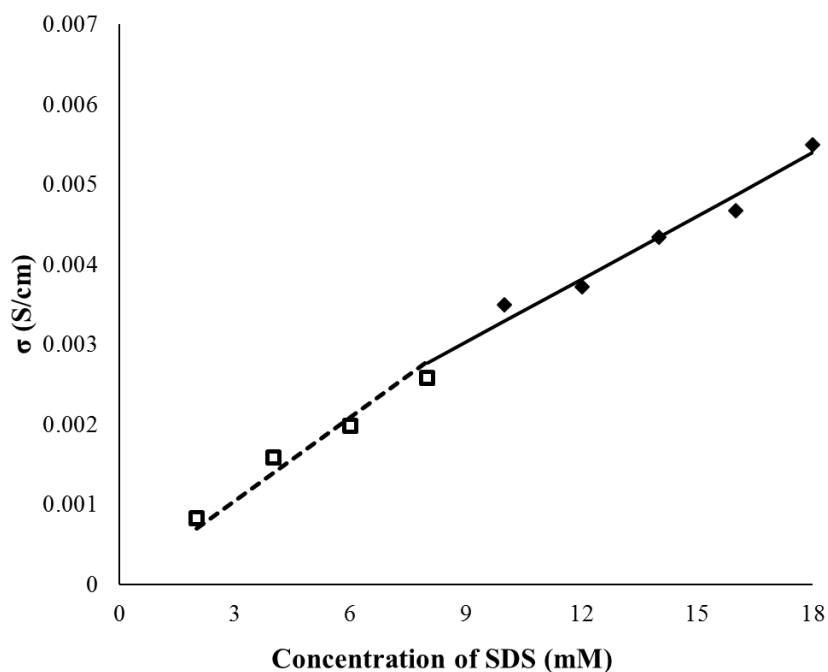


Figure 10.7. Specific conductance for different concentrations of SDS when the top electrode was cathode (Case I). The voltage applied was 40 V. The dotted line corresponds to the pre-micellar SDS concentration and has a slope of $347.48 \times 10^{-6} \text{ S cm}^{-1} \text{ mM}^{-1}$. The continuous line corresponds to the micellar regime and has a slope of $262.35 \times 10^{-6} \text{ S cm}^{-1} \text{ mM}^{-1}$. The ratio of the two slopes yields $\beta = 0.755$ listed in Table 10.1. The hollow and filled symbols correspond to the experimental data in the pre-micellar and micellar regimes, respectively.

Table 10.1. Micellar parameters.

Voltage	Case	SDS			DTAB		
		n	β	m	n	β	m
	No Voltage	56	0.854	48	83	0.892	74
15 V	Case I	56	0.835	47	83	0.877	73
15 V	Case II	56	0.829	46	83	0.874	73
25 V	Case I	56	0.812	45	83	0.846	70
25 V	Case II	56	0.809	45	83	0.844	70
40 V	Case I	56	0.755	42	83	0.813	67
40 V	Case II	56	0.759	42	83	0.810	67

The aggregation number, n listed in Table 10.1 is 56 for SDS, which is in the same range as the values reported [Quina et al. (1995); Evans (1956) and Shah et al. (2001)]. In particular, in Shah et al. (2001), the values of n for SDS revealed in several different approximations were $n=50$, 67, and 76. The aggregation number for 20 mM SDS solution found using a different technique, namely, the small-angle neutron scattering, was $n=55$ [Quina et al. (1995)]. Similarly, the aggregation number for DTAB was found $n=79$ [Kale et al. (1980)], close to the value $n=83$ we report.

It should be emphasized that micellization involves two characteristic times, the first one, τ_{fast} - of the fast process associated with exchange of monomers between micelles and the bulk aqueous phase, and the second one, τ_{slow} - of the slow process associated with micelle dissociation kinetics [Oh and Shah (1991)]. The average micellar lifetime, $\tau_{\text{mic}}(m)$ is associated with the slow process, and for surfactant concentration much greater than cmc is approximately equal to $\tau_{\text{mic}}(m) = n\tau_{\text{slow}}$ [Oh and Shah (1991); Leung and Shah (1986)]. For the surfactant

concentrations used in the present work, τ_{slow} is in the ms-range [Oh and Shah (1993)]. Hence the maximum micelle lifetime is in the order of 0.1 s, three orders of magnitude smaller than the characteristic film drainage time. Therefore, micellization and micelle disassembling processes are dynamic during the drainage process, while the micelle concentration and structure are, in fact, quasi-steady for a given surfactant. It should be emphasized that the degree of counter-ion binding β listed in Table 10.1 is close to 1, which means that the overall charge carried by micelles is relatively small. Moreover, micelles are located in the bulk outside the diffuse layers (cf. Fig. 10.3), i.e. in the electroneutral part of the film thickness. Even though the individual charge carriers drift there under the action of the applied electric field, their overall effects compensate each other in the electroneutral part and thus do not affect drainage kinetics.

10.4 Discussion of the experimental results

The ionic electrolyte solutions possess charges embedded in the free surfaces of the film. For example, the anionic SDS solution films have negatively charged hydrophilic heads of the surfactant molecules embedded in the free surfaces with each surfactant molecule having charge $-e$, with e being the counter-ion (proton) charge (see Fig. 10.3). On the other hand, the cationic DTAB solution films possess embedded positively charged hydrophilic heads of the surfactant molecules at the surface, with charge e . On the electrolyte side, counter-ions form the Stern layer rigidly attached to the surface charges (see Fig. 10.3) where the electric potential associated with the charges, drops dramatically from the ζ -potential of the surface φ_0 to the value φ_{SL} at the surface of the Stern layer in contact with the electrolyte. The two potentials are related as $\varphi_{\text{SL}} = \varphi_0 - 4\pi\delta\sigma_s / \epsilon_r$, where δ is the thickness of the Stern layer, the surface charge is σ_s , ϵ_r is the relative dielectric permittivity of water, and the Gaussian CGS units are used here and

hereinafter. Accordingly, the embedded surface charges and the rigidly attached counter-ions of the Stern layer can be considered as a charged surface with a charge σ_{SL} , which is much lower than the surface charge σ_s . The electrolyte layer near the Stern layer is polarized and forms the diffuse layer adjacent to the Stern layer. In the linearized Debye approximation $\varphi_{SL} = 4\pi\sigma_{SL}\lambda_D / \epsilon_r$, where λ_D is the Debye length. The diffuse layers are predominantly positively charged in the case of the anionic SDS (with cations Na^+ dominating there), and predominantly negatively charged in the case of the cationic DTAB (with anions Br^- dominating there).

The electric field imposed on the film triggers three different mechanisms. The first one is associated with the surface charge being subjected to the action of the imposed electric field, which means that the shear stress applied to the film surface appears, which can affect the surface elasticity. A non-uniform distribution of the surfactant molecules over the surface is the source of the surface elasticity ε [Levich and Technica (1962); Langevin and Sonin (1994)]. The concentration of the surfactant molecules in the absence of the electric field is higher near the film bottom due to the gravitational drainage. Therefore, the surface tension is higher near the film top, which pulls the surface upward against gravity, the effect associated with the surface elasticity $\varepsilon = -\Gamma(\partial\gamma / \partial\Gamma)$ (the Gibbs elasticity), where γ is the surface tension and Γ is the surfactant concentration at the surface (the effect of surfactant adsorption/desorption on the surface elasticity is negligibly small in the present case-see Appendix 10.A1). Due to the action of the electric field at the surfactant layer at the film surface with the attached Stern layer, the effective surface elasticity ε_{eff} arises as

$$\varepsilon_{\text{eff}} \approx \varepsilon - \sigma_{\text{SL}} (\Phi_{\text{bottom}} - \Phi_{\text{top}}) \quad (10.2)$$

with $(\Phi_{\text{bottom}} - \Phi_{\text{top}})$ being the imposed potential difference between the top and bottom electrodes, and σ_{SL} being the combined surface charge density accounting for the presence of the Stern layer.

In the case of SDS in Case I in Fig. 10.3, $(\Phi_{\text{bottom}} - \Phi_{\text{top}}) > 0$ and $\sigma_{\text{SL}} < 0$, i.e. the imposed electric field increases the surface elasticity, since it pushes the negatively charged surface layer downward enhancing the concentration gradient along the surface, and thus the surface elasticity. On the other hand, in the case of SDS in Case II in Fig. 10.3, $(\Phi_{\text{bottom}} - \Phi_{\text{top}}) < 0$ and $\sigma_{\text{SL}} < 0$. Then, the imposed electric field decreases the surface elasticity, since it pulls the negatively charged surface layer upward diminishing the concentration gradient along the surface, and thus the surface elasticity.

The second mechanism related to the electric field imposed on a film is the electroosmosis. It results from the action of the imposed electric field on the counter-ions in the diffuse layer. The velocity of the electroosmotic flow $u_{\text{eo}} = \varepsilon_r E_x (\varphi - \varphi_{\text{SL}}) / 4\pi\mu$, with $\varphi = \varphi_{\text{SL}} \exp(-y/\lambda_D)$ being the ion-related part of the total electric potential in the diffuse layer, ε_r being relative dielectric permittivity of water, E_x being the x-projection of the electric field strength of the imposed field, μ being the liquid viscosity, and λ_D being the Debye length. The electroosmotic Smoluchowski flows develop in the diffuse layers on the background of the gravitational drainage of the films. For example, in the case of SDS with the imposed field of Case I in Fig. 10.3, the electroosmotic flow will be directed upward, since $(\varphi - \varphi_{\text{SL}}) > 0$, $E_x < 0$, and thus $u_{\text{eo}} < 0$, which means that it is directed against the x-axis (i.e. upward). On the other hand, in the case of

SDS in Case II in Fig. 10.3, the electroosmotic flow will be directed downward, since in this case $(\varphi - \varphi_{SL}) > 0$, $E_x > 0$, and thus $u_{eo} > 0$.

The third mechanism related to the electric field imposed on a film results from the electroosmotic flow directed into a dead end (the upper or lower electrodes) in rectangular films, which can create an extra pressure gradient along the x-axis. This effect will be important to explain the “anomalous” behavior of the SDS solution in Case II (line 3) in Fig. 10.3. The electroosmotic flow entering a dead end is described by the following projection of the momentum balance equation on the x-axis

$$\mu \frac{\partial^2 u_{eo}}{\partial y^2} = \frac{\varepsilon_r E_x}{4\pi} \frac{\partial^2 \varphi}{\partial y^2} + \frac{dp}{dx} \quad (10.3)$$

where p is pressure

The continuity equation in this case reads

$$\int_0^{h/2} u_{eo} dy = 0 \quad (10.4)$$

with the film thickness being denoted as h.

The solution of Eq. (10.3) subjected to the symmetry condition at $y=h/2$ reads

$$u_{eo} = \frac{\varepsilon_r E_x}{4\pi\mu} (\varphi - \varphi_{SL}) + \frac{1}{\mu} \frac{dp}{dx} \left(\frac{y^2}{2} - y \frac{h}{2} \right) \quad (10.5)$$

while Eq. (10.4) reveals the pressure gradient as $dp/dx = -12\sigma_{SL} E_x \lambda_D / h^2$. Note that in Case II in Fig. 10.3 where $\sigma_{SL} < 0$ and $E_x > 0$, the pressure gradient $dp/dx > 0$, i.e. pressure increases toward the dead end (the lower electrode of the frame).

The pressure gradient due to the flow into a dead end (the upper or lower electrode) in rectangular films interferes with gravity acceleration, which yields the effective value of

$$g_{\text{eff}} = g \left[1 + 12 \sigma_{\text{SL}} E_x \lambda_D / (\rho g h_0^2) \right] \quad (10.6)$$

where h_0 is the initial film thickness at $t=0$.

In Case II in Fig. 10.3 for SDS where $\sigma_{\text{SL}} < 0$ and $E_x > 0$, the pressure build-up due to the electroosmotic flow into the lower dead end counteracts the gravity drainage, and can extend the film life time as the data 3 show in the top panel in Fig. 10.3, in a very counter-intuitive manner (since the electroosmotic flow is directed in the direction of gravitational drainage). On the other hand, in Case I in Fig. 10.3 for SDS this effect can accelerate drainage. However, it is counteracted by the traction of the electroosmotic flow directed upward, which can become dominant.

In Case I, the film stabilization is due to the traction imposed by the electroosmotic flow directed upward, which appears to be stronger than the associated pressure build-up near the upper dead end. In Case II, the film stabilization is due to the pressure build-up near the lower dead end, which is stronger than the traction imposed by the electroosmotic flow directed downward.

In the presence of the imposed electric field Eqs. (10.1) and (10.5) reveal that the drainage law [Sett et al. (2013)] given by Eqs. (10.A1) and (10.A2) takes the following form

$$h = h_0 - \frac{h_0(1-\Theta)}{\tau} t \quad (10.7)$$

Here the characteristic time

$$\tau = \frac{\varepsilon \left[1 - \sigma_{\text{SL},0} (\Phi_{\text{bottom}} - \Phi_{\text{top}}) / \varepsilon \right]}{\left[\rho (g_{\text{eff}} h_0)^{3/2} \right]} \quad (10.8)$$

is determined by the surface elasticity and gravity, as well as by the electric force acting directly on the surface charge, the electroosmotic flow, and the pressure gradient generated by the electroosmotic flow into the dead end. Also, the dimensionless electric parameter

$$\Theta = \frac{2\sigma_{SL,0}E_x}{\rho gh_0} \quad (10.9)$$

where $\sigma_{SL} \approx \sigma_{SL,0}$ is the initial surface charge density of the Stern layer.

The theoretical dependence for the film thickness is linear in time. Thus, its comparison to the experimental data uniquely determines the value of $B = -h_0(1-\Theta)/\tau$. On the other hand, the intermediary parameters affecting B , namely Θ and τ , depend only on a single unknown $\sigma_{SL,0}$ [cf. Eqs. (10.6), (10.8) and (10.9)] and thus the latter can be found from the measured value of B . Using the data for SDS for both polarities of the top electrode, the minimum and maximum initial surface charge density is then found as $|\sigma_{SL,0}| = 0.047 \text{ g}^{1/2}\text{cm}^{-1/2}\text{s}^{-1} (1.56 \times 10^{-7} \text{ C/m}^2)$ and $|\sigma_{SL,0}| = 0.177 \text{ g}^{1/2}\text{cm}^{-1/2}\text{s}^{-1} (5.9 \times 10^{-7} \text{ C/m}^2)$, respectively. As to our knowledge, there were no prior published reports of the combined surface charge density $\sigma_{SL,0}$ on the surface of vertical soap films accounting for the surface charge density associated with surfactant $\sigma_s = 0.23 \text{ C/m}^2$ (discussed below) and its partial and significant “neutralization” by the adjacent Stern layer. However, such significant reduction of $\sigma_{SL,0}$ in comparison to σ_s is quite expectable, since a dramatic reduction of the potential in the diffuse layer due to the presence of the Stern layer is well known.

Equations (10.7) and (10.8) show that the film lifetime t_f is

$$t_f = T_0 \frac{\left[1 - \sigma_{SL,0} (\Phi_{\text{bottom}} - \Phi_{\text{top}}) / \varepsilon\right]}{(1-\Theta) \left[1 + 6(\lambda_D / h_0) \Theta\right]^{3/2}} \quad (10.10)$$

where the film lifetime without the imposed electric field is T_0 given by Eq. (10.A2) in Appendix 10.A2.

Take for the estimate for SDS $\sigma_{SL,0}(\Phi_{\text{bottom}} - \Phi_{\text{top}})/\varepsilon \sim \mp 0.0118$ and $\Theta = 2\sigma_{SL,0}E_x/(\rho gh_0) \sim \pm 0.082$, which correspond to $\sigma_{SL,0} = -0.177 \text{ g}^{1/2}\text{cm}^{-1/2}\text{s}^{-1}$ and $(\Phi_{\text{bottom}} - \Phi_{\text{top}}) = \pm 40 \text{ V}$ (with the upper signs for Case I and the lower ones for Case II), as well as $6(\lambda_D/h_0) \sim 0.72$ and $\varepsilon \sim 2 \text{ g/s}^2$. Note also that the surface elasticity ε is found from the cut-off time T_0 measured without the electric field applied using Eq. (10.A2) of Appendix 10.A2 as $\varepsilon = T_0\rho(gh_0)^{3/2}$, as it was done in Sett et al. (2013).

Substituting these values in Eq. (10.10), we obtain for Case I $t_{f,I} \approx 1.01T_0$ and for Case II $t_{f,II} \approx 1.001T_0$, with both $t_{f,I}$ and $t_{f,II}$ being larger than T_0 , and $t_{f,I} > t_{f,II}$ in qualitative agreement with the data sets 2 and 3 in Fig. 10.3. In Case I, the film stabilization is due to the traction imposed by the electroosmotic flow directed upward, which appears to be stronger than the associated pressure build-up near the upper dead end. In Case II, the film stabilization is due to the pressure build-up near the lower dead end, which is stronger than the traction imposed by the electroosmotic flow directed downward.

Take for the estimate the Debye length $\lambda_D \approx \sqrt{\varepsilon_i k_B T / 8\pi e^2 c_\infty} \approx 3 \text{ nm}$ (where k_B is the Boltzmann constant, T is temperature, e is proton charge, and c_∞ is the bulk concentration of surfactant in solution). The specific conductance measured in the experiment at the moment when drainage begins is of the order of $7 \times 10^{-3} \text{ S/cm}$ (Fig. 10.6c, the curve corresponding to 25 V in Case I with the upper electrode being cathode) with the contributions from the bulk and surface conductivity and the electroosmotic flow. The surface conductance of the Stern layer

(with charge per unit area opposite in sign but close in the magnitude to the charge density associated with surfactant taken for the estimate as $\sigma_s = 0.23 \text{ C/m}^2$) is equal to $K_s = 2\mu_e |\sigma_s|$, where the electric mobility $\mu_e = D_b e / k_B T = 38 \times 10^{-9} \text{ m}^2 / (\text{Vs})$, and D_b is the bulk diffusion coefficient. The specific conductance in the bulk $\sigma_{\text{bulk}} = 2D_b e^2 c_\infty / k_B T$. The ratio $\delta_D = K_s / \sigma_{\text{bulk}} = |\sigma_s| / (e c_\infty)$ determines the thickness of the thinning film at which the surface conductance reaches the bulk one. This is the so-called Dukhin length [Dukhin (1993)]. For a 16 mM SDS solution (Fig. 10.6, the curve corresponding to 25 V in Case I) $\delta_D = 149 \text{ nm}$. This value of the film thickness is reached at $t=64 \text{ s}$. Then, at $t>64 \text{ s}$, the surface conductance becomes more and more dominant factor, and the measured electric conductance increases dramatically (Fig. 10.6). Indeed, the overall conductance presented in Fig. 10.6 is defined as $\sigma(t) = I(t) L_{\text{ver}} / [h(t) L_{\text{hor}} 2U]$, which incorporates contributions of the surface and bulk conductance as $\sigma(t) = K_s \delta_D^2 / [h(t)] + \sigma_{\text{bulk}} h_{\text{bulk}}(t) / [h(t)]$, where $h_{\text{bulk}}(t)$ is the part of the film thickness with the bulk conductance. When the film thins, the ratio $h_{\text{bulk}}(t) / [h(t)] \rightarrow 0$, and thus $\sigma(t) \rightarrow K_s \delta_D^2 / [h(t)]$, which tends to infinity, since $h(t) \rightarrow 0$.

The film stabilization effects demonstrated in the present work on an individual vertical film, can be employed for the foam stabilization as well, since the same physical mechanisms are involved [Exerowa and Kruglyakov (1997); Lawrence (1929); Zaniquelli and Galembeck (1985)]. This, indeed happens in the experiment with the gravity settler [Jun et al. (2012)], (cf. Fig. 10.8a) with the 16 mM SDS solution foam as the results shown in Figs. 10.8b and 10.8c reveal. The cap of the gravity settler and the base plate were made of aluminum, and these metallic ends served as the top and bottom electrodes, to which external voltage source was

connected as shown in Fig. 10.8a. The cylindrical column was of glass, serving as the dielectric gap between the two electrodes. The volume of liquid drained from the foam column in the cylindrical gravity settler was significantly diminished at both polarities applied compared to the case with no voltage applied. Therefore, the electric effects found and explained in the experiments with drainage from the individual films are fully at play at both polarities in the general case of foams.

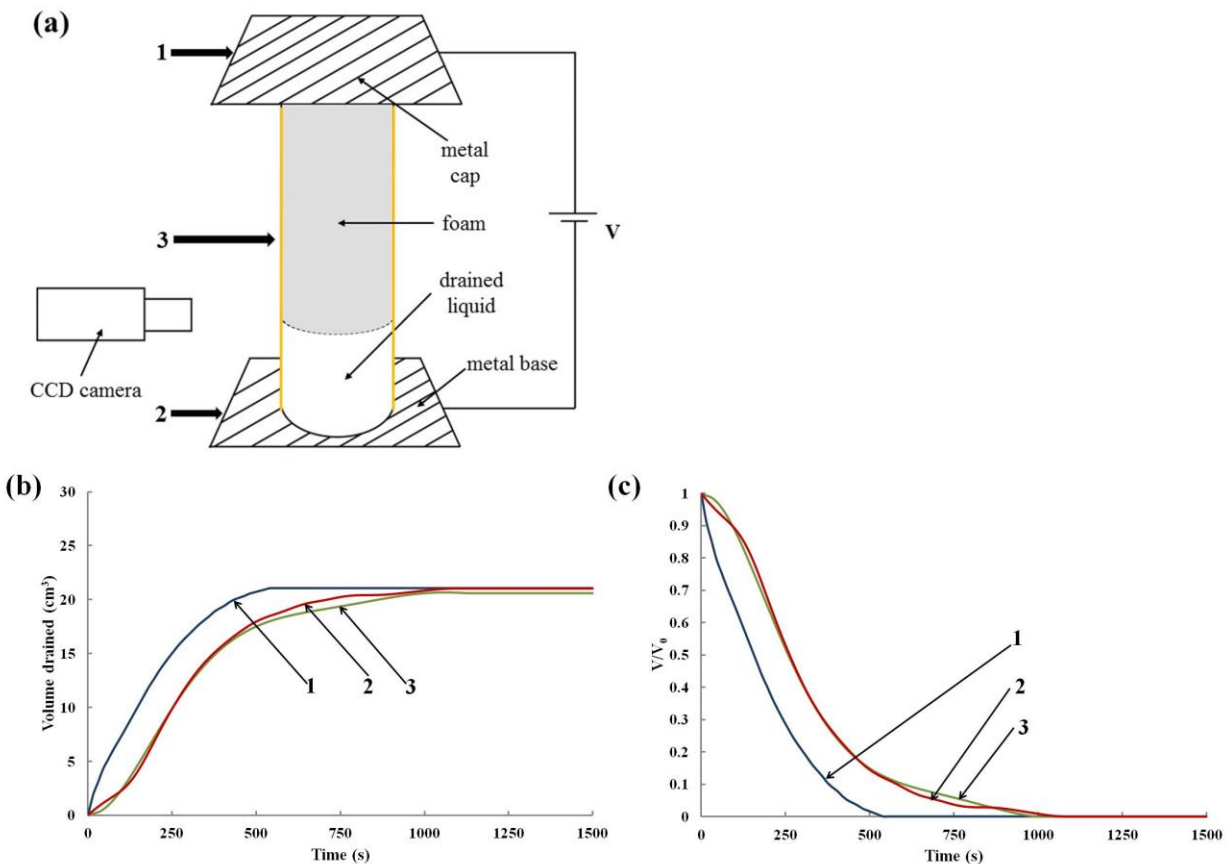


Figure 10.8. (a) Sketch of the experiments with gravity settler. (b) Volume of liquid drained. (c) Drainage curves with V being the instantaneous volume of liquid in the foam rendered dimensionless by the initial total volume of liquid in the foam V_0 . The results obtained for the 16 mM SDS solution foam at voltage of 40 V applied to the foam for the first 1500 s. Curve 1

(blue) -no voltage applied, 2 (red) -top electrode is cathode (Case I), 3 (green) -top electrode is anode (Case II).

10.5 Conclusion

Vertical plane films of anionic and cationic surfactants, in distinction from non-ionic surfactants, can be stabilized against gravitational drainage, which can be significantly decelerated, on a frame with the upper and lower parts being electrodes sustaining the electric field. The application of the electric field to vertical plane films of anionic and cationic surfactants trigger three physical mechanisms: (i) the surface charge redistribution, which affects surface elasticity, (ii) the electroosmotic flow in the diffuse layer, and (iii) pressure build-up near the film end to which the electroosmotic flow is directed.

The film stabilization against drainage is rather counter-intuitive, since it is observed irrespective of the applied polarity, albeit the duration of the decelerated drainage depends on the polarity. As our results show, while surface elasticity can be increased or decreased depending on the applied polarity, the electrical stabilization of the film drainage and its duration mostly stems from the following two competing phenomena: the first one being the traction imposed by the electroosmotic flow, and the second one being the pressure build-up near the end of the frame. When the polarity is such that the electroosmotic flow is directed upward (against gravity), the pressure build-up happens near the upper end of the frame and counteracts the electroosmotic flow, albeit being weaker. On the other hand, in cases where the electroosmotic flow is directed downward (in the gravity direction), pressure build-up happens near the lower end of the frame, albeit being stronger. In both cases, the stronger effect acts against gravity and stabilizes drainage, albeit to a different degree. The electrical stabilization was observed not only

in the case of individual vertical films of surfactant solutions but also on foams in a gravity settler with electrodes on the top and bottom.

Electrokinetic phenomena are in focus as an attractive means of micromixing and transport in microchannels [Wu and Li (2008)], in situations where liquid electrolytes are polarized near solid walls with the embedded or induced charges and the electrokinetic flows arise in such polarized near-wall layers when they are subjected to an imposed electric field. Free surfactant films considered in our work present an interesting case of a micro- and even a nanochannel with no solid walls. Then, the individual surfactant films similar to those studied here can be used as an instrument in studies of the micellization process and micelles structures, as well as transport and self-organization, e.g. crystallization, of different charged solutes, in particular, biologically important compounds.

Appendix

10.A1 The effect of the surfactant exchange between the surface and the bulk on the surface elasticity

The effect of the exchanges of surfactants between the surface and bulk is estimated using comparison between the characteristic adsorption/desorption time τ_{ads} and the time spent by surfactants in the dynamic meniscus accompanying film withdrawal from the bulk $\tau_{\text{dyn}} \approx L_{\text{ver}} / u_{\text{withdrawal}}$, where $u_{\text{withdrawal}}$ is the frame withdrawal velocity. In the present experiments $L_{\text{ver}}=4$ cm and $u_{\text{withdrawal}} \approx 2$ cm/s. Therefore, $\tau_{\text{dyn}} \approx 2$ s. On the other hand, τ_{ads} is at least of the order of 100 s. Since $\tau_{\text{dyn}} \ll \tau_{\text{ads}}$ contribution of the adsorption/desorption of surfactant is negligible. Moreover, it is negligible even on the scale of the entire drainage experiment in Figs. 10.3 and 10.4, which is about 40-90 s. The conclusion about the negligible

effect of surfactant adsorption/desorption on the surface elasticity value in the present case is in agreement with the estimates in [Sett et al. (2013); Levich and Technica (1962); Langevin and Sonin (1994)]. Indeed, both the bulk and surface liquid elements are equally stretched when a film is formed. Therefore, concentration gradient across the film is negligibly small, and diffusion-driven supply of surfactant required for adsorption at a depleted section might be sustained only by the bulk and surface diffusion along the film. The characteristic times of these processes are $\tau_{Db} \approx a^2 / D_b$ and $\tau_{Ds} \approx a^2 / D_s$, respectively, where D_b and D_s denote the bulk and surface diffusion coefficients, respectively, and $a \sim L_{vet}/10 \sim 10^{-1}$ cm. Taking $D_b \approx 10^{-5} \text{ cm}^2/\text{s}$ and $D_s \approx 10^{-7} \text{ cm}^2/\text{s}$ as in [Sett et al. (2013); Langevin and Sonin (1994)], one obtains $\tau_{Db} \approx 10^3 \text{ s}$ and $\tau_{Ds} \approx 10^5 \text{ s}$, much longer than the drainage process of 40-90 s. Therefore, the effect of the surfactant adsorption/desorption on the surface elasticity is negligibly small in the present case.

10.A2 Surface elasticity and drainage in the absence of the electric field

In the absence of the electric field, it was shown in the framework of the quasi-one-dimensional theory [Sett et al. (2013)] that the film thickness close to its top is given by the following linear dependence on time

$$h(x, t) = h_0 \left(1 - \frac{t}{T_0} \right) \quad (10.A1)$$

where the time T_0 is

$$T_0 = \frac{\varepsilon}{\rho (gh_0)^{3/2}} \quad (10.A2)$$

with h_0 being the initial thickness, ρ being liquid density and g being gravity acceleration. It should be emphasized that the quasi-one-dimensional drainage character can be sustained in the presence of the imposed electric field (cf. Appendix 10.A3).

Surface elasticity and its importance deserve several additional comments. When lipid layers, proteins and fatty acids, polymers or biopolymers are present in a surface layer or a film, surface viscosity and/or surface viscoelasticity, as well as bulk viscosity and/or viscoelasticity, become an additional or even dominating factor compared to surface elasticity [Bhamla et al. (2014)]. It should be emphasized that in some cases such surfactants also introduce a significant surface rigidity. Under such conditions, drainage through thin liquid films, especially in contact with a solid surface on one side, resembles lubrication flow in a journal bearing rather than drainage of films of the low molecular weight SDS and DTAB solutions studied in Sett et al. (2013) and the present work. The drainage process is radically different in these cases. Indeed, the dependences of the film thickness on time revealed in the experiments of Sett et al. (2013) for plane and spherical films surrounded by air on both sides are all linear from the initial thickness h_0 of about 1 μm to the black film of about 30 nm. This behavior is fully explained and accounted for by surface elasticity Sett et al. (2013). On the contrary, very thick spherical films, which are affected by surface viscosity and viscoelasticity at the free surface and are in contact with a solid surface on the other side, reveal the highly nonlinear dependences of the film thickness on time in the range from about 100 μm down to about 10 μm [Bhamla et al. (2014)].

10.A3 The imposed electric field

In the present case, a further analysis is required to elucidate to what extent the electric field imposed by the frame-like electrodes depicted in Fig. 10.1b is uniform for the quasi-one-dimensional approach still being applicable. This implies solving the Laplace equation for the electric potential Φ in a rectangle with, for example, $\Phi = -1$ on the top electrode, $\Phi = 1$ on the bottom electrode and $\Phi = 0$ at the dielectric insets (Φ is rendered dimensionless by potential U). Assume that a rectangle is located in the complex plane $\omega = \xi + i\eta$, where i is the imaginary unit, and has lengths $2L$ in the ξ -direction and L' in the η -direction, rendered dimensionless by an arbitrary length scale ℓ . Such a rectangle can be conformally mapped onto the upper half-plane of the complex plane $z = X + iY$, with all its sides being mapped onto the real axis X . This is achieved by the Schwarz-Christoffel mapping [Polya and Latta (1974)], which yields the mapping function for rectangle as $z = \text{sn}(\omega)$, with $\text{sn}(\omega)$ being the Jacobian elliptic sine function. Since the boundary conditions for Φ are mapped onto the real axis X , the solution in the z -plane is given by the Poisson integral [Polya and Latta (1974)], while the solution in the physical plane ω is restored via the mapping function. Then, the complex potential χ is introduced, and the conjugate strength of the electric field is found as $\bar{E} = -d\chi/d\omega$. For the frames symmetric relative to the η -axis this yields

$$\bar{E} = E_{\xi} - iE_{\eta} = \frac{2}{\pi i} \left(\frac{X_1}{X_1^2 - z^2} + \frac{X_2}{X_2^2 - z^2} \right) \sqrt{(1 - z^2)(1 - k^2 z^2)} \quad (10.A3)$$

where $z = \text{sn}(\omega)$, $X_1 = \text{sn}(\omega_1)$, and $X_2 = \text{sn}(\omega_2)$, with subscripts 1 and 2 corresponding to the lower and upper right vertices of the rectangle, respectively (with $\eta_1 = 0$). Also, k is determined by L as $L = K(k^2)$, with K denoting the complete elliptic integral of the 1st kind, and $L' = K(k'^2)$, where $k' = \sqrt{1 - k^2}$.

The electric fields imposed on the surfactant solution films by different electrodes are illustrated in Fig. 10.A1, where κ is the dimensionless distance of the ends of the dielectric insets from the lower and upper vertices along the vertical rectangle sides. In Figs. 10.A1a and 10.A1b the field in the central part of the rectangular frames with dimensional horizontal and vertical sides of $L_{\text{hor}} = 2L\ell = 3.708\ell$ and $L_{\text{ver}} = L'\ell = 1.854\ell$ is sufficiently uniform, and the electric field strength at $\xi=\eta=0$ is $E_{\eta} = 1.07U/\ell$ in Fig. 10.A1a and $E_{\eta} = 1.087U/\ell$ in Fig. 10.A1(b), with variation in the η -direction at $\xi=0$ of about 1 % in both cases. However, for the frames of Figs. 10.A1c and 10.A1d such variation is about 50%.

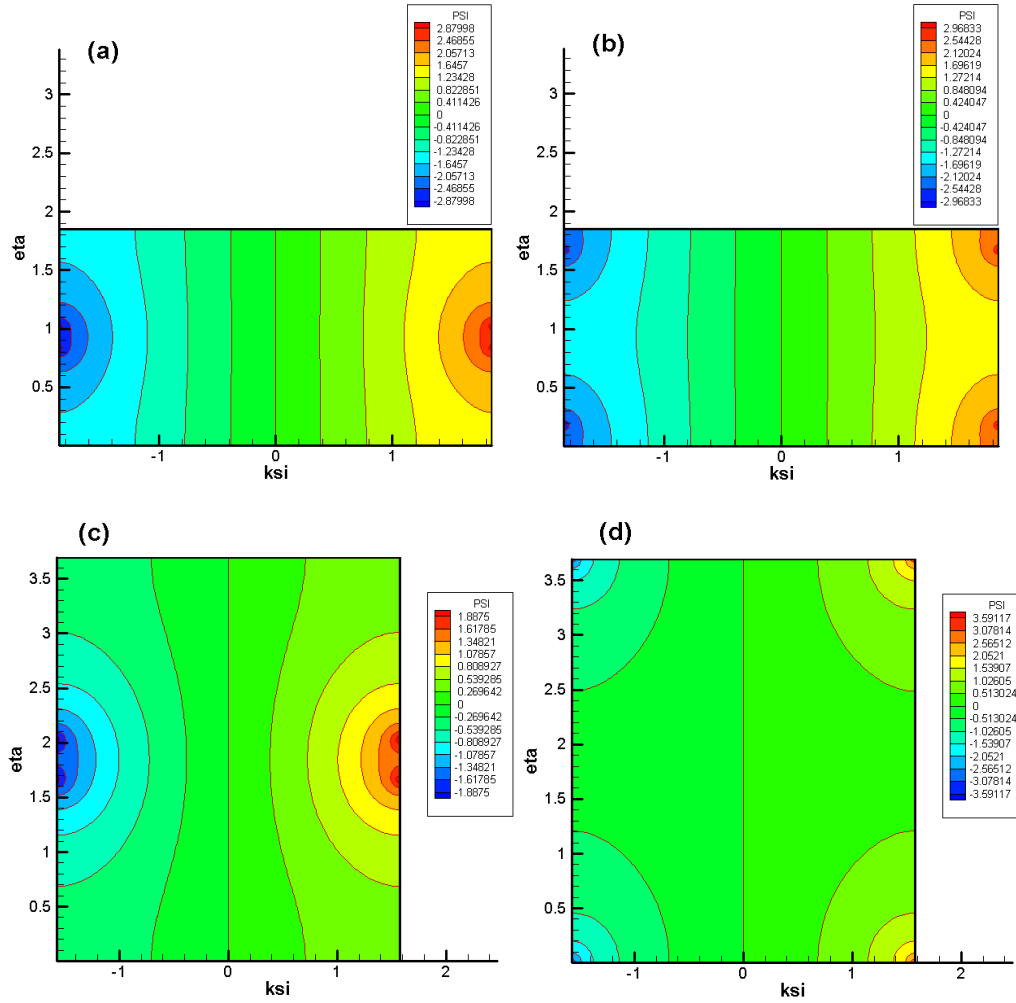


Figure 10.A1. The imposed electric field structure. The field-strength lines are shown on the color map of the imaginary part ψ of the complex potential. (a) $k = k' = 1/\sqrt{2}$, $\kappa = 0.45$; (b) $k = k' = 1/\sqrt{2}$, $\kappa = 0.001$; (c) $k = 0.1$, $\kappa = 0.45$; (d) $k = 0.1$, $\kappa = 0.001$. Here parameter κ determines equal dimensionless distances of the ends of the dielectric insets in the vertical sides of the wire frames from the corresponding vertices.

CHAPTER 11

CONCLUSION

In the present work, various aspects governing the drainage of thin surfactant films were investigated. A novel experimental setup was designed to characterize the physical properties of such thin films like surface elasticity and disjoining pressure by measuring time dependent film thickness using the interferometric technique. The calculated values of the surface elasticity and disjoining pressure were found to be similar to those in literature as established by the other methods. Thereby the present inexpensive and simple technique is established as a useful novel tool. The effect of different forces counteracting to gravitational drainage, namely the concentrational Marangoni effect (the surface elasticity), disjoining pressure, ionic effect of salts and electrokinetic phenomena were elucidated.

Several new phenomena were observed during drainage. The fluffy aggregates formed by the bilayers of trisiloxane surfactants created high disjoining pressure during the later stages of drainage thereby stabilizing them and extending them much longer than ordinary films. These findings could be directly correlated to foamability and foam stability of the trisiloxane and mixed surfactant solutions, creating foam having high foamability and stability. These highly stabilized foams were then used in gypsum slurry important for the manufacturing of dry wallboards, which led to a significant decrease in total water consumption in the entire manufacturing process.

The addition of salts to surfactant solution led to a very interesting result where we found that ionic salts have a critical concentration till which they act as foaming agents and beyond which they acts as defoamers.

The application of the electric field to planar foam films led to their stabilization, irrespective of the polarity and contrary to general intuition. The observed novel phenomena were explained by an interplay between the electroosmotic flow and the pressure rise appearing in the flow into a dead end.

Foams are used widely in numerous industries and understanding their physical properties and the intrinsic physical mechanisms is necessary for a better utilization and application of different surfactants. The findings of the present work are useful for understanding foams from the perspective of their drainage from thin lamellae, and can be valuable in applications in all industries pertaining to foams.

CHAPTER 12

CITED LITERATURE

- Afanasyev, Y. D., Andrews, G. T., & Deacon, C. G. (2011). Measuring soap bubble thickness with color matching. *American Journal of Physics*, 79(10), 1079-1082.
- Alexander, S. (1977). Adsorption of chain molecules with a polar head a scaling description. *Journal de Physique*, 38(8), 983-987.
- Alexandridis, P., Holzwarth, J. F., & Hatton, T. A. (1994). Micellization of poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) triblock copolymers in aqueous solutions: thermodynamics of copolymer association. *Macromolecules*, 27(9), 2414-2425.
- Bahri, M. A., Hoebeke, M., Grammenos, A., Delanaye, L., Vandewalle, N., & Seret, A. (2006). Investigation of SDS, DTAB and CTAB micelle microviscosities by electron spin resonance. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 290(1), 206-212.
- Basheva, E. S., Kralchevsky, P. A., Danov, K. D., Ananthapadmanabhan, K. P., & Lips, A. (2007). The colloid structural forces as a tool for particle characterization and control of dispersion stability. *Physical Chemistry Chemical Physics*, 9(38), 5183-5198.
- Bauduin, P., Renoncourt, A., Touraud, D., Kunz, W., & Ninham, B. W. (2004). Hofmeister effect on enzymatic catalysis and colloidal structures. *Current opinion in colloid & interface science*, 9(1), 43-47.
- Baumgardt, K., Klar, G., & Strey, R. (1982). On the Concentration Dependence of the Mean Aggregation Number of Ionic Micelles as Determined by Stopped-Flow Experiments. *Berichte der Bunsengesellschaft für physikalische Chemie*, 86(10), 912-915.
- Bazilevsky, A. V., & Rozhkov, A. N. (2012). Motion of a foam lamella in a circular channel under a relaxing small pressure jump. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 414, 457-465.
- Berg, S., Adelizzi, E. A., & Troian, S. M. (2004). Images of the floating world: Drainage patterns in thinning soap films. *Physics of Fluids*, 16(9), S6-S6.
- Berg, S., Adelizzi, E. A., & Troian, S. M. (2005). Experimental study of entrainment and drainage flows in microscale soap films. *Langmuir*, 21(9), 3867-3876.
- Bergeron, V. (1997). Disjoining pressures and film stability of alkyltrimethylammonium bromide foam films. *Langmuir*, 13(13), 3474-3482.

- Bergström, M., & Pedersen, J. S. (1999). Structure of pure SDS and DTAB micelles in brine determined by small-angle neutron scattering (SANS). *Physical Chemistry Chemical Physics*, 1(18), 4437-4446.
- Berr, S. S., Coleman, M. J., Jones, R. R. M., & Johnson Jr, J. S. (1986). Small-angle neutron scattering study of the structural effects of substitution of tetramethylammonium for sodium as the counterion in dodecyl sulfate micelles. *The Journal of Physical Chemistry*, 90(24), 6492-6499.
- Bezzobotov, V. Y., Borbely, S., Cser, L., Farago, B., Gladkih, I. A., Ostanevich, Y. M., & Vass, S. (1988). Temperature and Concentration Dependence of Properties of Sodium Dodecyl Sulfate Micelles Determined from Small Angle Neutron Scattering Experiments. *The Journal of Physical Chemistry*, 92(20), 5738-5743.
- Bhamla, M. S., Giacomini, C. E., Balemans, C., & Fuller, G. G. (2014). Influence of interfacial rheology on drainage from curved surfaces. *Soft matter*, 10(36), 6917-6925.
- Bhuiyan, L. B., Bratko, D., & Outhwaite, C. W. (1991). Electrolyte surface tension in the modified Poisson-Boltzmann approximation. *The Journal of Physical Chemistry*, 95(1), 336-340.
- Bonhomme, O., Liot, O., Biance, A. L., & Bocquet, L. (2013). Soft nanofluidic transport in a soap film. *Physical review letters*, 110(5), 054502.
- Boström, M., Kunz, W., & Ninham, B. W. (2005). Hofmeister effects in surface tension of aqueous electrolyte solution. *Langmuir*, 21(6), 2619-2623.
- Boström, M., Williams, D. R. M., & Ninham, B. W. (2004). Why the properties of proteins in salt solutions follow a Hofmeister series. *Current opinion in colloid & interface science*, 9(1), 48-52.
- Boström, M., Williams, D. R., & Ninham, B. W. (2001). Surface tension of electrolytes: specific ion effects explained by dispersion forces. *Langmuir*, 17(15), 4475-4478.
- Boys, C. V. (1958). Soap bubbles, their colours and the forces which mold them (Vol. 542). Courier Corporation.
- Brown, W., Fundin, J., & Miguel, M. D. G. (1992). Poly (ethylene oxide)-sodium dodecyl sulfate interactions studied using static and dynamic light scattering. *Macromolecules*, 25(26), 7192-7198.

- Carey, E., & Stubenrauch, C. (2010). Foaming properties of mixtures of a non-ionic (C 12 DMPO) and an ionic surfactant (C 12 TAB). *Journal of colloid and interface science*, 346(2), 414-423.
- Carey, E., & Stubenrauch, C. (2013). Free drainage of aqueous foams stabilized by mixtures of a non-ionic (C 12 DMPO) and an ionic (C 12 TAB) surfactant. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 419, 7-14.
- Cates, M. E., & Candau, S. J. (1990). Statics and dynamics of worm-like surfactant micelles. *Journal of Physics: Condensed Matter*, 2(33), 6869.
- Chang, H. C., & Yeo, L. Y. (2010). *Electrokinetically driven microfluidics and nanofluidics* (pp. 39-40). Cambridge, UK:Cambridge University Press.
- Chang, H. C., Yossifon, G., & Demekhin, E. A. (2012). Nanoscale electrokinetics and microvortices: how microhydrodynamics affects nanofluidic ion flux. *Annual Review of Fluid Mechanics*, 44, 401-426.
- Craig, V. S. J., Ninham, B. W., & Pashley, R. M. (1993a). Effect of electrolytes on bubble coalescence. *Nature*, 364(6435), 317-319.
- Craig, V. S., Ninham, B. W., & Pashley, R. M. (1993b). The effect of electrolytes on bubble coalescence in water. *The Journal of Physical Chemistry*, 97(39), 10192-10197.
- Croonen, Y., Geladé, E., Van der Zegel, M., Van der Auweraer, M., Vandendriessche, H., De Schryver, F. C., & Almgren, M. (1983). Influence of salt, detergent concentration, and temperature on the fluorescence quenching of 1-methylpyrene in sodium dodecyl sulfate with m-dicyanobenzene. *The Journal of Physical Chemistry*, 87(8), 1426-1431.
- Culick, F. E. C. (1960). Comments on a ruptured soap film. *Journal of applied physics*, 31(6), 1128-1129.
- Danov, K. D., Kralchevska, S. D., Kralchevsky, P. A., Ananthapadmanabhan, K. P., & Lips, A. (2004). Mixed solutions of anionic and zwitterionic surfactant (Betaine): Surface-tension isotherms, adsorption, and relaxation kinetics. *Langmuir*, 20(13), 5445-5453.
- de Gennes, P. G. (1987). Polymers at an interface; a simplified view. *Advances in Colloid and Interface Science*, 27(3), 189-209.
- de Gennes, P. G. (2001). "Young" soap films. *Langmuir*, 17(8), 2416-2419.
- Debrégeas, G., De Gennes, P. G., & Brochard-Wyart, F. (1998). The life and death of "bare" viscous bubbles. *Science*, 279(5357), 1704-1707.

Derjaguin, B. V. (1989). *Theory of Stability of Colloids and Thin Films*. Consultants Bureau/Plenum Publishing Co., New York.

Derjaguin, B. V., Churaev, V. N., & Muller, V. M. (1987). *Surface Forces*. Plenum Press, New York.

Dickinson, E. (2010). Food emulsions and foams: Stabilization by particles. *Current Opinion in Colloid & Interface Science*, 15(1), 40-49.

Dole, M. (1938). A theory of surface tension of aqueous solutions. *Journal of the American Chemical Society*, 60(4), 904-911.

Dole, M., & Swartout, J. A. (1940). A twin-ring surface tensiometer. I. The apparent surface tension of potassium chloride solutions. *Journal of the American Chemical Society*, 62(11), 3039-3045.

Dominguez, A., Fernandez, A., Gonzalez, N., Iglesias, E., & Montenegro, L. (1997). Determination of critical micelle concentration of some surfactants by three techniques. *Journal of Chemical Education*, 74, 1227.

Dorshow, R. B., Bunton, C. A., & Nicoli, D. F. (1983). Comparative study of intermicellar interactions using dynamic light scattering. *The Journal of Physical Chemistry*, 87(8), 1409-1416.

Dos Santos, A. P., & Levin, Y. (2011). Ion specificity and the theory of stability of colloidal suspensions. *Physical review letters*, 106(16), 167801.

Dukhin, S. S. (1993). Non-equilibrium electric surface phenomena. *Advances in Colloid and Interface Science*, 44, 1-134.

Edwards, D. A., Brenner, H., & Wasan, D. T. (1991). *Interfacial Transport Phenomena*. Butterworth-Heinemann, Boston.

Ennis, J., Kjellander, R., & Mitchell, D. J. (1995). Dressed ion theory for bulk symmetric electrolytes in the restricted primitive model. *The Journal of chemical physics*, 102(2), 975-991.

Evans, H. C. (1956). 117. Alkyl sulphates. Part I. Critical micelle concentrations of the sodium salts. *Journal of the Chemical Society (Resumed)*, 579-586.

Exerova, D., & Kruglyakov, P. M. (1998). *Foam and Foam Films: Theory, Experiment, Application*. Elsevier, Amsterdam.

Finet, S., Skouri-Panet, F., Casselyn, M., Bonnete, F., & Tardieu, A. (2004). The Hofmeister effect as seen by SAXS in protein solutions. *Current opinion in colloid & interface science*, 9(1), 112-116.

Georgieva, D., Cagna, A., & Langevin, D. (2009). Link between surface elasticity and foam stability. *Soft Matter*, 5(10), 2063-2071.

Germick, R. J., Rehill, A. S., & Narsimhan, G. (1994). Experimental investigation of static drainage of protein stabilized foams—comparison with model. *Journal of food engineering*, 23(4), 555-578.

Görgényi, M., Dewulf, J., Van Langenhove, H., & Héberger, K. (2006). Aqueous salting-out effect of inorganic cations and anions on non-electrolytes. *Chemosphere*, 65(5), 802-810.

Hamburger, H. J. (1886). Ueber den Einfluss chemischer Verbindungen auf Blutkörperchen im Zusammenhang mit ihren Moleculargewichten.

Hayter, J. B., & Penfold, J. (1983). Determination of micelle structure and charge by neutron small-angle scattering. *Colloid and Polymer Science*, 261(12), 1022-1030.

He, M., Hill, R. M., Lin, Z., Scriven, L. E., & Davis, H. T. (1993). Phase behavior and microstructure of polyoxyethylene trisiloxane surfactants in aqueous solution. *The Journal of Physical Chemistry*, 97(34), 8820-8834.

Heydweiller, A. (1910). Concerning the physical characteristics of solutions in correlation. II. Surface tension and electronic conductivity of watery salt solutions. *Ann. Phys*, 33, 145-185.

Hill, R. M. (1999). *Silicone Surfactants*. Marcel Dekker, New York.

Hofmeister, F. (1888a). On the understanding of the effects of salts. *Arch. Exp. Pathol. Pharmacol.* (Leipzig), 24, 247-260.

Hofmeister, F. (1888b). Zur lehre von der wirkung der salze. *Archiv für experimentelle Pathologie und Pharmakologie*, 25(1), 1-30.

Hofmeister, F. (1890). On the theory of the action of salts, *Arch. Exp. Pathol. Pharmacol.*, Leipzig, 27, 395-413.

Hofmeister, F. (1891). Die Beteiligung gelöster Stoffe an Quellungsvorgängen. *Arch. f. exper. Path.*, 28, 210.

Hunter, T. N., Pugh, R. J., Franks, G. V., & Jameson, G. J. (2008). The role of particles in stabilising foams and emulsions. *Advances in Colloid and Interface Science*, 137(2), 57-81.

Isenberg, C. (1992). *The Science of Soap Films and Bubbles*.

Israelachvili, J. (1992). *Interfacial and Surface Forces*. Academic Press, London.

Ivanov, I. B., Ananthapadmanabhan, K. P., & Lips, A. (2006). Adsorption and structure of the adsorbed layer of ionic surfactants. *Advances in colloid and interface science*, 123, 189-212.

Ivanov, I. B., Slavchov, R. I., Basheva, E. S., Sidzhakova, D., & Karakashev, S. I. (2011). Hofmeister effect on micellization, thin films and emulsion stability. *Advances in colloid and interface science*, 168(1), 93-104.

Jarvis, N. L., & Scheiman, M. A. (1968). Surface potentials of aqueous electrolyte solutions. *The Journal of Physical Chemistry*, 72(1), 74-78.

Jenkins, F. A., & White, H. E. (1957). *Fundamentals of optics*. Tata McGraw-Hill Education.

Jones, G., & Ray, W. A. (1935). The surface tension of solutions. *Journal of the American Chemical Society*, 57(5), 957-958.

Jones, G., & Ray, W. A. (1937). The surface tension of solutions of electrolytes as a function of the concentration. I. A differential method for measuring relative surface tension. *Journal of the American Chemical Society*, 59(1), 187-198.

Jones, G., & Ray, W. A. (1941a). The Surface Tension of Solutions of Electrolytes as a Function of the Concentration II*. *Journal of the American Chemical Society*, 63(1), 288-294.

Jones, G., & Ray, W. A. (1941b). The surface tension of solutions of electrolytes as a function of the concentration. III. Sodium chloride. *Journal of the American Chemical Society*, 63(12), 3262-3263.

Jones, G., & Ray, W. A. (1942). The surface tension of solutions of electrolytes as a function of the concentration. IV. Magnesium sulfate. *Journal of the American Chemical Society*, 64(12), 2744-2745.

Jones, M. N. (1967). The interaction of sodium dodecyl sulfate with polyethylene oxide. *Journal of colloid and interface science*, 23(1), 36-42.

Jun, S., Pelot, D. D., & Yarin, A. L. (2012). Foam consolidation and drainage. *Langmuir*, 28(12), 5323-5330.

Jungwirth, P., & Tobias, D. J. (2001). Molecular structure of salt solutions: a new view of the interface with implications for heterogeneous atmospheric chemistry. *The Journal of Physical Chemistry B*, 105(43), 10468-10472.

Kale, K. M., Cussler, E. L., & Evans, D. F. (1980). Characterization of micellar solutions using surfactant ion electrodes. *The Journal of Physical Chemistry*, 84(6), 593-598.

- Karakashev, S. I. (2014). How to determine the adsorption energy of the surfactant's hydrophilic head? How to estimate easily the surface activity of every simple surfactant? *Journal of colloid and interface science*, 432, 98-104.
- Karakashev, S. I., & Ivanova, D. S. (2010a). Thin liquid film drainage: Ionic vs. non-ionic surfactants. *Journal of colloid and interface science*, 343(2), 584-593.
- Karakashev, S. I., & Nguyen, A. V. (2009). Do liquid films rupture due to the so-called hydrophobic force or migration of dissolved gases? *Langmuir*, 25(6), 3363-3368.
- Karakashev, S. I., Ivanova, D. S., Angarska, Z. K., Manev, E. D., Tsekov, R., Radoev, B., Slavchov, R., & Nguyen, A. V. (2010b). Comparative validation of the analytical models for the Marangoni effect on foam film drainage. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 365(1), 122-136.
- Karakashev, S. I., Manev, E. D., & Nguyen, A. V. (2008a). Effect of double-layer repulsion on foam film drainage. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 319(1), 34-42.
- Karakashev, S. I., Manev, E. D., Tsekov, R., & Nguyen, A. V. (2008b). Effect of ionic surfactants on drainage and equilibrium thickness of emulsion films. *Journal of colloid and interface science*, 318(2), 358-364.
- Karakashev, S. I., Nguyen, A. V., & Manev, E. D. (2007). A novel technique for improving interferometric determination of emulsion film thickness by digital filtration. *Journal of colloid and interface science*, 306(2), 449-453.
- Karakashev, S. I., Nguyen, A. V., Manev, E. D., & Phan, C. M. (2005). Surface foam film waves studied with high-speed linescan camera. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 262(1), 23-32.
- Karakashev, S. I., Nguyen, P. T., Tsekov, R., Hampton, M. A., & Nguyen, A. V. (2008c). Anomalous ion effects on rupture and lifetime of aqueous foam films formed from monovalent salt solutions up to saturation concentration. *Langmuir*, 24(20), 11587-11591.
- Karakashev, S. I., Stöckelhuber, K. W., & Tsekov, R. (2011). Wetting films on chemically patterned surfaces. *Journal of colloid and interface science*, 363(2), 663-667.
- Karakashev, S., Tsekov, R., & Manev, E. (2001). Adsorption of alkali dodecyl sulfates on air/water surface. *Langmuir*, 17(17), 5403-5405.
- Karapetsas, G., Craster, R. V., & Matar, O. K. (2011). On surfactant-enhanced spreading and superspreading of liquid drops on solid surfaces. *Journal of Fluid Mechanics*, 670, 5-37.

- Kjellander, R. (1995). Modified Debye-Hückel approximation with effective charges: an application of dressed ion theory for electrolyte solutions. *The Journal of Physical Chemistry*, 99(25), 10392-10407.
- Koehler, S. A., Hilgenfeldt, S., & Stone, H. A. (2000). A generalized view of foam drainage: experiment and theory. *Langmuir*, 16(15), 6327-6341.
- Koelsch, P., Viswanath, P., Motschmann, H., Shapovalov, V. L., Brezesinski, G., Möhwald, H., & Schollmeyer, H. (2007). Specific ion effects in physicochemical and biological systems: Simulations, theory and experiments. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 303(1), 110-136.
- Kornev, K. G., Neimark, A. V., & Rozhkov, A. N. (1999). Foam in porous media: thermodynamic and hydrodynamic peculiarities. *Advances in colloid and interface science*, 82(1), 127-187.
- Kunz, W. (2010). Specific ion effects in colloidal and biological systems. *Current Opinion in Colloid & Interface Science*, 15(1), 34-39.
- Kunz, W., Henle, J. W. N. B., & Ninham, B. W. (2004a). 'Zur Lehre von der Wirkung der Salze' (about the science of the effect of salts): Franz Hofmeister's historical papers. *Current Opinion in Colloid & Interface Science*, 9(1), 19-37.
- Kunz, W., Nostro, P. L., & Ninham, B. W. (2004b). The present state of affairs with Hofmeister effects. *Current Opinion in Colloid & Interface Science*, 9(1), 1-18.
- Langevin, D., & Sonin, A. A. (1994). Thinning of soap films. *Advances in colloid and interface science*, 51, 1-27.
- Langmuir, I. (1917). The constitution and fundamental properties of solids and liquids. II. Liquids. 1. *Journal of the American Chemical Society*, 39(9), 1848-1906.
- Lawrence, A. S. C. (1929). Soap films: a study of molecular individuality. G. Bell.
- Leontidis, E. (2002). Hofmeister anion effects on surfactant self-assembly and the formation of mesoporous solids. *Current opinion in colloid & interface science*, 7(1), 81-91.
- Leung, R., & Shah, D. O. (1986). Dynamic properties of micellar solutions: I. Effects of short-chain alcohols and polymers on micellar stability. *Journal of colloid and interface science*, 113(2), 484-499.
- Levich, V. G. (1962). *Physicochemical Hydrodynamics*. Prentice Hall, Englewood Cliffs.
- Levich, V. G., & Technica, S. (1962). *Physicochemical hydrodynamics (Vol. 689)*. Englewood Cliffs, NJ: Prentice-hall.

- Lewith, S. (1887). Zur lehre von der Wirkung der Salze. Archiv für experimentelle Pathologie und Pharmakologie, 24(1-2), 1-16.
- Limbeck, R. V. (1888). Zur Lehre von der Wirkung der Salze. Archiv für experimentelle Pathologie und Pharmakologie, 25(1), 69-86.
- Lucassen, J. (1981). Dynamic properties of free liquid films and foams. In Anionic Surfactants (pp. 217-265). Marcel Dekker The Netherlands.
- Lurie, A. I. (2005). Theory of Elasticity. Springer, Berlin.
- Lyklema, J., Scholten, P. C., & Mysels, K. J. (1965). Flow in thin liquid films. The Journal of Physical Chemistry, 69(1), 116-123.
- Magrabi, S. A., Dlugogorski, B. Z., & Jameson, G. J. (2001). Free drainage in aqueous foams: model and experimental study. AIChE journal, 47(2), 314-327.
- Maldarelli, C. (2011). On the microhydrodynamics of superspreading. Journal of Fluid Mechanics, 670, 1-4.
- Marc̃elja, S. (2006). Selective coalescence of bubbles in simple electrolytes. The Journal of Physical Chemistry B, 110(26), 13062-13067.
- Markin, V. S., & Volkov, A. G. (2002). Quantitative theory of surface tension and surface potential of aqueous solutions of electrolytes. The Journal of Physical Chemistry B, 106(45), 11810-11817.
- Markovich, T., Andelman, D., & Podgornik, R. (2014). Surface tension of electrolyte solutions: A self-consistent theory. EPL (Europhysics Letters), 106(1), 16002.
- Marrucci, G. (1969). A theory of coalescence. Chemical engineering science, 24(6), 975-985.
- Marrucci, G., & Nicodemo, L. (1967). Coalescence of gas bubbles in aqueous solutions of inorganic electrolytes. Chemical Engineering Science, 22(9), 1257-1265.
- Miles, G. D., Ross, J., & Shedlovsky, L. (1950). Film drainage: A study of the flow properties of films of solutions of detergents and the effect of added materials. Journal of the American Oil Chemists' Society, 27(7), 268-273.
- Miller, R., & Liggieri, L. (Eds.). (2009). Interfacial rheology. CRC Press.
- Morrison, I. D., & Ross, S. (2002). Colloidal Dispersions: Suspensions, Emulsions and Foams. Wiley Interscience, New York.

- Münzer, E. (1898). Zur Lehre von der Wirkung der Salze. *Naunyn-Schmiedeberg's Archives of Pharmacology*, 41(1), 74-96.
- Murray, B. S., & Ettelaie, R. (2004). Foam stability: proteins and nanoparticles. *Current opinion in colloid & interface science*, 9(5), 314-320.
- Mysels, K. J. (1959). *Soap films: studies of their thinning and a bibliography*. Pergamon press.
- Mysels, K. J. (1968). Dynamic processes in soap films. *The Journal of general physiology*, 52(1), 113-124.
- Mysels, K. J. (1986). Surface tension of solutions of pure sodium dodecyl sulfate. *Langmuir*, 2(4), 423-428.
- Mysels, K. J., & Cox, M. C. (1962). An experimental test of Frankel's law of film thickness. *Journal of Colloid Science*, 17(2), 136-145.
- Mysels, K. J., & Jones, M. N. (1966). Direct measurement of the variation of double-layer repulsion with distance. *Discussions of the Faraday Society*, 42, 42-50.
- Mysels, K. J., Cox, M. C., & Skewis, J. D. (1961). The measurement of film elasticity. *The Journal of Physical Chemistry*, 65(7), 1107-1111.
- Newton, I. (1704). *Opticks: or a treatise of the reflexions, refractions, inflexions and colours of light*.
- Nguyen, A. V., & Schulze, H. J. (2004). *Colloidal Science of Flootation*. Marcel Dekker, Inc.
- Nierstrasz, V. A., & Frens, G. (1999). Marginal regeneration and the Marangoni effect. *Journal of colloid and interface science*, 215(1), 28-35.
- Nierstrasz, V. A., & Frens, G. (2001). Marangoni flow driven instabilities and marginal regeneration. *Journal of colloid and interface science*, 234(1), 162-167.
- Nikolov, A. D., Kralchevsky, P. A., Ivanov, I. B., & Wasan, D. T. (1989). Ordered micelle structuring in thin films formed from anionic surfactant solutions: II. Model development. *Journal of colloid and interface science*, 133(1), 13-22.
- Noskov, B. A., Aleksandrov, D. A., Gumennik, E. V., Krotov, V. V., & Miller, R. (1998). The dynamic surface elasticity of sodium dodecyl sulfate solutions in the frequency range 0.8-5 Hz. *Colloid journal of the Russian Academy of Sciences*, 60(2), 204-210.
- Noskov, B. A., Alexandrov, D. A., & Miller, R. (1999). Dynamic surface elasticity of micellar and nonmicellar solutions of dodecyldimethyl phosphine oxide. Longitudinal wave study. *Journal of colloid and interface science*, 219(2), 250-259.

- Oh, S. G., & Shah, D. O. (1991). Relationship between micellar lifetime and foamability of sodium dodecyl sulfate and sodium dodecyl sulfate/1-hexanol mixtures. *Langmuir*, 7(7), 1316-1318.
- Oh, S. G., & Shah, D. O. (1993). The effect of micellar lifetime on the rate of solubilization and detergency in sodium dodecyl sulfate solutions. *Journal of the American Oil Chemists' Society*, 70(7), 673-678.
- Onsager, L., & Samaras, N. N. (1934). The Surface Tension of Debye-Hückel Electrolytes. *The Journal of Chemical Physics*, 2(8), 528-536.
- Ostwald, W. (1886). *Lehrbuch der allgemeinen Chemie* (Vol. 2). W. Engelmann.
- Particle Sciences Technical Brief (2012). Phase Behavior of Surface-active Solutes. Particle Sciences, Drug Development Services, Vol 6.
- Pashley, R. M., & Craig, V. S. J. (1997). Effects of electrolytes on bubble coalescence. *Langmuir*, 13(17), 4772-4774.
- Pitzer, K. S. (1973). Thermodynamics of electrolytes. I. Theoretical basis and general equations. *The Journal of Physical Chemistry*, 77(2), 268-277.
- Pitzer, K. S., & Kim, J. J. (1974). Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes. *Journal of the American Chemical Society*, 96(18), 5701-5707.
- Pitzer, K. S., & Mayorga, G. (1973). Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. *The Journal of Physical Chemistry*, 77(19), 2300-2308.
- Pitzer, K. S., & Mayorga, G. (1974). Thermodynamics of electrolytes. III. Activity and osmotic coefficients for 2-2 electrolytes. *Journal of Solution Chemistry*, 3(7), 539-546.
- Plateau, J. (1873). *Statique expérimentale et théorique des liquides soumis aux seules forces moléculaires* (Vol. 2). Gauthier-Villars.
- Poiseuille, J. L. (1844). *Recherches expérimentales sur le mouvement des liquides dans les tubes de très-petits diamètres*. Imprimerie Royale.
- Polya, G., & Latta, G. (1974). Complex variables.
- Prince, M. J., & Blanch, H. W. (1990). Transition electrolyte concentrations for bubble coalescence. *AIChE Journal*, 36(9), 1425-1429.

Pringsheim, N., Pfeffer, W., & Strasburger, E. (1858). *Jahrbücher für wissenschaftliche Botanik* (Vol. 1). Wilh. Engelmann.

Prins, A., Arcuri, C., & Van Den Tempel, M. (1967). Elasticity of thin liquid films. *Journal of Colloid and Interface Science*, 24(1), 84-90.

Prud'homme, R. K. (1995). *Foams: Theory: Measurements: Applications* (Vol. 57). CRC Press.

Quina, F. H., Nassar, P. M., Bonilha, J. B., & Bales, B. L. (1995). Growth of sodium dodecyl sulfate micelles with detergent concentration. *The Journal of Physical Chemistry*, 99(46), 17028-17031.

Ramani, M. V., Kumar, R., & Gandhi, K. S. (1993). A model for static foam drainage. *Chemical engineering science*, 48(3), 455-465.

Randles, J. E. B. (1957). Ionic hydration and the surface potential of aqueous electrolytes. *Discussions of the Faraday Society*, 24, 194-199.

Rao, A. A., Wasan, D. T., & Manev, E. D. (1982). Foam stability—effect of surfactant composition on the drainage of microscopic aqueous films. *Chemical Engineering Communications*, 15(1-4), 63-81.

Raoult, F. M. (1888). By Raoult's method of determining the lowering of the freezing point in very dilute solutions. London, Brown and Morris.

Ruckenstein, E. (2012). Superspreading: A possible mechanism. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 412, 36-37.

Sakai, M. (1988). Physico-chemical properties of small bubbles in liquids. In *Dispersed Systems* (pp. 136-142). Steinkopff.

Santini, E., Ravera, F., Ferrari, M., Stubenrauch, C., Makievski, A., & Krägel, J. (2007). A surface rheological study of non-ionic surfactants at the water–air interface and the stability of the corresponding thin foam films. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 298(1), 12-21.

Saulnier, L., Boos, J., Stubenrauch, C., & Rio, E. (2014). Comparison between generations of foams and single vertical films—single and mixed surfactant systems. *Soft matter*, 10(29), 5280-5288.

Schurtenberger, P., Mazer, N., & Känzig, W. (1983). Static and dynamic light scattering studies of micellar growth and interactions in bile salt solutions. *The Journal of Physical Chemistry*, 87(2), 308-315.

Setschenow, J. Z. (1889). Über die konstitution der salzlosungen auf grund ihres verhaltens zu kohlen-säure. *Z. physik. Chem*, 4, 117-125.

Sett, S., Karakashev, S. I., Smoukov, S. K., & Yarin, A. L. (2015). Ion-specific effects in foams. *Advances in colloid and interface science*, 225, 98-113.

Sett, S., Sahu, R. P., Pelot, D. D., & Yarin, A. L. (2014b). Enhanced Foamability of Sodium Dodecyl Sulfate Surfactant Mixed with Superspreader Trisiloxane-(poly)ethoxylate. *Langmuir*, 30(49), 14765-14775.

Sett, S., Sahu, R. P., Sinha-Ray, S., & Yarin, A. L. (2014a). Superspreaders Versus “Cousin” Non-Superspreaders: Disjoining Pressure in Gravitational Film Drainage. *Langmuir*, 30(10), 2619-2631.

Sett, S., Sahu, R. P., Sinha-Ray, S., & Yarin, A. L. (2016). Experimental Investigation of Eletrokinetic Stabilization of Gravitational Drainage of Ionic Surfactants Films. *Electrochimica Acta*, 187, 693-703.

Sett, S., Sinha-Ray, S., & Yarin, A. L. (2013). Gravitational drainage of foam films. *Langmuir*, 29(16), 4934-4947.

Shah, S. S., Jamroz, N. U., & Sharif, Q. M. (2001). Micellization parameters and electrostatic interactions in micellar solution of sodium dodecyl sulfate (SDS) at different temperatures. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 178(1), 199-206.

Shah, S. S., Saeed, A., & Sharif, Q. M. (1999). A study of micellization parameters and electrostatic interactions in micellar solution of sodium dodecyl sulfate. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 155(2), 405-412.

Shanks, P. C., & Franses, E. I. (1992). Estimation of micellization parameters of aqueous sodium dodecyl sulfate from conductivity data. *The Journal of Physical Chemistry*, 96(4), 1794-1805.

Sheludko, A. (1967). Thin liquid films. *Advances in Colloid and Interface Science*, 1(4), 391-464.

Slavchov, R. I., & Novev, J. K. (2012). Surface tension of concentrated electrolyte solutions. *Journal of colloid and interface science*, 387(1), 234-243.

Slavchov, R. I., Karakashev, S. I., & Ivanov, I. B. (2014). Ionic surfactants and ion-specific effects: adsorption, micellization, thin liquid films. *Surfactant science and technology, retrospects and prospects*. CRC Press, New York.

Sonin, A. A., Bonfillon, A., & Langevin, D. (1994). Thinning of soap films: The role of surface viscoelasticity. *Journal of colloid and interface science*, 162(2), 323-330.

Squires, T. M., & Bazant, M. Z. (2004). Induced-charge electro-osmosis. *Journal of Fluid Mechanics*, 509, 217-252.

Squires, T. M., & Quake, S. R. (2005). Microfluidics: Fluid physics at the nanoliter scale. *Reviews of modern physics*, 77(3), 977.

Stein, H. N. (1993). The drainage of free liquid films. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 79(1), 71-80.

Stubenrauch, C., & Miller, R. (2004). Stability of foam films and surface rheology: an oscillating bubble study at low frequencies. *The Journal of Physical Chemistry B*, 108(20), 6412-6421.

Stubenrauch, C., & von Klitzing, R. (2003). Disjoining pressure in thin liquid foam and emulsion films—new concepts and perspectives. *Journal of Physics: condensed matter*, 15(27), R1197.

Stubenrauch, C., Shrestha, L. K., Varade, D., Johansson, I., Olanya, G., Aramaki, K., & Claesson, P. (2009). Aqueous foams stabilized by n-dodecyl- β -D-maltoside, hexaethyleneglycol monododecyl ether, and their 1: 1 mixture. *Soft Matter*, 5(16), 3070-3080.

Tanford, C. (1980). *The Hydrophobic Effect: Formation of Micelles and Biological Membranes* 2d Ed. J. Wiley.

Taylor, G. (1959). The dynamics of thin sheets of fluid. III. Disintegration of fluid sheets. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 253(1274), 313-321.

Theander, K., & Pugh, R. J. (2003). Synergism and foaming properties in mixed nonionic/fatty acid soap surfactant systems. *Journal of colloid and interface science*, 267(1), 9-17.

Tobias, D. J., & Hemminger, J. C. (2008). Chemistry. Getting specific about specific ion effects. *Science (New York, NY)*, 319(5867), 1197-1198.

Valkovska, D. S., Danov, K. D., & Ivanov, I. B. (2002). Stability of draining plane-parallel films containing surfactants. *Advances in colloid and interface science*, 96(1), 101-129.

Venzmer, J. (2011). Superspreading—20years of physicochemical research. *Current Opinion in Colloid & Interface Science*, 16(4), 335-343.

Venzmer, J. (2013). Personal communication

Venzmer, J., & Wilkowski, S. P. (1998). Trisiloxane surfactants-Mechanisms of spreading and wetting. ASTM Special Technical Publication, 1347, 140-154.

Wagner, C. (1924). The surface tension of dilute solutions of electrolytes. *Phys. Z*, 25, 474-477.

Walderhaug, H., & Knudsen, K. D. (2008). Microstructures in aqueous solutions of a polyoxyethylene trisiloxane surfactant and a cosurfactant studied by SANS and NMR self-diffusion. *Langmuir*, 24(19), 10637-10645.

Weaire, D., & Hutzler, S. (1999). *The Physics of Foams*. Oxford University Press, Oxford.

Weissenborn, P. K., & Pugh, R. J. (1995a). Surface tension and bubble coalescence phenomena of aqueous solutions of electrolytes. *Langmuir*, 11(5), 1422-1426.

Weissenborn, P. K., & Pugh, R. J. (1995b). Coalescence of bubbles in aqueous solutions of electrolytes (No. CONF-9510120--). Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO (United States).

Weissenborn, P. K., & Pugh, R. J. (1996). Surface tension of aqueous solutions of electrolytes: relationship with ion hydration, oxygen solubility, and bubble coalescence. *Journal of Colloid and Interface Science*, 184(2), 550-563.

Wu, Z., & Li, D. (2008). Micromixing using induced-charge electrokinetic flow. *Electrochimica Acta*, 53(19), 5827-5835.

Xia, J., Dubin, P. L., & Kim, Y. (1992). Complex formation between poly (oxyethylene) and sodium dodecyl sulfate micelles: Light scattering, electrophoresis, and dialysis equilibrium studies. *The Journal of Physical Chemistry*, 96(16), 6805-6811.

Yossifon, G., & Chang, H. C. (2008). Selection of nonequilibrium overlimiting currents: universal depletion layer formation dynamics and vortex instability. *Physical review letters*, 101(25), 254501.

Young, C. Y., Missel, P. J., Mazer, N. A., Benedek, G. B., & Carey, M. C. (1978). Deduction of micellar shape from angular dissymmetry measurements of light scattered from aqueous sodium dodecyl sulfate solutions at high sodium chloride concentrations. *The Journal of Physical Chemistry*, 82(12), 1375-1378.

Zaniquelli, M. E. D., & Galembeck, F. (1985). Modification of foam drainage by electroosmotic effect. *Langmuir*, 1(6), 647-651.

Zhao, J., & Zou, W. (2013). Foams stabilized by mixed cationic gemini/anionic conventional surfactants. *Colloid and Polymer Science*, 291(6), 1471-1478.

CHAPTER 13

APPENDIX

The following are the statements from the Publisher granting permission to use previously published articles of the present author in this thesis. Permission granted by American Chemical Society addresses the work on gravitational drainage from sections 2.1, 3.1, as well as Chapter 4; on superspreaders versus “cousin” non-superspreaders from sections 2.2, 3.2 and Chapter 5; and also for the work on enhanced foamability from sections 2.3 and 3.3, and Chapter 7. These sections are reproduced by permission of American Chemical Society and the link of the papers is as follows:

<http://pubs.acs.org/doi/abs/10.1021/la4003127>

<http://pubs.acs.org/doi/abs/10.1021/la404754d>

<http://pubs.acs.org/doi/abs/10.1021/la503542b>

Permission granted by Elsevier addresses the work on ion specific effects from sections 2.4 and 3.5, as well as Chapter 9, and also for the work on electrokinetic effect from sections 2.5 and 3.6, as well as Chapter 10. These sections are reproduced by permission of Elsevier and the link of the papers is as follows:

<http://www.sciencedirect.com/science/article/pii/S0001868615001487>

<http://www.sciencedirect.com/science/article/pii/S0013468615308483>

1/26/2016

Rightslink® by Copyright Clearance Center



RightsLink®

Home

Account
Info

Help



Title: Gravitational Drainage of Foam Films
Author: S. Sett, S. Sinha-Ray, A. L. Yarin
Publication: Langmuir
Publisher: American Chemical Society
Date: Apr 1, 2013
 Copyright © 2013, American Chemical Society

Logged in as:
 Soumyadip
 Sett

LOGOUT

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

1/26/2016

Rightslink® by Copyright Clearance Center



RightsLink®

Home

Account
Info

Help

**Title:**Superspreaders Versus "Cousin"
Non-Superspreaders: Disjoining
Pressure in Gravitational Film
DrainageLogged in as:
Soumyadip Sett

LOGOUT

Author:S. Sett, R. P. Sahu, S. Sinha-Ray,
et al**Publication:** Langmuir**Publisher:** American Chemical Society**Date:** Mar 1, 2014

Copyright © 2014, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

1/26/2016

Rightslink® by Copyright Clearance Center



RightsLink®

Home

Account
Info

Help

**Title:**

Enhanced Foamability of Sodium Dodecyl Sulfate Surfactant Mixed with Superspreader Trisiloxane-(poly)ethoxylate

Logged in as:

Soumyadip Sett

LOGOUT

Author:

S. Sett, R. P. Sahu, D. D. Pelot, et al

Publication: Langmuir**Publisher:** American Chemical Society**Date:** Dec 1, 2014

Copyright © 2014, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

ELSEVIER LICENSE TERMS AND CONDITIONS

Jan 26, 2016

This is a License Agreement between Soumyadip Sett ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Soumyadip Sett
Customer address	842 W Taylor St. CHICAGO, IL 60607
License number	3796591112047
License date	Jan 26, 2016
Licensed content publisher	Elsevier
Licensed content publication	Advances in Colloid and Interface Science
Licensed content title	Ion-specific effects in foams
Licensed content author	Soumyadip Sett, Stoyan I. Karakashev, Stoyan K. Smoukov, Alexander L. Yarin
Licensed content date	November 2015
Licensed content volume number	225
Licensed content issue number	n/a
Number of pages	16
Start Page	98
End Page	113
Type of Use	reuse in a thesis/dissertation
Portion	full article
Format	both print and electronic
Are you the author of this Elsevier article?	Yes
Will you be translating?	No
Title of your thesis/dissertation	Dynamics of Thin Surfactant Films
Expected completion date	May 2016

Estimated size (number of pages)	250
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD

ELSEVIER LICENSE TERMS AND CONDITIONS

Jan 26, 2016

This is a License Agreement between Soumyadip Sett ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Soumyadip Sett
Customer address	842 W Taylor St. CHICAGO, IL 60607
License number	3796600042806
License date	Jan 26, 2016
Licensed content publisher	Elsevier
Licensed content publication	Electrochimica Acta
Licensed content title	Experimental Investigation of Electrokinetic Stabilization of Gravitational Drainage of Ionic Surfactants Films
Licensed content author	Soumyadip Sett, Rakesh P. Sahu, Suman Sinha-Ray, Alexander L. Yarin
Licensed content date	1 January 2016
Licensed content volume number	187
Licensed content issue number	n/a
Number of pages	11
Start Page	693
End Page	703
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	full article
Format	both print and electronic
Are you the author of this Elsevier article?	Yes
Will you be translating?	No
Title of your thesis/dissertation	Dynamics of Thin Surfactant Films

Expected completion date	May 2016
Estimated size (number of pages)	250
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD

CHAPTER 14

CURRICULUM VITAE

SOUMYADIP SETT

Department of Mechanical and Industrial Engineering, University of Illinois at Chicago (UIC)
842 West Taylor Street, Chicago, Illinois 60607-7022

Education

University of Illinois at Chicago, Chicago, IL *Aug. 2011 – May 2016*

- Ph.D. Candidate, Mechanical and Industrial Engineering
- Advisor: Professor Alexander L. Yarin
- GPA: 3.91/4.0

Jadavpur University, Kolkata, India *Aug 2007 – July 2011*

- Bachelor of Engineering, Power Engineering
- Graduated first class with honors, Marks 85.6%

Awards and Honors

- Received Dean's Scholar Award (2015), the most distinguished award offered by UIC to graduate students for outstanding academic contributions.
- Received Chicago Consular Corps Scholarship (2015) for outstanding academic performance as foreign student studying at UIC.
- Received Litvin Graduate Honor Award (2014) from Mechanical and Industrial Engg. Department, UIC, in recognition of academic achievement and service to the department and graduate student community.
- Received Chancellor's Student Service Award (2014) from University of Illinois at Chicago in recognition of volunteer service to the university and community.
- Received Travel Award from Graduate Student Council at UIC for presenting conference paper in American Physical Society Spring Meeting in March 2015.
- Student Presenter Award from UIC to present conference paper in March 2014.

Publications

1. Sett, S.; Sinha-Ray, S.; Yarin, A.L. Gravitational Drainage of Foam Films. *Langmuir*, 2013, 29(16), 4934 – 4947.
2. Sett, S.; Sahu, R.P.; Sinha-Ray, S.; Yarin, A.L. Superspreaders Versus “Cousin” Nonj-Superspreaders: Disjoining Pressure in Gravitational Film Drainage. *Langmuir*, 2014, 30(10). 2619-2631.
3. Sett, S.; Sahu, R.P.; Pelot, D.D.; Yarin, A.L. Enhanced Foamability of Sodium Dodecyl Sulfate Surfactant Mixed with Superspreader Trisiloxane-(poly)ethoxylate. *Langmuir*, 2014, 30(49), 14765-14775.

4. Sahu, R.P.; Sett, S.; Yarin, A.L.; Pourdeyghi, B. Impact of Aqueous Suspension Drops onto Non-Wettable Porous Membranes : Hydrodynamic Focusing and Penetration of Nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2015, 467, 31-45.
5. Sett, S.; Lee, M.W.; Yarin, A.L. Biodegradable and Biocompatible Soy Protein/Polymer/Adhesive Sticky Nano-textured Patches for Prevention of Esca Fungi Invasion into Pruning Cuts and Wounds of Vines. *Journal of Materials Chemistry B*, 2015, 3(10), 2147-2162.
6. Sett, S.; Karakashev, S.I.; Smoukov, S.K.; Yarin, A.L. Ion-Specific Effects in Foams. *Advances in Colloid and Interface Science*, 2015, 225, 98-113.
7. Sett, S.; Sahu, R.P.; Sinha-Ray, S.; Yarin, A.L. Experimental Investigation of Electrokinetic Stabilization of Gravitational Drainage of Ionic Surfactant Films. *Electrochimica Acta*, 2016, 187, 693-703.

Teaching experience

- Fall 2014: Laboratory Instructor for Fluid Mechanics (ME211)
- Fall 2013: Teaching Assistant (TA), Fluid Mechanics (ME 211)
- Spring 2013: Teaching Assistant (TA), Numerical Methods in Mech Engg (ME 428)
- Spring 2012: Teaching Assistant (TA), Fluid Mechanics (ME 211)

Students mentored

- Shalin Patel (BS UIC) – Spring 2014
- Martin Weith (BS UIC) – Fall 2014
- Maninder Singh (BS UIC) – Summer 2014 and Summer 2015
- Kais Kawar (BS UIC) – Fall 2015

Professional societies

- Student member of American Physical Society.
- Student member of Materials Research Society.