RICE UNIVERSITY

Effect of Oils, Soap and Hardness on the Stability of Foams

by

Hui Zhang

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

Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

Clarence A. Miller, Louis Calder Professor
Chemical Engineering

George J. Hirasaki, A. J. Hartsook Professor
Chemical Engineering

Kirk H. Raney, Research Engineer
Shell Chemical L.P.

Mason B. Tomson, Professor
Civil and Environmental Engineering

HOUSTON, TEXAS
SEPTEMBER, 2003
INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI Microform 3122565

Copyright 2004 by ProQuest Information and Learning Company.
All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346
Abstract

Effect of Oils, Soap and Hardness on Stability of Foams

by

Hui Zhang

A systematic study of foam stability in the presence of model nonpolar oils and their mixtures with oleic acid was conducted for two commonly used surfactants (anionic and nonionic) under neutral and alkaline conditions with different amounts of dissolved calcium. In some cases insoluble calcium soap or microemulsions formed in situ. Measurements of the rate of collapse of a foam column were supplemented by microscopic observations of individual foam and "pseudoemulsion" films and by measurement of equilibrium and dynamic surface and interfacial tensions.

In the absence of calcium soap use of equilibrium values of conventional entry E, spreading S, and bridging B coefficients was adequate to explain the effect of oils on stability of foams containing the nonionic surfactant. For the anionic surfactant E must be modified to account for electrostatic repulsion in the pseudoemulsion film. Calcium soap particles at the oil-water interface facilitate entry of oil drops and the associated bridging of foam films or Plateau borders, producing a substantial antifoam effect. When this synergistic effect occurs, conventional values of E govern oil entry. In some cases for oils that were mixtures of triolein and oleic acid foam is unstable during foam formation and initial foam drainage but stable at later times, behavior which is explained by calculating transient values of E, S, and B.

Addition of n-dodecanol produced significant stabilization of foams of the anionic surfactant containing dispersed oil drops both when calcium soap was present and when
high levels of calcium had destabilized the foam at neutral pH. ESB theory proved useful in predicting this effect. An amine oxide surfactant was less effective as a foam booster.

In the absence of oil, calcium soap particles can destabilize foams of both surfactants. A model for predicting the precipitation boundary including the enhancement of calcium content in the electrical double layers of surfactant micelles yielded results in agreement with experiment. Foam was less stable while precipitation was occurring (hours) than at equilibrium, perhaps because calcium oleate, which initially formed at the interfaces, was extracted as oleate concentration decreased to its equilibrium value.
Acknowledgements

At this very delightful time of my life, I want to express my sincere appreciation to the many people and organizations who have helped this work. I am particularly grateful to:

Professor Clarence A. Miller, my thesis advisor, for his resourceful guidance and assistance in my research and in improving the quality of this thesis. The continuous support and inspiration from him and his wife, Mrs. Hilary Miller, are invaluable gifts to me.

Dr. Kirk H. Raney, Professor George J. Hirasaki and Professor Mason B. Tomson for serving on my thesis committee. Without their advice and generous assistance, this work could not have been achieved.

Dr. Peter R. Garrett, whose insights and ardent assistance greatly advanced this work.

The faculty and staff of the Department of Chemical Engineering at Rice University, and my fellow students in the Interfacial Phenomena Laboratory, for their help and collaboration.

This work was funded by the National Science Fundation. My collaboration with Mr. Greg Shpakoff and Mr. Paul Tortorici from Shell Chemical L.P. has been very beneficial.

Especially, my dear husband, Min Liu, my parents and my sisters for their endless love and encouragement.
# Table of Contents

<table>
<thead>
<tr>
<th>Chapter 1 Project Scope and Objectives</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chapter 2 Background</strong></td>
<td>4</td>
</tr>
<tr>
<td>2.1 Foam</td>
<td>4</td>
</tr>
<tr>
<td>2.1.1 Foam Generation and Foam Structure</td>
<td>4</td>
</tr>
<tr>
<td>2.1.2 Foam Characterization</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Liquid Film</td>
<td>6</td>
</tr>
<tr>
<td>2.2.1 Surface Tension Gradients and Thin Film Structure</td>
<td>6</td>
</tr>
<tr>
<td>2.2.2 Forces in Thin Liquid Films</td>
<td>7</td>
</tr>
<tr>
<td>2.2.2a Capillary Pressure</td>
<td>7</td>
</tr>
<tr>
<td>2.2.2b Disjoining Pressure</td>
<td>8</td>
</tr>
<tr>
<td>2.2.3 Perturbation on Planar Film</td>
<td>11</td>
</tr>
<tr>
<td>2.2.4 Drainage of Liquid Film</td>
<td>13</td>
</tr>
<tr>
<td>2.3 Antifoams and Defoaming Mechanisms</td>
<td>15</td>
</tr>
<tr>
<td>2.3.1 Entry, Spreading and bridging coefficients</td>
<td>15</td>
</tr>
<tr>
<td>2.3.2 Entry Barrier</td>
<td>17</td>
</tr>
<tr>
<td>2.3.3 Liquid Antifoams</td>
<td>21</td>
</tr>
<tr>
<td>2.3.3a Spreading-fluid Entrainment</td>
<td>21</td>
</tr>
<tr>
<td>2.3.3b Bridging-dewetting Mechanism</td>
<td>21</td>
</tr>
<tr>
<td>2.3.3c Oil-bridge Stretching Mechanism</td>
<td>24</td>
</tr>
<tr>
<td>2.3.3d Bridging of Plateau Borders</td>
<td>27</td>
</tr>
<tr>
<td>2.4 Solid Antifoams</td>
<td>27</td>
</tr>
</tbody>
</table>
2.5 Synergistic Antifoam Action by Hydrophobic Solid Particles and Insoluble oils 28

2.6 Foam Boosting Additives and Foam Stability 29

Chapter 3 Materials and Experimental Procedures 31

3.1 Materials 31

3.2 Videomicroscopy Configuration 32

3.3 Experimental Procedures 34

3.3.1 Foam Stability Testing 34

3.3.2 Interfacial/Surface Tension Measurement 36

3.3.3 Horizontal Contacting Experiment 36

3.3.4 Optical Observation of Individual Foam Film in Scheludko Cell 38

3.3.5 Observation of Asymmetric Oil-Water-Air Films 39

3.3.6 Vertical Foam Cell 40

3.3.7 Turbidity Measurement 41

3.3.8 Ultrafiltration 41

3.3.9 Titration 42

Chapter 4 Foam of Commercial Surfactants 43

4.1 Experiments with Anionic Surfactant N25-3S 43

4.1.1 Foam Formation Rate and Foam Stability 43

4.1.2 Dynamic Surface Tension 45

4.1.3a Film thinning behavior- at different surfactant concentrations 46

4.1.3b Film thinning behavior-at different hardness levels 48

4.1.4 Vertical foam cell 52
4.1.5 Discussion 53
  4.1.5a Effect of surfactant concentration on foam behavior 53
  4.1.5b Effect of hardness on foam stability and film drainage 55

4.2 Experiments with Nonionic Surfactant N25-7 58
  4.2.1 Foamability and Foam Stability 58
  4.2.2 Dynamic Surface Tension 59
  4.2.3 Thin Film Behavior 60
  4.2.4 Discussion 63

4.3 Summary 64

Chapter 5 Mechanism for Defoaming Action in Aqueous systems
  by Oils and Calcium Soap 66

5.1 Introduction 66

5.2 Effect of Pure Oils on Foam Stability 67
  5.2.1 Foam Stability 67
  5.2.2 Individual Foam Films 69
  5.2.3 Vertical Foam Cell 70
  5.2.4 ESB Analysis 71

5.3 Effect of Oil Mixtures on Foam Stability 72
  5.3.1 Foam Stability 72
  5.3.2 Video-microscopy Contacting Experiment 74
  5.3.3 Horizontal Foam Films 77
  5.3.4 Stability of Oil-Water-Air Asymmetric Films 78
  5.3.4a Experiments with anionic surfactant N25-3S 78
5.3.4b Experiments with Nonionic surfactant N25-7  81
5.3.4c Experiments with preformed calcium soap particles  82
5.3.5 ESB Analysis  84
5.3.6 Synergism between Oil Drops and Insoluble Soap Particles  88
5.4 Mechanism  89
5.5 Summary  92

Chapter 6 Effect of Fatty Acid and Sodium Soap on Foam behavior  94
6.1 Introduction  94
6.2 Horizontal Contacting Experiment  96
   6.2.1 Experiments in the Absence of N25-3S or N25-7  96
   6.2.2 Experiments in the Presence of N25-3S or N25-7  98
   6.2.3 Discussion of Contacting Results  100
6.3 Horizontal Foam Films  100
6.4 Oil-water-air Asymmetric Films  103
6.5 Foam Stability and ESB Analysis  105
6.6 Summary  109

Chapter 7 Effect of Hardness in the Presence of Oils on Foam Stability  110
7.1 Introduction  110
7.2 Experimental Results  111
   7.2.1 Foam Stability  111
   7.2.2 Video-microscopy Contacting Experiment  114
   7.2.3 Horizontal Foam Films  115
   7.2.4 Oil-water-air Asymmetric Films  116
7.3 Discussion 121
7.4 Summary 124

Chapter 8 Foam Boosting Study 126
8.1 Introduction 126
8.2 Experimental Results with Lauric Alcohol (LA) 126
  8.2.1 Foam Stability 127
  8.2.2 Dynamic and Equilibrium Surface Tension 131
  8.2.3 Pseudoemulsion Films 132
8.3 Experiments with Amine Oxide (C\textsubscript{14}DMAO) 134
  8.3.1 Foam Stability 134
    8.3.1a Results with C16/HOI 134
    8.3.1b Results with TO/HOI 135
  8.3.2 Pseudoemulsion Films 137
8.4 Discussion 141
  8.4.1 Foam-stabilizer Efficacy 141
  8.4.2 Comments on Drainage of Pseudoemulsion Films 145
8.5 Summary 147

Chapter 9 Defoaming Effect of Calcium Soap 148
9.1 Introduction 148
9.2 Experimental Results 148
  9.2.1 Turbidity 148
  9.2.2 Foam Stability - Experiments with Fresh Solutions 151
  9.2.3 Foam Stability - Aging Study 155
9.2.4 Dynamic and Equilibrium Surface Tension 158

9.2.5 Individual Foam Film 159

9.2.5a pH9 solution of 0.01%N25-3S + 0.001%NaOl + 300ppmCa²⁺ 160

9.2.5b pH9 solution of 0.01%N25-3S + 0.005%NaOl + 300ppmCa²⁺ 161

9.2.5c pH9 solution of 0.01%N25-3S + 0.01%NaOl + 300ppmCa²⁺ 162

9.2.5d pH9 solution of 0.01%N25-3S + 0.04%NaOl + 300ppmCa²⁺ 162

9.3 Discussion 163

9.3.1 Effect of Alkalinity on Foam stability in the Presence of Calcium 163

9.3.2 Defoaming by Calcium Soap 164

9.4 Precipitation of Calcium Soap in Micellar Solution of N25-3S 168

9.5 Summary 180

Chapter 10 Conclusions and Future Studies 182

10.1 Conclusions for This Thesis Work 182

10.1.1 ESB Theory 182

10.1.2 Adjusting Foam Stability 183

10.1.3 Effect of Calcium soap on Foam stability in the Absence of Oils 184

10.2 Possibilities for Future Research 185

10.2.1 Drainage of Foam Film and Pseudoemulsion Film 185

10.2.2 Stabilization of Foams with Nonionic Surfactants 185

10.2.3 Others 186

Reference 187

Appendix I Experiment with Preformed Calcium Soap 192
Appendix II  Micelle Modeling-nomenclature  XI  194

Appendix III  Summary of experimental results in Chapter 5  195

Appendix IV  Summary of experimental results in Chapter 6  196

Appendix V  Summary of experimental results in Chapter 7  197

Appendix VI  Summary of experimental results in Chapter 8 - 0.01wt%N25-3S with n-dodecanol as foam booster  198

Appendix VII  Summary of experimental results in Chapter 8 - 0.01wt%N25-3S with C_{14}DMAO as foam booster  199
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Foam structure</td>
<td>4</td>
</tr>
<tr>
<td>2.2</td>
<td>Velocity profile of the draining liquid inside a vertical film</td>
<td>7</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic profile of thin liquid film</td>
<td>7</td>
</tr>
<tr>
<td>2.4</td>
<td>A typical disjoining pressure isotherm</td>
<td>10</td>
</tr>
<tr>
<td>2.5</td>
<td>Sinusoidal perturbations in a thin liquid foam film</td>
<td>12</td>
</tr>
<tr>
<td>2.6</td>
<td>Schematic presentation of the main stages of foam film evolution as observed in the Scheludko cell</td>
<td>14</td>
</tr>
<tr>
<td>2.7</td>
<td>Oil lens, definition of $\Theta^* (\theta_{ow})$ and unstable bridge configurations</td>
<td>23</td>
</tr>
<tr>
<td>2.8</td>
<td>Schematic profile of several defoaming mechanisms</td>
<td>26</td>
</tr>
<tr>
<td>2.9</td>
<td>Suggest antifoaming mechanism of bridging the plateau border by antifoams</td>
<td>27</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic drawing of video microscope system</td>
<td>34</td>
</tr>
<tr>
<td>3.2</td>
<td>Foam stability testing equipment</td>
<td>36</td>
</tr>
<tr>
<td>3.3</td>
<td>Horizontal contacting method</td>
<td>37</td>
</tr>
<tr>
<td>3.4</td>
<td>Schematic Diagram of Microinjection System</td>
<td>37</td>
</tr>
<tr>
<td>3.5</td>
<td>Schematic profile of Scheludko capillary cell</td>
<td>39</td>
</tr>
<tr>
<td>3.6</td>
<td>Schematic presentation of the observation of pseudoemulsion films</td>
<td>40</td>
</tr>
<tr>
<td>3.7</td>
<td>Schematic profile of vertical foam cell</td>
<td>40</td>
</tr>
<tr>
<td>3.8</td>
<td>Schematic Diagram of Vertical-Stage Microscope</td>
<td>41</td>
</tr>
<tr>
<td>4.1</td>
<td>Foam formation rate at different surfactant concentrations</td>
<td>43</td>
</tr>
<tr>
<td>4.2</td>
<td>Foam stability at different hardness levels</td>
<td>44</td>
</tr>
<tr>
<td>4.3</td>
<td>Foamability at different hardness levels</td>
<td>44</td>
</tr>
</tbody>
</table>
Figure 4.4 Effect of hardness on stability of foams of 0.01%N25-3S solution

Figure 4.5 Dynamic surface tension at different surfactant concentrations

Figure 4.6 Effect of hardness on dynamic surface tension

Figure 4.7 Consecutive thinning stages of film made by 0.01%N25-3S

Figure 4.8 Part of the thinning process of film made by 0.05 wt% N25-3S solution

Figure 4.9 Thinning process of film made by 0.1wt% N25-3S

Figure 4.10 Film made from solution of 0.01wt%N25-3S + 20ppm hardness

Figure 4.11 Film made by solution of 0.01wt%N25-3S + 300ppm hardness

Figure 4.12 Film produced from solution of 0.01wt%N25-3S + 300ppm hardness

Figure 4.13 Black spots and white ridges in film produced from

0.01%N25-3S + 300ppmCa\(^{2+}\) solution

Figure 4.14 Film made from solution of 0.01%N25-3S + 3000ppm hardness

Figure 4.15 Results of vertical foam cell

Figure 4.16 Foam quality as a function of hardness

Figure 4.17 Oscillatory form of Π(h) isotherm

Figure 4.18 Schematic presentation of the shifts of disjoining pressure

isotherms as hardness level increases

Figure 4.19 Foam formation rate at different surfactant concentrations

Figure 4.20 Effect of hardness on foam stability and foam formation

Figure 4.21 Dynamic surface tension at different N25-7 concentrations

Figure 4.22 Equilibrium films obtained from 0.01wt%

and 0.05wt% N25-7 solutions

Figure 4.23 Film produced with 0.1wt%N25-7 solution
Figure 4.24 Sequence of the thinning process of film produced with solution containing 0.1wt% N25-7 and 300ppm hardness 62

Figure 4.25 Origin of white spots 63

Figure 5.1 Effect of pure oils on the stability of foams with 0.01wt% N25-3S 68

Figure 5.2 Effect of pure oils on the stability of foams with 0.1wt% N25-7 68

Figure 5.3 Plot of foam height versus time 69

Figure 5.4 Typical cases in films made by 0.01%N25-3S solution containing hexadecane 70

Figure 5.5 Foam in vertical cell of solution containing 0.01wt%N25-3S & 0.02wt% hexadecane 71

Figure 5.6 Effect of oil mixtures on stability of foams with 0.01wt%N25-3S 73

Figure 5.7 Effect of oil mixtures on stability of foams with 0.1wt%N25-7 74

Figure 5.8 Effect of C16/HO1 on decay behavior of foams with 0.01wt%N25-3S and 0.1wt%N25-7 74

Figure 5.9 A drop of C16/HO1 mixture contacted the pH9 solution containing 0.01wt% N25-3S and 300ppm hardness 75

Figure 5.10 A drop of TO/HO1 contacted the pH9 solution containing 0.01wt% N25-3S and 300ppm hardness 75

Figure 5.11 A drop of C16/HO1 in pH9 solution containing 0.1wt%N25-7 & 300ppmCa$^{2+}$ 76

Figure 5.12 A drop of TO/HO1 in pH9 solution containing 0.1wt%N25-7 & 300ppmCa$^{2+}$ 77
Figure 5.13 Foam films produced with pH9 solution of 0.01wt% N25-3S containing 0.01wt% C16/HOl and 300ppm Ca^{2+}  

78

Figure 5.14 Pseudoemulsion films  

79

Figure 5.15. Asymmetrically draining stable pseudoemulsion film formed between oil phase (TO/HOl) and aqueous phase (0.01wt% N25-3S +300ppm Ca^{2+}, pH9)  

80

Figure 5.16 Pseudoemulsion film formed by TO/HOl in pH9 solution containing 0.1wt%N25-7 and 300ppm calcium  

81

Figure 5.17 calcium oleate particles dispersed in hexadecane  

84

Figure 5.18 Pseudoemulsion films between hexadecane (containing 10wt% preformed calcium soap particles) and 0.01wt% N25-3S solution  

84

Figure 5.19 Synergistic effect between oil drops and soap particles on foam stability 

89

Figure 5.20 Foam of solution containing oil (system III)  

89

Figure 5.21 Schematic presentation of a drop (or particle) in foam film  

91

Figure 5.22 Bridging of water-oil-air asymmetric film by spherical particle  

92

Figure 6.1 A C16/HOl drop in pH9 DI water  

97

Figure 6.2 A C16/HOl drop in pH9 solution of 0.01wt%N25-3S  

98

Figure 6.3 A TO/HOl drop in pH9 solution of 0.01wt%N25-3S  

99

Figure 6.4 A C16/HOl drop in pH9 solution of 0.1wt%N25-7  

90

Figure 6.5 Consecutive stages of the drainage of a film produced from pH9 solution containing 0.01wt% N25-3S and 0.02wt% C16/HOl  

101

Figure 6.6 Films produced from pH 9 solution containing 0.1wt%N25-7 and 0.1wt% C16/HOl  

102
Figure 6.7 (a) pH 9 solution containing 0.1wt%N25-7 and 0.1wt% C16/HO1 under reflected light. (b) Unstable thin film produced with such solution

Figure 6.8 Consecutive stages of the drainage of a pseudoemulsion film formed between a drop of C16/HO1 and pH 9 solution of 0.01wt%N25-3S

Figure 6.9 Consecutive thinning process of a pseudoemulsion film formed by a drop of TO/HO1 in pH 9 solution of 0.01wt% N25-3S

Figure 6.10 Effect of C16/HO1 on foam stability at different pH

Figure 6.11 Effect of TO/HO1 on foam stability at different pH

Figure 6.12 Foam stability of N25-3S, NaO1 and their mixture

Figure 7.1 Effect of C16/HO1 on foam stability at different hardness concentrations

Figure 7.2 Effect of TO/HO1 on foam stability at different hardness concentrations

Figure 7.3 a drop of C16/HO1 in the 0.01wt% solution of N25-3S containing 2000ppm hardness

Figure 7.4 Thinning process of a pseudoemulsion film formed by a drop of C16/HO1 in solution containing 0.01wt% N25-3S and 300pp hardness

Figure 7.5 Thinning process of a pseudoemulsion film formed by a drop of TO/HO1 in solution containing 0.01wt% N25-3S and 300ppm hardness

Figure 7.6 Rupture of a pseudoemulsion film formed by a drop of C16/HO1 in solution containing 0.01wt% N25-3S and 2000ppm hardness

Figure 7.7 Thinning process of a pseudoemulsion film formed by a drop of TO/HO1 in solution containing 0.01wt% N25-3S and 2000ppm hardness

Figure 7.8 Comparison of the defoaming stability of hexadecane and C16/HO1 at high hardness
Figure 8.1 Foam stability of solutions containing C16/HO1, calcium soap and different amount of LA

Figure 8.2 Comparison of different foam appearance

Figure 8.3 Foam stability of solutions containing C16/HO1, high hardness and different amount of LA

Figure 8.4 Foam stability of solutions containing TO/HO1, high hardness and different amount of LA

Figure 8.5 Surface tension of pH9 solutions containing N25-3S, 300ppm hardness and dodecanol

Figure 8.6 Pseudoemulsion film between TO/HO1 and 0.01%N25-3S + 0.001% LA + 300ppmCa, pH9 solution

Figure 8.7 A pseudoemulsion film between TO/HO1 and pH9 solution containing 0.01%N25-3S, 0.005%C_{14}DMAO and 300ppm hardness

Figure 8.8 Foam of pH9 solutions containing C16/HO1, 300ppmCa and C_{14}DMAO

Figure 8.9 Foam stability of solutions containing C16/HO1, 2000ppm Ca and different amount of C_{14}DMAO

Figure 8.10 Foam of pH9 solutions containing TO/HO1, 300ppmCa and C_{14}DMAO

Figure 8.11 Foam of pH7 solutions containing TO/HO1, 2000ppmCa and C_{14}DMAO

Figure 8.12 A pseudoemulsion film between C16/HO1 and pH9 solution containing 0.01%N25-3S, 0.005%C_{14}DMAO and 300ppm hardness

Figure 8.13 A pseudoemulsion film (d = 800μm) between TO/HO1 and pH9 solution containing 0.01%N25-3S, 0.0001wt%C_{14}DMAO and 300ppm hardness.

Figure 8.14 A pseudoemulsion film between TO/HO1 and pH9 solution containing
0.01%N25-3S, 0.001wt%C_{14}DMAO and 300ppm hardness.

Figure 8.15 A pseudoemulsion film between TO/HOl and pH9 solution containing 0.01%N25-3S, 0.005wt%C_{14}DMAO and 300ppm hardness

Figure 8.16 Schematic of thick rim formation process in pseudoemulsion film

Figure 9.1 Foam stability with 0.01%N25-3S at different amounts of sodium oleate

Figure 9.2 Effect of pH on foam stability with 0.01%N25-3S and 300ppm hardness

Figure 9.3 Foam stability with 0.02%N25-3S at different amounts of sodium oleate

Figure 9.4 Foam stability with N25-7 at different amounts of sodium oleate

Figure 9.5 Comparison of foam stability between fresh and aged solutions

Figure 9.6 Comparison of foam stability between fresh and aged solutions

Figure 9.7 Comparison of foam stability between fresh and aged solutions of N23-3S in the presence of oil

Figure 9.8 Comparison of foam stability between fresh and aged solutions of N25-7 in the presence of oil

Figure 9.9 Dynamic surface tensions with N25-3S and soap

Figure 9.10 Dynamic surface tensions with N25-7 and soap

Figure 9.11 Foam film with pH9 solution containing 0.01%N25-3S, 0.001%NaOl, 300ppm Ca^{2+}

Figure 9.12 Foam film with pH9 solution containing 0.01%N25-3S, 0.005%NaOl and 300ppm Ca^{2+}

Figure 9.13 Foam film with pH9 solution containing 0.01%N25-3S, 0.01%NaOl, 300ppm Ca^{2+}

Figure 9.14 Foam film with pH9 solution containing 0.01%N25-3S,
0.04%NaOl, 300ppm Ca$^{2+}$

Figure 9.15 Geometry of Plateau border 167

Figure 9.16 Schematic of double layer 172

Figure 9.17 Comparison of Donnan potential and Stern layer potential 174

Figure 9.18 Donnan potential and calcium binding as a function of surfactant concentration 176

Figure 9.19 Measured and predicted $f_{Ca^{2+}}$ 176

Figure 9.20 Precipitation boundary of calcium oleate in micellar solution of N25-3S 178

Figure 9.21 Plot of calcium versus N25-3S for a constant value of NaOl at precipitation boundary 180
List of Tables

Table 5.1 Semi-equilibrium Entry, Spreading, Bridging coefficients and foam stability for solutions of 0.01wt% N25-3S and 0.1wt% N25-7 with pure oily soils

Table 5.2 Equilibrium Entry, Spreading, Bridging coefficients and foam stability for solutions of 0.01wt% N25-3S and 0.1wt% N25-7 with oil mixtures

Table 5.3 Dynamic and Semi-equilibrium E, S, and B with N25-3S

Table 5.4 Dynamic and semi-equilibrium E, S, and B with N25-7

Table 6.1 Semi-equilibrium Entry, Spreading, Bridging coefficients for solutions of 0.01wt% N25-3S and 0.1wt% N25-7 with C16/HOl

Table 6.2 Semi-equilibrium Entry, Spreading, Bridging coefficients for solutions of 0.01wt% N25-3S and 0.1wt% N25-7 with TO/HOl

Table 6.3 Anionic surfactant concentration in aqueous system containing emulsified oil mixtures

Table 7.1 Entry, Spreading, Bridging coefficients and foam stability for C16/HOl and TO/HOl

Table 7.2 Equilibrium Entry, Spreading, Bridging coefficients for C16/HOl and hexadecane

Table 8.1 Entry, Spreading, Bridging coefficients for C16/HOl with calcium soap and LA

Table 8.2 Semi-equilibrium Entry, Spreading, Bridging coefficients for C16/HOl with 2000ppm hardness and LA

Table 8.3 Semi-equilibrium Entry, Spreading, Bridging coefficients for TO/HOl with 2000ppm hardness and LA
Table 8.4 Semi-equilibrium Entry, Spreading, Bridging coefficients for C16/HO1 with calcium soap and C₁₄DMAO

Table 8.5 Semi-equilibrium Entry, Spreading, Bridging coefficients for C16/HO1 with 2000ppm hardness and C₁₄DMAO

Table 8.6 Semi-equilibrium Entry, Spreading, Bridging coefficients for TO/HO1 with calcium soap and C₁₄DMAO

Table 8.7 Semi-equilibrium Entry, Spreading, Bridging coefficients for TO/HO1 with 2000ppm hardness and C₁₄DMAO

Table 8.8 Influences of C₁₄DMAO and LA on surface and interfacial tensions

Table 9.1(a) Transmittance of pH9 solution of 0.01%N25-3S+20ppm

(b) Transmittance of pH9 solution of 0.01%N25-3S+300ppm

(c) Transmittance of pH9 solution of 0.01%N25-3S+3000ppm

(d) Transmittance of pH9 solution of 0.02%N25-3S+300ppm

(e) Transmittance of pH9 solution of 0.05%N25-3S+300ppm

Table 9.2 Transmittance as function of time and concentration of NaO1 for 0.1%N25-7 with 300ppm hardness

Table 9.3 Defoaming effect of calcium soap at different hardness level

Table 9.4 Equilibrium surface tension of solutions containing soap and hardness

Table 9.5 Filtration data of N25-3S at different concentrations

Table 9.6 Filtration data of N25-3S and N25-7 at different hardness levels

Table 9.7 Results of ultrafiltration

Table 9.9 Calculation of precipitation boundary at 300ppm hardness

Table 9.10 Transmittance measurement
Chapter 1 Project Scope and Objectives

This study aimed to provide fundamental understanding of the effect of oily and/or soap additives on foam stability. A wide range of conditions was considered which involved a nonionic and anionic surfactant; a pure hydrocarbon (n-hexadecane), a pure triglyceride (triolein) and their mixtures with oleic acid as oils; and effect of alkalinity and hardness individually and combined. Some of these conditions yielded insoluble calcium soap or microemulsion (perhaps L₃ phase in triolein system) as an additional phase formed in situ. One major objective of this work was to determine the entry, spreading and bridging coefficients (E, S, and B) to see to what extent classical ESB analysis can predict foam stability of this wide range of conditions representative of those in cleaning applications.

Compared with most previous studies on foam stability which have dealt with chemically inert materials such as hydrocarbons, silicone oils and their mixture with hydrophobic solid particles, the novelty of this work on foam was not only the use of liquid triglycerides or hydrocarbons and their mixtures with fatty acids as oils, but also greater emphasis than in previous studies on dynamic effects, e.g., changes in properties of air-water and oil-water interfaces as a function of time and formation of intermediate phases at the interface between oil and surfactant solution as they equilibrate.

The other objective is to improve the understanding of effect of calcium soap with and without oil on foam stability. The defoaming effect of calcium and magnesium soaps is well known but not well understood.
Necessary background information on foam, thin liquid films, foam boosting additives, antifoams and defoaming mechanisms is provided in Chapter 2. Experimental procedures and all equipment set-ups are described in Chapter 3.

Chapter 4 presents the properties such as foamability, foam stability and thin film drainage of a commercial anionic surfactant Neodol® 25-3S (N25-3S) and a commercial nonionic surfactant Neodol® 25-7 (N25-7), which are the two principal surfactants used in this study related to dishwashing and laundry applications. Also, effect of hardness on foam behavior and foam film drainage is discussed in detail.

Chapter 5 describes how oily soils and calcium soap affect foam stability. The first part presents results with pure oils in the absence of calcium soap. Entry barrier caused mainly by the electrical double layer forces in pseudoemulsion film is emphasized. The second part presents results in the presence of both oil and insoluble calcium soap. A synergism between oil and soap particles and a possible mechanism of instability are discussed.

Chapter 6 studies foam properties of an alkali/acidic oil systems, i.e., pH9 solution containing oil mixtures with oleic acid. Interesting dynamic phenomena observed at the oil-water interface, in foam films, and in pseudoemulsion films are described. None of the experiments discussed in this chapter has hardness, i.e. there is no formation of insoluble soap.

In Chapter 7, effect of hardness on foams of 0.01wt% N25-3S is investigated in the presence of oily additives. The most striking result is the great reduction in foam stability at 2000ppm hardness for hexadecane, triolein and their mixtures with oleic acid.
All the experiments were performed at neutral pH. So formation of insoluble calcium soap is negligible.

Chapter 8 describes the investigated effect of two potential boosters, n-dodecanol (LA) and tetradecyl dimethyl amine oxide (C_{14}DMAO), on foam stability for two situations where foam was highly unstable for both C16/HOI (the mixture of hexadecane and oleic acid at weight ratio of 9 to 1) and TO/HOI (the mixture of triolein and oleic acid at weight ratio of 9 to 1) with N25-3S. The first condition is pH9 solution of 0.01wt%N25-3S plus 300ppm hardness, where calcium soap is present. The other is 0.01wt%N25-3S plus 2000ppm hardness at neutral pH, where negligible calcium soap is present.

Chapter 9 focuses on the effect of calcium soap, which was formed by adding both sodium oleate and calcium chloride to alkaline, oil-free solutions of N25-3S and N25-7, on foam stability. It was found that the fresh and aged surfactant solutions containing calcium soap particles produced foams of different stability. Also, the precipitation of calcium soap in surfactant micellar solutions is considered. A model to estimate the association of calcium with surfactant micelles and to predict precipitation boundary of calcium oleate was presented. The model was justified by data obtained with ultrafiltration and turbidity measurement.

Finally, the last chapter summarizes the major findings of this work, and the directions of future work are discussed.
Chapter 2 Background

2.1 Foam

Foam is a disperse system, consisting of gas bubbles that are separated by liquid layers. Foams have various scientific and technological applications in areas such as thermal insulation, fire fighting, ore flotation, food industry, washing etc. [Bikerman, 1953].

2.1.1 Foam Generation and Foam Structure

Like other disperse system foams can be obtained by condensation and dispersion methods [Exerowa and Kruglyakov, 1998]. Condensation method for generating foam involves creation of gas bubbles in the solution by decreasing external pressure or by increasing temperature or as a result of chemical reaction.

In the dispersion method foam results from dispersing gas into bubbles by injecting it into the foaming solution through capillaries, porous plates, or gauzes or by blowing gas through gauzes wetted with a surfactant solution. Gas dispersion can be obtained also by shaking a vessel partially filled with a solution, by simultaneous flow of gas and liquid in a tube, by mechanical mixing of gas and liquid with a stirrer, perforated disks or other devices, by pouring liquid on the surface of the same solution, by sucking gas into a flowing liquid, etc.

The structure of a typical foam formed by, say, shaking a surfactant solution in a cylindrical vessel is shown schematically in Figure 1.1[Garrett, 1993]. In the lower part of the foam, bubbles are spherical (so-called kugelschaum) and of small size with a relatively low gas

![Figure 2.1 Foam structure](image)
volume fraction. As the liquid drains out of the foam, the bubbles distort to form polyhedra. This polyhedral foam (polyederschaum) consists of plane-parallel films joined by channels called Plateau borders. This structure has relatively high gas volume fraction and low density so it first forms at the top of the foam column.

2.1.2 Foam Characterization

The main physicochemical parameters of foam are: volume or foam height if the cross-section area is constant; expansion factors (ratio of the total foam volume to the volume of the liquid in it); dispersity, which is characterized by the distribution function of the gas bubbles by size, specific surface, and the partition of the liquid between the films and the Plateau-Gibbs borders.

The collapse of a foam is the result of four processes that occur in the foam simultaneously [Kruglyakov 1988]: foam syneresis, which consists of outflow of liquid from the films into the Plateau-Gibbs borders and, subsequently out of the borders; coalescence of the bubbles; diffusion growth of the bubbles; evaporation of liquid from the foam. Processes 2 and 3 are accompanied by structural rearrangements of the films and the borders. Usually process 4 can be strongly slowed down or even completely stopped. Its role is, therefore, less fundamental.

In principle, drainage of foams and foam collapse are independent processes. In fact, however, there is a considerable interplay between them. The stability of foams against coalescence and diffusion expansion of bubbles is characterized by the variation of the dispersity with time. In foams that are in contact with the atmosphere the whole volume (or height) of the foam diminishes with time. This process takes place simultaneously with the internal foam collapse, which does not change the foam
volume. The time for complete destruction (or the disappearance of a certain portion of a column) is a parameter widely used as a characteristic of foam stability.

The properties of thin liquid films separating the bubbles (rate of thinning, equilibrium thickness, elasticity, stability etc.) have decisive influence on all processes in a foam and its stability. The study of the various physicochemical properties of thin films in foams, for the present, is very difficult or even impossible in most cases. However, direct and precise measurements can be conducted in free (model) films using special methods and modern apparatus. Great progress in understanding the essence of the different processes and phenomena that take place in foam films has been achieved on the basis of investigations of the free films, especially microscopic films which serve as an adequate model of the film structure in polyhedral foam.

2.2 Liquid Film

2.2.1 Surface Tension Gradients and Thin Film Structure

It's not possible to obtain long-living foams from pure liquid because the presence of surface-active material is necessary for freshly formed foam film to survive. Consider a vertical plane-parallel film in a gravity field for example. For the film to persist, the draining liquid inside the film should take a parabolic velocity profile as shown in Figure 2.2b, instead of a plug flow as shown in Figure 2.2a where all elements of the film accelerated downward, tearing the film apart. A parabolic velocity profile means that velocity gradients exist and exert a viscous stress at the air-liquid surface. And this stress must be and can only be balanced by a tangential force acting in the plane of the surface, that is the gradient of surface tension. In pure liquid this prerequisite cannot be satisfied.
In summary, the introduction of a surfactant into a liquid significantly changes the properties of gas dispersions and liquid films. It lowers the surface tension at the gas/liquid interface, facilitates the dispersion of gas and reduces the size of bubbles, and changes the velocity and regime of bubble rise [Exerowa & Kruglyakov, 1998].

For surfactant solution, a thin liquid film consists of two surface layers bounding a liquid interior. The surface active material present in the liquid phase is preferentially adsorbed at the surface. A typical diagram of a liquid film is shown in Figure 2.3. The thinning of the liquid film is governed by forces within the film which are discussed in the following section.

**Figure 2.3 Schematic profile of thin liquid film**

2.2.2 Forces in Thin Liquid Films

2.2.2a Capillary Pressure
The main driving force for film drainage is the capillary pressure. In the case of an axisymmetrical film, two regions can be observed (see Figure 2.3). The first region is located near the center of the film where the curvature of the interface is small. Thus according to the Young-Laplace equation, the pressure in the first region is nearly equal to the pressure in the disperse phase. The second region, located at the periphery of the film, is called the meniscus region or Plateau border. Here the shape of the interface is concave and, according to the Young-Laplace equation, the pressure in the meniscus region is less than that in the disperse phase. The pressure difference between the center of the film and the meniscus causes the fluid to drain out of the film. The capillary pressure is defined as the pressure difference between the disperse phase and the liquid in the meniscus region. For a horizontal axisymmetrical planar film of radius $R_f$ formed in a capillary ring of internal radius $R_c$, neglecting gravity effects, Eserowa et al [1966] expressed the capillary pressure $P_c$ as:

$$P_c = 2\sigma \frac{R_c}{R_c^2 - R_f^2} \quad (\text{Eq. 2-1})$$  

where $\sigma$ is the interfacial tension.

Note that for $R_f << R_c$, one gets: $P_c = \frac{2\sigma}{R_c}$. \hspace{1cm} (Eq. 2-2)

2.2.2b Disjoining Pressure

Studies on film drainage indicate that when a film reaches a thickness of about 100nm, other forces besides gravity and capillary pressure forces influence its drainage. These forces have a molecular origin and are called by Derjaguin [1955] the disjoining pressure $\Pi$. It represents the excess pressure acting normal to a film interface that results from the overlap of molecular interactions between the interfacial layers. This pressure is a function of the film thickness and can be either positive (disjoining) or
negative (conjoining). In an equilibrium and flat film, the disjoining pressure is equal to the capillary pressure.

A schematic of the disjoining pressure isotherm for a typical ionic surfactant stabilized liquid film is pictured in Figure 2.4. Three primary components of the disjoining pressure are identified and their contributions indicated here:

One is the London-van der Waals attraction term, \( \Pi_{vw} \), which acts to thin a symmetric film. Using the theory of London [1937], which gives the interaction energy between two atoms, the van der Waals disjoining pressure \( \Pi_{vw} \) can be expressed as a function of the film thickness \( 2h \) [Boer 1936, Scheludko 1967].

\[
\Pi_{vw} = -\frac{A}{6\pi(2h)^3} \quad (\text{Eq. 2-3})
\]

Here \( A \) is the Hamaker constant [Hamaker 1937], which can be calculated or determined experimentally. Scheludko and Exerowa [1960] found an average value for the Hamaker constant of \( 7.5\times10^{-13} \text{erg} \) for aqueous films. Lyklema and Mysels [1965], using equilibrium aqueous foam films, obtained a value of \( 6\times10^{-13} \text{erg} \) for the Hamaker constant.

Another component of the disjoining pressure is the electrical double-layer repulsion, \( \Pi_{el} \). The interfaces of films often bear a charge that results from the adsorption of charged surfactant molecules on the surfaces. A double-layer system is thus established in which the surface charge is balanced by the net charge residing in a diffuse layer of counter-ions that extends from the surface into the interior. For films thinner than about 100nm, the electrostatic repulsion due to overlap of diffuse layers of the two surfaces becomes significant. Verwey and Overbeek[1948], Derjaguin and
Laudau [1941] gave a good approximation for the pressure $\Pi_{el}$ due to electrostatic repulsion:

$$\Pi_{el} = 64nk\Theta^2 \exp(-\kappa(2h-2\delta)) \quad \text{(Eq. 2-4)}$$

Where $n =$ number of counterions per cubic centimeter in the bulk solution.

$$\Theta = \tanh(ze\psi / 4kT)$$

$$\kappa^{-1} = (8\pi\varepsilon^2 z^2 n / ekT)^{-1/2}$$

$\kappa^{-1}$ is called the Debye-Hückel characteristic length.

$\delta =$ thickness of the adsorbed monolayer

$\varepsilon =$ dielectric constant for the solvent

$2h =$ thickness of the film

$z =$ valency

$e =$ electronic charge

$\psi =$ potential at the interface

$T =$ temperature

$k =$ Boltzmann constant

Figure 2.4 A typical disjoining pressure isotherm

The third component, $\Pi_{sh}$, is a short range-repulsive pressure. It is called the structural (steric) or hydration disjoining which prevents further thinning [Jones et al., 1966].

These components combine to produce the thick solid line in Figure 2.4, which represents the shape of the disjoining pressure isotherm. It is important to note that thermodynamically stable film can exist only in negatively sloping regions of the isotherm [de Vries, 1958]. In Figure 2.4 the portion of the curve with a positive slope
separates the isotherm into two stable regions, thick (~50nm) common black films (CBF) and thinner (~4nm) Newton black films (NBF). It's worth noting that these designations are somewhat restrictive because they pertain only to systems that give a 180° net optical phase shift due to reflections at the interfaces. Typically, asymmetric films (e.g. oil-water-air pseudoemulsion films) exhibit refractive index changes that produce a zero net phase shift. Hence, below approximately 50nm these films produce white instead of black films. CBF will form if electrical forces are strong enough to balance the combined effect of capillary pressure and the van der Waals forces. In contrast, if electrical forces are weak, the equilibrium thickness of NBF is determined by the short range-repulsive disjoining pressure. Kashchiev [1987] has shown that the theory of rupture by hole nucleation of a bi-layer film can predict the stability of Newton black films.

The dashed lines (labeled as $P_{C1}$ and $P_{C2}$ in Figure 2.4) represent two different capillary pressures applied to the film. When the capillary pressure intersects the isotherm in the negative sloping regions a (meta)stable film will be formed at the corresponding thickness. Therefore, from Figure 2.4 we see that $P_{C1}$ can produce two films with different equilibrium thickness (CBF or NBF) while only thin Newton black films can exist at $P_{C2}$. At even higher capillary pressures rupture of the film is inevitable.

2.2.3 Perturbation on Planar Film

Thickness perturbations, of a thermal or mechanical nature, may be considered to be of a wavelike nature. A symmetrical sinusoidal thickness perturbation is shown in Figure 2.5. Here the thin part of the film is subject to two opposing forces. A capillary
pressure due to the surface tension tends to suck liquid back into the thin part of the film, and a disjoining force tends to push liquid away.

![Diagram showing liquid movement due to disjoining force and capillary force](image)

Figure 2.5 Sinusoidal perturbations in a thin liquid foam film

![Unperturbed Film surfaces](image)

The magnitude of the capillary pressure is determined by the curvature of the film surface. For a given amplitude of the perturbation, the curvature is determined by the wavelength. Thus, the longer the wavelength, the less marked the curvature and the weaker the capillary pressure. Vrij and Overbeek[1969] deduce a critical wavelength above which disjoining forces will dominate over the capillary pressure and the perturbation will spontaneously grow. When the amplitude of the fastest growing perturbation equals the thickness of the film, film rupture is supposed to occur.

Clearly this description ignores any contribution to disjoining forces from stabilizing interactions across a thin film due to adsorbed surfactant. These could arise from overlapping double layers or steric factors due to interaction of bulky surfactant head groups. With many surfactants at sufficiently high concentrations (and therefore adsorption levels) or with suitable amount electrolyte, the growth of perturbations at a particular critical thickness results not in foam film rupture but in the formation of spots of thin metastable film. These spots then grow to cover the whole film area and finally
form a thin film that appears black in reflected light because destructive interference of reflected light occurs.

The concentration at which this transition from rupture to black spot formation occurs is $C_{\text{black}}$. Values for $C_{\text{black}}$ in microscopic films have been measured for a number of surfactants [Exerowa, 1978]. In the case of aqueous solutions of surfactants $C_{\text{black}}$ is generally lower than the CMC.

2.2.4 Drainage of Liquid Film

Thin liquid films are frequently used as a model to study foam stability [Singh et al., 1996; Ivanov, 1980; Malhotra and Wasan, 1987]. The lifetime of such a film depends on both the rate of drainage and the transition phenomenon which occurs when it reaches a critical thickness. The process of film thinning in the absence of antifoam is conveniently divided into the following stages (see Figure 2.6): (1) two bubbles approach to each other; (2) bubbles deform slightly under hydrodynamic interaction; (3) strong deformation usually leads to a film of non-uniform thickness, with a thicker lens-shaped region (usually called a dimple) near the center of the film. However, no dimple is formed under some conditions [Velev et al., 1995]; (4) Sometimes the dimple disappears gradually and forms an essentially plane parallel film (called axisymmetric drainage). Sometimes the dimple leaves the film rapidly and spontaneously due to hydrodynamic instability produced by surface tension driven flow. This is called asymmetric drainage [Joye et al., 1994 & 1996]. The film typically contains several channels (with dynamic regions thicker than the surrounding planar portions of the film) after dimple expulsion, and then gradually thins down to the order of $100\text{nm}$, at which thickness the channels almost disappear; (5) sometimes stepwise transitions in the film thickness through
formation and expansion of thinner spots can be observed. Such a method of liquid film thinning is called “stratification” in the literature [Nikolov & Wasan, 1989; Bergeron & Radke, 1992; Pollard & Radke, 1994] and comes about due to oscillatory structural forces, created by the micelles; (6) if the film doesn’t break during further thinning, it gradually reaches an equilibrium thickness stabilized by the disjoining pressure.

**Figure 2.6** Schematic presentation of the main stages of foam film evolution as observed in the Scheludko cell. Two concave surfaces approach each other (A) and first form a film with a thicker central region (dimple) surrounded by a thinner boundary (B). After the expulsion of the dimple, an almost planner film crossed by several thicker regions (channels) is formed (C). With further film thinning, the channels disappear (D). Several stepwise transitions sometimes observed in a process called “stratification” at film thickness less than 100nm (E). The film eventually reaches its equilibrium thickness (F).

When a foam forms above a bulk liquid phase, liquid drains from the individual films into the Plateau borders (the junctions of the films) and from the latter into the bulk liquid.
2.3 Antifoams and Defoaming Mechanisms

2.3.1 Entry, Spreading and Bridging Coefficients

Existing knowledge of how oils and solid particles either alone or in combination affect foam stability has been reviewed by Garrett [1993] and Aveyard et al. [1994]. Central to the effect of oils is whether or not small oil drops dispersed within an aqueous surfactant solution will "enter" the air-water surface. A strong indicator of whether the drop will enter is given by the so-called classical entry coefficient $E$:

$$E = \gamma_{AW} + \gamma_{OW} - \gamma_{AO} \quad \text{(Eq. 2-5)}$$

Where $\gamma_{WA}, \gamma_{OW}, \gamma_{OA}$ are the air-water, oil-water, and air-oil tensions respectively. Entry is expected for positive values of $E$. As is readily seen, $-E$ is the spreading coefficient of water on oil. Thus, entry does not occur if water spreads spontaneously on oil.

If the drop can enter the interface, other coefficients are generally considered to be important. One is the spreading coefficient $S$ of oil on water:

$$S = \gamma_{AW} - \gamma_{OW} - \gamma_{AO} \quad \text{(Eq. 2-6)}$$

The oil spreads for $S \geq 0$, carrying along some water and thereby producing local thinning of the foam film which can lead to rupture.

The second is the bridging coefficient $B$, defined as follows [Garrett 1980]:

$$B = \gamma_{AW}^2 + \gamma_{OW}^2 - \gamma_{AO}^2 \quad \text{(Eq. 2-7)}$$

Even when $S \leq 0$, so that the oil drop forms a lens at the air-water surface instead of spreading, the foam will become unstable once the drop has entered its other surface so that it spans the film, provided that $B > 0$ [Garrett 1980, 1993].

As emphasized particularly by Aveyard et al [1994], $E$ may have very different values for the initial un-equilibrated fluids and the final situation after equilibrium is
reached, so that one must consider the extent of equilibrium that exists in the system of interest as well as time-dependent effects. To represent a foam system at equilibrium, E, S, and B should be calculated with three tensions which do not change with time and where both fluids, antifoam and foaming liquid, are mutually saturated. In this current work time-dependent effect of tensions, especially air-water surface tension, on foam stability is of great interest. So sometimes $\gamma_{AW}$ that changes with time is selected to calculated E, S, B, and the resulting values are denoted as dynamic entry, spreading and bridging coefficients. Another type of E, S, B calculation used throughout chapters 5-8 utilizes values of $\gamma_{AW}$ and $\gamma_{AO}$ where the foaming liquid is saturated with antifoam but the antifoam droplets are not saturated with respect to the foaming liquid. Also, $\gamma_{OW}$ is measured by spinning drop tensiometer where oil to water ratio is much higher (more than 20 times) than that in foam column. That is, although the three tensions used for calculation are time-independent values, only $\gamma_{AW}$ but not $\gamma_{OW}$ and $\gamma_{AO}$ are in all cases the correct values for a foam system where everything is at equilibrium. E, S, B calculated in this way are denoted as semi-equilibrium entry, spreading and bridging coefficients in this thesis.

Following is a summary of the relations between E, S and B for a liquid foam system containing antifoam. At equilibrium Antonov’s rule requires that the spreading coefficient of one liquid on another be zero or negative. Hence $S \leq 0$ and $E \geq 0$, the latter since $-E$ is itself a spreading coefficient as noted above. If $E > 0$, one can have either $S < 0$, in which case $B > 0$ or $B = 0$ or $B < 0$ depending on values of tensions, or $S = 0$, in which case $B = \gamma_{AW}^2 + \gamma_{OW}^2 - (\gamma_{AW} - \gamma_{OW})^2 > 0$. If $E = 0$, one must have $S < 0$ and $B = \gamma_{AW}^2 + \gamma_{OW}^2 - (\gamma_{AW} + \gamma_{OW})^2 < 0$. In addition for non-equilibrium situations: if $E >$
0 and $S > 0$, one must have $B > 0$; if $E < 0$, one must have $S < 0$ and $B < 0$. It’s noteworthy that if $B > 0$, $\gamma_{AO}^2 < \gamma_{AW}^2 + \gamma_{OW}^2 < (\gamma_{AW} + \gamma_{OW})^2$, i.e. $\gamma_{AW} + \gamma_{OW} > \gamma_{AO}$ or $E > 0$. So if $E > 0$ and $S < 0$, $B$ can be either positive or negative. But if $B > 0$, it must be that $E > 0$.

Among the dynamic and semi-equilibrium entry, spreading and bridging coefficients presented in this thesis, it’s sometimes seen that both $E > 0$ and $S > 0$. This is because they don’t represent a foam system at equilibrium. In some cases $\gamma_{AW}$ is still decreasing with time. In some cases $\gamma_{OW}$ may not the correct equilibrium value for a specific foam system, because oil to water ratio in foam is much smaller than that in a spinning capillary tube where $\gamma_{OW}$ is measured. Also, $\gamma_{AW}$ may not be at equilibrium since a thin layer of oil would exist at equilibrium in foam system but may not always exist in experiments with spinning drop tensiometer. Here $S = 0$ at equilibrium if such spreading occurs since $\gamma_{AW} = \gamma_{OW} + \gamma_{AO}$ at equilibrium. When $E < 0$, water spreads on oil, so $\gamma_{AO}$ measured in absence of water is not true equilibrium value in foam system where there would be a water film at oil-air surface. True value of $E$ at equilibrium is zero under these conditions.

2.3.2 Entry Barrier

The positive bridging coefficient indicates that the oil bridges would be unstable if they are formed in the foam films [Garrett, 1993; Denkov et al., 1999]. On the other hand, the formation of oil bridges from pre-emulsified oil drops requires the rupture of the asymmetric oil-water-air films, formed between the drops and the solution surface. Recently, results obtained with some surfactant–oil couples demonstrated a straightforward correlation between the foam stability and the entry barrier, which
prevents the emergence of pre-emulsified oil drops on the solution surface [Arnaudov et al., 2001; Basheva et al., 2000; Marinova and Denkov, 2001]. The primary reason for this correlation is that any mechanism of foam destruction by emulsified oil should include the stage of formation and rupture of asymmetric oil-water-air film which was named by Wasan et al [1988] as “pseudoemulsion film”. As noticed long ago by Kruglyakov [1988] and Kulkarni et al. [1977], these asymmetric films might be stabilized by various surface forces (electrostatic, van der Waals, etc.) which suppress the drop entry and impede the antifoam action of oil. Furthermore, if the asymmetrical film is stable, the introduction of oil into the foaming solution might lead to a foam boosting effect [Koczo et al., 1994]. Hence the oil drop entry is a key stage in the overall process of foam destruction by oils.

The classical entry coefficient E is derived from the change of energy when the oil drop enters the air-water interface. The definition of E doesn’t consider an energy barrier that must be overcame for drop entry and doesn’t consider the properties of the pseudoemulsion film, e.g., the geometry of the system or the influence of thin-film forces. Therefore the entering coefficient E is a thermodynamic property, which determines whether the particular configuration of the oil drop is energetically favorable or not, but cannot predict the fate of the oil drops under dynamic conditions which exist within the draining foam film. So its application to some processes is severely limited.

Several different parameters have been suggested in the literature to quantify the entry barriers for oil drops. Lobo and Wasan [1993] suggested to use the energy of interaction per unit area in the asymmetrical oil-water-air film, f, as a criterion of its stability

\[
f = - \int_{h \to \infty}^{h_0} \Gamma_{AS} dh \quad \text{(Eq. 2-8)}
\]
where $\Pi_{AS}(h)$ is the disjoining pressure, $h_E$ is the equilibrium thickness of the asymmetric film at a certain capillary pressure (which has to be specified).

In a parallel study, Bergeron et al. [1993] suggested the so-called generalized entry coefficient, $E_g$, and presented a thorough analysis of this situation. In their work, thin-film forces are readily incorporated into $E_g$ by replacing the oil-gas surface tension in the definition of classical $E$ (Eq. 2-5) with the tension of the aqueous film, $\gamma_f$, which is written in terms of the disjoining pressure isotherm:

$$\gamma_f(h_f) = \gamma_{AW} + \gamma_{OW} + \int_0^{\Pi_{AS}(h_f)} hd\Pi_{AS} \quad (\text{Eq.2-9})$$

The result is a modified entry coefficient $E_g$:

$$E_g = -\int_0^{\Pi_{AS}(h_E)} hd\Pi_{AS} \quad (\text{Eq.2-10})$$

where the lower limit of the integral corresponds to $\Pi_{AS}(h\to\infty)=0$. $h_E$ is the equilibrium thickness of the thin film at a particular disjoining pressure. As also shown by Bergeron et al. [1993], the classical entry coefficient, $E$, can be obtained as a particular case of $E_g$ in the limit $h_E\to0$.

Eq.2-10 relates the generalized entry coefficient to the disjoining pressure isotherm and, therefore, to pseudoemulsion film properties. For pseudoemulsion films that are not highly curved at equilibrium, $\Pi(h_E) = P_c$ [Manlowe and Radke, 1990]. Even when the films are curved, the disjoining pressure (and hence the limits of the integration in Eq2-10) can be evaluated from the capillary pressure and the film curvature [Manlowe and Radke, 1990; Toshev and Platikanov, 1992].
The determination of the value of $E_g$ requires the knowledge of the disjoining pressure isotherm, $\Pi_{AS}(h)$, which is a non-trivial task. When $E_g$ is calculated, the comparison with the antifoam efficiency of different oils is viable. A negative $E_g$ defines the system as non-entering and a positive one defines entering.

Bergeron et al. [1993] measured the disjoining pressure isotherms of planar films and asymmetric oil-water-air films for several surfactant-oil couples. They found a good correlation between the stability of the asymmetric films and the stability of foams in porous media, in the presence of oil. Furthermore, they showed that the destabilizing effect of oil is indeed caused by a lower stability of the asymmetric oil-water-air films as compared to the stability of the foam air-water-air film. It's reasonable to deduce that this criterion shouldn't be restricted to foam in porous media but applies for foam in general.

In the same study, another possible quantity as a measure of the asymmetric film stability was also discussed, namely, the critical capillary pressure leading to rupture of the asymmetric film. A similar idea had been used before [Khatib et al., 1988] to explain the collapse of foams in porous media in the absence of oil. As shown by Aronson et al. [1994], the measured value of the foam collapse pressure (which acts as to suck liquid from the foam) was close to the rupture pressure of a single foam film, as determined by the porous plate method [Mysels and Jones, 1964].

Indeed, the critical capillary pressure seems to be the most adequate measure of the film stability in such systems, because the capillary pressure is the actual external variable that compresses the film surfaces toward each other, against the repulsive surface forces (disjoining pressure) stabilizing the film.
Recently, another experimental tool became available for quantifying the entry barriers of oil drops. Hadjiiski et al. [1996] developed the so-called film trapping technique (FTT), which consists of trapping oil drops in a wetting film, formed from surfactant solution on a solid substrate, and subsequently measuring the critical capillary pressure that leads to drop entry on the fluid surface of the wetting film.

2.3.3 Liquid Antifoams

2.3.3a Spreading-fluid Entrainment

Ross [1950] has advanced a hypothesis concerning the rupture of foam films by oil droplets for which \( E > 0 \) and \( S > 0 \). Such oil droplets will emerge into the air-foaming liquid surface and spread as a duplex film (see Figure 2.8A). If the oil droplet emerges into both surfaces of a film, a duplex film of oil would simultaneously spread over both surfaces of the foam film. This would squeeze out the original liquid in the film to produce a region composed entirely of antifoam oil where rupture would occur.

2.3.3b Bridging-dewetting Mechanism

Many examples of systems were found for which \( E > 0 \) and \( S < 0 \) but where antifoam effects are pronounced [Tsuge et al., 1984; Garrett, 1993 & 1994]. Spreading liquids that are poor antifoam agents were also known [Frye, 1989a]. It's then proposed that a configuration consisting of an oil droplet bridging a thin plane-parallel aqueous film may be unstable. Some direct evidence for this mechanism has been presented by Dombrowski and Fraser [1954], who made a photographic investigation of the effect of dispersed particles and oil droplets on the disintegration of thin sheets of water or alcohol formed from spray nozzles. They found that particles or oil drops which were wetted by these liquids had no effect on the manner of disintegration of the film. On the other hand
particles or oil droplets which were not wetted by these liquids had a marked effect causing perforation of films when their size was of the order of the thickness of the film. Dippenaar[1982] observed bridging of water lamellae by hydrophobic particles using cinematography.

Garrett [1980] gave an analysis of the effect of non-spreading oil droplets on the stability of aqueous films. He considered the consequences attendant upon the adoption of a bridging configuration by, for example, a hydrophobic oil drop in a plane-parallel symmetrical aqueous film. In order to adopt such a configuration the drop must dewet so that $E > 0$ but must not spread so that $S < 0$. The three-phase contact lines made by the drop at the film surfaces are assumed to satisfy Neumann's triangle of surface tension forces (see Figure 2.7a). Garrett showed that if such an oil lens bridges a plane-parallel foam film by emerging into both air-water surfaces, then no configuration of mechanical stability is available to the lens if the angle $\theta^*$, formed by the tangents to the air-water and oil-water surfaces so denoted as $\theta_{ow}$ later on, is $> 90^\circ$. Using a vector force balance at the three-phase contact point, $\theta_{ow}$ can be related to the three interfacial tensions by

$$\cos \theta_{ow} = \frac{\gamma_{AO}^2 - \gamma_{AW}^2 - \gamma_{OW}^2}{2\gamma_{AW} \gamma_{OW}} \quad (\text{Eq. 2-11})$$

Thus critical condition for rupture ($\theta_{ow} > 90^\circ$, $\cos \theta_{ow} < 0$) can be expressed as $\gamma_{AO}^2 - \gamma_{AW}^2 - \gamma_{ow}^2 < 0$, that is actually $B > 0$.

The condition of $B > 0$ ($\theta_{ow} > 90^\circ$) gives rise to unstable bridging configurations. When the air-water surfaces are everywhere planar as shown in Figure 2.7b, it's obvious by inspection that the Laplace pressure drop across the oil-air surface $\Delta P_{OA} > 0$ and that
across the oil-water surface $\Delta P_{OW} < 0$. In this situation $\Delta P_{OA} > \Delta P_{OW}$ and an unbalanced capillary force will cause enhanced rates of drainage in the aqueous film away from the lens. If, on the other hand, the air-water surface is nonplanar, a configuration similar to that shown in Figure 2.7c occurs. Here again there is a capillary pressure enhancing the rate of drainage away from the droplet. In this case it is possible, as suggested by Frye and Berg [1989b], to envisage a process where the oil lens is completely dewetted from the foam film to form a hole, as shown in Figure 2.7d where thinning of the aqueous film causes the lens to expand and ultimately results in coincidence of the upper and lower three-phase contact lines.

Figure 2.7 Oil lens, definition of $\theta^*$ ($\theta_{ow}$) and unstable bridge configurations

So even if $S \leq 0$, the oil drop may forms a lens at the air-water surface instead of spreading, the foam film will become unstable once the drop has entered its other surface so that it spans the film provided $B > 0$. Calculations of the time for film rupture upon bridging [Frye, 1987] indicated that rapid film rupture should occur if the contact angle is more than $5^\circ$ to $10^\circ$ above this critical contact angle. It also should be noted that if the
curvature of the air-water interfaces is concave or $\theta_{ow} < 90^\circ$, the resulting pressure difference pulls liquid toward the drop, acting to stabilize the film [Garrett, 1980].

The bridging-dewetting mechanism is now widely considered to be more important than spreading in breaking foams. But as discussed by Bergeron et al. [1997], the two mechanisms discussed above do not necessarily exclude each other - a spreading of the oil could facilitate the bridging by reducing the local film thickness. Or as shown by Denkov et al. [1999], an oil layer having a thickness of several nanometers may substantially facilitate the entry of the oil drops into the film surface and the formation of unstable bridges.

2.3.3c Oil-bridge Stretching Mechanism

Garrett pointed out in a later study [1993] that the process depicted in Figure 2.7c–d would not apply as $\theta_{ow} \rightarrow 180^\circ$, when the curvature of the oil-air surfaces will of necessity become concave if the oil-water surface is to remain cylindrical. In this case the point of rupture could be at the center of the expanding oil lens as the two concave air-oil surfaces approach one another. In fact, this picture (biconcave oil bridge which ruptures in the center) was observed by Denkov et al. [1999] in some systems they studied. They found the antifoam particles destroy the foam lamella by the formation of unstable oil bridges, which afterward stretch and eventually rupture, due to uncompensated capillary pressures across the different interfaces. They named the process the bridging-stretching mechanism. It is illustrated in Figure 2.8C.

Theoretical analysis of this antifoam action was given by Denkov [1999] in another paper. The author stated that, in Garrett's model [1980] the film surfaces were assumed to be perfectly flat and it was not clear in advance whether the observed surface
deformation could change significantly the predictions of the theoretical model. In his study, the deformability of the foam film surfaces has been explicitly taken into account. This modification makes the model much more complex, and a variety of possible configurations of the meniscus surrounding it has to be considered. The theoretical results of the author show that oil bridges might be in equilibrium with the meniscus surrounding them even if the bridging coefficient B is positive. The equilibrium configuration of the bridge and the contiguous meniscus could be either stable or unstable, depending on the relative size of the bridge as compared to the film thickness. At positive B the small bridges might be in stable or unstable equilibrium, while the large bridges are always in an unstable equilibrium. The critical volume separating stable from unstable bridges depends on the three-phase contact angles (i.e. on the value of B). Once shifted from their equilibrium state, the unstable bridges spontaneous expand (due to lack of balance of the capillary pressure jumps at oil-air and oil-water interfaces) and eventually rupture the foam film. At negative values of B, the bridges are in stable equilibrium with the contiguous meniscus, just as predicted by Garrett [1980, 1993].

Figure 2.8 is a schematic illustration of the defoaming mechanisms discussed above. For all of these mechanisms, the first critical step is drop entry, which requires both a positive entry coefficient E and a small entry barrier.
Figure 2.8 Schematic profile of several defoaming mechanisms

(A) Spreading-fluid entrainment: The spreading of the oil over the foam film surface leads to Marangoni-driven flow of water radially from the oil drop, resulting in a local film thinning and rupture. (B) Bridging-dewetting mechanism: The formation of an oil bridge between the two film surfaces could lead to dewetting of the hydrophobic antifoam particle, with subsequent rupture of the foam lamella. (C) Bridging- Stretching mechanism: After an oil bridge is formed, it stretches due to uncompensated capillary pressures. Finally, the oil bridge ruptures in its thinnest central region.
2.3.3d Bridging of Plateau Borders

Instead of direct bridging in the foam lamella, a series of papers from Wasan’s laboratory [Koczo et al., 1992 &1994] emphasized that bridging also happens in Plateau borders. On the basis of direct observation of foam rupture events and single film studies, they proposed that the oil drops (with particles inside) move to the plateau borders of the draining foam. The drops get trapped in the thinning plateau borders and enter the air-solution surface forming a lens when the pseudoemulsion film is destabilized. On further foam drainage, the lens gets trapped and enters another surface at the Plateau border forming a bridge and the foam ruptures at the bridge. This mechanism is illustrated in Figure 2.9. This conclusion is supported by the work of Wang et al. [1999].

2.4 Solid Antifoams

It has been found that hydrophobic solids may exhibit striking antifoam action. For example, Kulkarni et al. [1977] noted that spraying hydrophobic silica particles onto some foams resulted in rapid destruction of bubbles contacted by the solid particles.

Some authors take the view that antifoam solid particles act by a bridging mechanism [Garrett, 1979], an approach quite similar to the bridging mechanism of the insoluble oil as discussed before. But there are some differences that should be noted: a)
When the particle enters the air-water surface, the orientation it will attain in the surface depends on its shape and on the contact angle. b) Compared with liquid antifoams, there is no deformation or elongation of solid particles during film thinning. c) Entry of particles into the air-water interfaces is the prerequisite for antifoam effect to take place. Aronson [1986] noted that solids of similar molecular composition did enter and that solids with asperities entered more often than smooth-shaped solids.

2.5 Synergistic Antifoam Action by Hydrophobic Solid Particles and Insoluble oils

Actually many antifoam formulations are complex combinations of different components. Antifoam formulations with high efficiency are generally a combination of hydrophobic solid particles (e.g. hydrophobic silica) dispersed in oil which may be emulsified in an aqueous medium. When the two components are used together, synergistic action occurs. It’s widely accepted that the main role of the solid particles in the mixed antifoams is to destabilize the oil-water-air film, thus facilitating drop entry. The subsequent oil spreading or bridging then leads to a rapid rupture of the aqueous film. This helps to overcome the shortcomings of both liquid antifoams, e.g., the deformability and dispersibility make it difficult for liquid droplets to enter both film interfaces and solid antifoams, e.g., it’s sometimes difficult to obtain contact angles large enough for spontaneous dewetting to occur at high surfactant concentration when they are used alone [Frye et al. 1989a]. As a result of this synergistic effect, the mixed solid-liquid formulations have typically much higher efficiency than the individual components (oil or solid particles) taken separately.
2.6 Foam Boosting Additives and Foam Stability

Foam is undesirable in many practical applications, such as in the case of automatic dishwasher detergents, paints, food products, distillation columns, sewage plants, and many industrial processes where additives are used to eliminate or control the foam. However, in some practical applications, where copious and long-lasting foam is desirable such as in the case of hand dish washing detergents, soaps, shampoos, shaving creams, beer, bubble bath, and fire-fighting agents, additives are used to increase foam stability [Bikerman, 1973].

There are various ways by which additives can help to stabilize foams such as: increasing the elasticity of the foam film; slowing down the drainage of liquid in the lamellae; decreasing the diffusion of gas across the lamellae; increasing the thickness of the electrical double layer; increasing the surface and bulk viscosity of the foam film. While some additives may contribute by one particular mechanism, others may offer a stabilizing effect with several mechanisms operating simultaneously. Lai and Dixit [1996] grouped the wide variety of foam additives into 6 categories: organic compounds, electrolyte, finely divided particles, polymers, copolymers and liquid crystals.

Surface active organic compounds are the most commonly used foam additives in practical applications. These organic additives typically stabilize foam by enabling the surfactant molecules to form a closely packed foam film that exhibits more elasticity and more resistance to drainage, and consequently is less susceptible to external disturbance. Among the best known from this class of additive are fatty alcohols, fatty acids, alkanolamides, amine oxides, and various other surfactants.
For anionic or cationic foaming systems, nonionic additives are typically the preferred choice. The effectiveness of these nonionic additives is dependent upon their surface activity and how easily they can be incorporated into the foam films. The complexing ability of the additive with the surfactant in the foam film also plays an important role in stabilizing foam, as is the case with amine oxides added to an anionic surfactant system. Another important consideration in selecting an effective foam additive is the compatibility between the hydrophobes of the foaming surfactants and that of the additives. In general, a compound having hydrocarbon chain with length comparable to the hydrocarbon length of the surfactant functions as an effective foam stabilizer.

It has been shown that the foam-enhancing and stabilizing effect of an additive is related to its ability to decrease CMC of the foaming surfactant [Schick and Fowkes, 1957]. An additive with polar groups capable of forming multiple hydrogen bonds is expected to be an effective foam stabilizer. The superior foam stabilizing effect of alkanol amides may be attributed to this factor.
Chapter 3 Materials and Experimental Procedures

3.1 Materials

As foaming agents, the commercial anionic surfactant Neodol®25-3S (denoted as N25-3S later on) and nonionic surfactant Neodol®N25-7 (denoted as N25-7 later on) were used. The former is an alkyl ethoxy sulfate sodium salt with a straight C$_{12}$-C$_{15}$ hydrocarbon chain and an average of three ethylene oxide (EO) groups. It is of typical use in hand dishwashing and shampoo products. The latter is a linear alcohol ethoxylate also with a C$_{12}$-C$_{15}$ hydrocarbon chain but with an average of seven EO groups. It is representative of nonionic surfactants that are used in combination with anionic surfactants in household laundry products. These two surfactants were both supplied by Shell Chemical L.P. (Houston, Texas). n-dodecanol (or lauric alcohol, LA) and N,N-dimethylmyristal amine oxide (C$_{14}$DMAO) were used as ‘foam booster’. LA was purchased from J. T. Baker Chemical Co. (‘Baker$^{\text{TM}}$ Grade). C$_{14}$DMAO was obtained from Hoechst and recrystallized twice from acetone at university of Bayreuth.

As antifoaming agents, liquid oils including triolein (with a purity of 99%, from Fluka Chemie), n-hexadecane (with a purity of 99%, from the Humphrey Chemical Company), and and their mixtures with oleic acid (with a purity of 95%, from Fisher Scientific Company) were studied as models of nonpolar lubricating oils, vegetable oils and nonpolar/polar sebum soil respectively. In subsequent sections, the mixture of hexadecane and oleic acid at weight ratio of 9 to 1 is denoted as C16/HOI, and the mixture of triolein and oleic acid at weight ratio of 9 to 1 is denoted as TO/HOI.

Sodium oleate used to produce preformed calcium soap particles was a commercial pure powder with assay of fatty acid (as oleic acid) > 82%, free alkali (as
NaOH < 0.5%, purchased from Sigma-Aldrich Company. Sodium oleate used in other studies was purchased from Fluka Chemie with a purity ≥ 99%. Calcium chloride (from Alfa Products, reagent grade) was dissolved in deionized water to prepare hard water. The concentration of hardness was calculated as CaCO₃ in accordance with the usual convention, i.e., the concentration that would exist if the same amount of calcium had been added as CaCO₃. Alkalinity was provided by sodium hydroxide purchased from Fisher Scientific with assay of NaOH ≥ 98.5%. Water used for experiments was doubly distilled and deionized.

3.2 Videomicroscopy Configuration

The videomicroscopy system in our laboratory consists of microscopes, cameras, temperature controllers, video micrometer, time code generators, video recording and editing systems and NeXT workstation (Figure 3.1).

The microscope used for oil contacting and thin film experiments was the Nikon Optiphot-Pol model with usual horizontal stage. A CCTV video camera Javelin JE-7362 (Javelin, CA) was connected on the top of the microscope, allowing simultaneous observation through microscope eyepiece and on a video monitor. Four objectives of 4X, 10X, 20X and 40X magnification (Nikon) were used to study dynamic behavior at different scales. A polarizer was placed on top of the field lens and adjusted for a cross-polarized view with a built-in analyzer in the top section of microscope. This configuration enabled direct detection of liquid crystalline phase formation.

Temperature controller was used to maintain a Mettler FP-5 microscope hot stage at the desired temperature. The hot stage was specifically modified and placed on top of a
Nikon X-Y positioner so that drops could be observed during and right after injection while the sample was maintained at constant temperature.

Another microscope was built with vertical stage configuration. No eyepieces were present with the vertical microscope and the image was sent directly to video monitor with a Javelin JE-3642RGB video camera. Three objectives of 1X, 4X and 10X magnification (Nikon) were used. Polarizing optics were included to identify formation of birefringent liquid crystalline phases.

The signal from both cameras first goes into the video micrometer (JV-6000, Javelin), which was used to measure the sizes of images in X, Y and diagonal directions. The output signal then goes to time code generators (Bio-Electronics TC-3 or Cypher Btx), and finally to video recorders (see Figure 3.1).

Experiments were recorded by a Panasonic AG-7750P S-VHS recorder with NTSC format which has a built in Time Base Corrector (TBC). With NTSC format video signals were recorded into either normal or super VHS format with 30 frames per second. Recording images could be seen on a color monitor with information of real time (from time code generators) and size measurements (from video micrometer).

For editing purposes, a video editor Panasonic AG-A750 and an S-VHS player Panasonic AG-7650P were added to the system. Further image processing could be done with NeXT workstation.
3.3 Experimental Procedures

3.3.1 Foam Stability Testing

A foam test apparatus (see Figure 3.2) which Shell Chemical Company obtained from SEN, Inc. was used for the foaming studies. Foam is formed in a clear plexiglass
cylinder by entrainment of air from a valve in the surfactant solution that is pumped through a recycle loop. The point where the recycle pipe joins the foam cylinder is about 2cm below the 0-cm mark of the cylinder. The experimental procedure consists of filling the apparatus by pouring approx. 440cc solution from above the cylinder (with the faucet closed) to the 0-cm mark. The pump is turned on for five minutes without the air valve open to provide uniform mixing of the solution. Air is then allowed into the recycle line, and foam is generated. The elapsed time in seconds when the 20-cm mark is reached by the foam is recorded and used to calculate an average foam formation rate. The pump is then shut off, and foam decay in the graduated cylinder is monitored. To study the effect of oil, liquid oils were added in increments to the aqueous solution. After each oil addition, the solution was circulated for five minutes prior to the foam formation step to provide for uniform emulsification and solubilization of the oil phase. All initial tests were performed at room temperature using deionized water. However, the temperature of the surfactant solution did increase slightly during each test due to warming by the pump. In general, the surfactant solution temperature was controlled in the range of 25°C to 28°C during a single test.

Among the advantages of this apparatus for measurement of foam formation rate and stability are the relatively small volume of aqueous solution and auxilliary ingredients required for each study. In addition, the rapid formation of foam (typically less than three minutes) and easy clean-up procedure allow for performance of many tests in a short time-frame.
3.3.2 Interfacial/Surface Tension Measurement

A University of Texas Model 300 Spinning Drop Tensiometer, equipped with video camera (JEM6222, Javelin) and video micrometer (VIA-100, Boecheler), was utilized to measure interfacial/surface tensions for time periods longer than 1 minute. With the video system, we can also observe drop shape and some interfacial phenomena. Surface tensions for time period shorter than 1 minute were measured by SITA-online t60 (SITA Messtechnik GmbH, Germany), which applies the maximum bubble pressure method. The range of bubble lifetime is from 30 to 60000 milliseconds.

3.3.3 Horizontal Contacting Experiment

The aqueous phase was imbibed into a rectangular optical glass cell (50mm×4mm×0.4mm, Vitro Dynamics Inc., Cat. No.2540) by capillary action. The glass cell was then sealed at one end and attached to a standard microslide (3 inch ×1 inch) with photopolymer adhesive (Norland Products Inc. Adhesive No. 63) which was cured with ultraviolet light of 250-380nm by a fiber optical gun (Norland Products Inc.). The cell was then observed by the microscope in Figure 3.1.
Microinjection system (Picospritzer II shown in Figure 3.4) was used to inject oil drops (with sizes in the range of 100–200µm) into the aqueous phase. Picospritzer II is a system with a high speed solenoid valve that supplies repeatable pressure pulses. Nitrogen was used as driving gas. Micropipettes were pulled from capillaries with outside diameters of 1mm and inner-diameters from 50-150µm purchased from Drummond Scientific Co. (Cat.No. 1-000-0300).
3.3.4 Optical Observation of Individual Foam Film in Scheludko Cell

Millimeter sized foam films were observed in reflected monochromatic light by using the method of Scheludko and Exerowa [Scheludko & Exerova 1957; Scheludko 1967]. The film was illuminated and observed in a direction perpendicular to its surfaces (see Figure 3.5). After surfactant solution was loaded in the capillary cell (i.d. = 3 mm, height = 1.2mm), liquid was sucked out by slowly withdrawing the syringe plunge until dimple begins to form. Drainage continued spontaneously thereafter under capillary pressure. Time recording was turned on at the moment the dimple began to form. Time code is in the form of 00:00:00:00, which means hour: minute: second: frame. Time resolution is 33 milliseconds, i.e., there are 30 frames per second. The glass cell was covered and small amount water was preloaded under capillary cell to prevent film evaporation. Most of the films were observed under 4× optical objective. Enlarged images were obtained through 10× optical objective. In order to study the effect of oils on the stability of foam films, a suitable amount of oil was added to surfactant solution. Before being loaded into the capillary cell, the solution was shaken intensively by hand in a test tube to achieve mixing and emulsification.

The interference of light reflected from the upper and lower surfaces of the foam film leads to appearance of dark and bright interference fringes, each of them corresponding to a given film thickness. The difference Δh in the film thickness between two neighboring dark (or bright) fringes is: Δh = λ/2n ≈ 203nm, λ = 546nm is the wavelength of the illuminating light and n=1.332 is the refractive index of the surfactant solution. One can easily distinguish changes in the film thickness on the order of Δh/4 ≈ 50nm (bright to gray, gray to dark and so on)[Denkov et al 1999]. More refined
procedures of light intensity detection [Scheludko & Exerova 1957; Scheludko 1967; Nikolov & Wasan 1989; Bergeron & Radke 1992] which are not employed here can lead to even higher accuracy in the film thickness determination.

Figure 3.5 Schematic profile of Scheludko capillary cell

![Schematic profile of Scheludko capillary cell](image)

**3.3.5 Observation of Asymmetric Oil-Water-Air Films**

A millimeter sized pseudoemulsion film was formed by pressing an oil drop underneath the solution surface and observed in reflected monochromatic light (see Figure 3.6), an adaptation of the work of Marinova and Denkov [2001]. The process of film formation and film thinning can be observed in detail when a relatively large drop of oil attached to the tip of a capillary (i.d. = 1mm) approaches the surface of the surfactant solution. The capillary is placed in the center of a glass cell, which consists of two concentric glass cylinders fused at one end to a glass plate. The inner glass cylinder has a relatively small free air-water interface (less than 1 cm$^2$) and was filled with surfactant solution during experiments. The outer glass cylinder has a relatively large size (i.d. = 3.0cm) and water is placed inside to provide a vapor-saturated environment. The glass cell was carefully covered to suppress the evaporation from the film.
3.3.6 Vertical Foam Cell

Visual observation of foam behavior was implemented by making foam on a small scale in a rectangular glass cell vertically oriented (Figure 3.7). The procedure consists of filling the cell with a small amount of liquid, and then injecting air by a syringe to make foam. By changing the position of slide holder, different parts of the foam can be observed. The glass cell was observed by the vertical-stage microscope as shown in Figure 3.8.

Figure 3.7 Schematic profile of vertical foam cell
3.3.7 Turbidity Measurement

Turbidity was measured by Brinkmann PC 800 colorimeter. The original measured datum is the percentage of transparency, T%, of the solution. Turbidity was then calculated from 1-T%. The colorimeter was first calibrated with fresh DI water, which gives 100T%, before each measurement.

3.3.8 Ultrafiltration

To measure the association of calcium and sodium with micelles, the activities of electrolytes in equilibrium with the micelles need to be determined. The technique used here was ultrafiltration. Hutchinson [1959] showed that, for sufficiently high rates of filtration, surfactant monomer can be separated from surfactant micelles by filtration.
through UF membranes. UF membranes used were Amicon® YM3 with 3,000 nominal molecular weight limit (NMWL) from Millipore Corp. The material is regenerated cellulose.

Surfactant and electrolyte solutions were charged to stirred filtration cells of 50 to 55mL capacity and forced through with 330kPa [48psi] nitrogen pressure. Filtration rates were 0.48 to 0.53 g/min. During each filtration, successive samples of filtrate were collected and analyzed for surfactant, calcium and chloride. The composition of the retentate was determined by material balance.

3.3.9 Titration

Concentration of anionic surfactant and calcium ion were analyzed by potentiometric titration. The apparatus was an automatic titrator, Metrohm Titrino Model 716, purchased from Brinkman Instruments. Titrations were automatically evaluated using the inflection point of the sigmoidal titration curve. The inflection point corresponds to the reaction equivalent point.

For analysis of anionic surfactant, the titrant solution is 0.004M benzethonium chloride (Hyamine 1622), reagent, ordered from Gallord-Schlesinger, Inc. The indicator is a combination anionic surfactant specific electrode purchased from Pheonix Electrode Co., Cat. No. SUR1502R. For analysis of calcium ion, the titrant is reagent EDTA, a product of FisherChemicals. The indicator is a calcium ion-specific electrode purchased from Phoenix Electrode Co.
Chapter 4 Foam of Commercial Surfactants

In this chapter, investigations of foams from solutions of anionic surfactant N25-3S and nonionic surfactant N25-7 are described. Besides studies of foamability and foam decay in foam column, dynamic surface tension and horizontal thin film drainage were tested to interpret foam stability results. Also, effect of hardness (mainly CaCl₂) on foam behavior was considered. We first studied foam/film property of the anionic surfactant, then performed similar work on the nonionic surfactant as comparison.

4.1 Experiments with Anionic Surfactant N25-3S

4.1.1 Foam Formation Rate and Foam Stability

Foam was generated at surfactant concentrations of 0.01wt%, 0.05wt% and 0.1wt% respectively. 0.01wt% (0.229mmol/l) is the measured critical micelle concentration (CMC) of this surfactant (data from Shell Chemical). Foam decay from an initial height of 20cm was recorded after half an hour. The results show that N25-3S produces very stable foam, e.g. foam decay was almost zero at 0.1wt% and only 3cm at 0.01wt%. Foam formation rate increased with increasing surfactant concentration, as shown in Figure 4.1.

With surfactant concentration being fixed at 0.01wt%, foam was generated with 100ppm, 200ppm and 300ppm hardness present (refer chapter 3.1 for the definition of...
concentration of hardness). The results show that hardness increases foam stability (as shown in Figure 4.2) but decreases foam formation rate (as shown in Figure 4.3). Stability tests at other hardness levels show that hardness increased foam stability up to 800 ppm. But when hardness was increased to very large values that are well beyond those of interest for dishwashing and detergency, e.g. 2000 ppm, foam stability decreased (as shown in Figure 4.4). No surfactant precipitation was observed during experiments at all these studied hardness levels.

Figure 4.2 Foam stability at different hardness levels

Figure 4.3 Foamability at different hardness levels

Figure 4.4 Effect of hardness on stability of foams of 0.01% N25-3S solution
4.1.2 Dynamic Surface Tension

Dynamic surface tensions (D.S.T.) at different concentrations of N25-3S were measured. The results in Figure 4.5 show that D.S.T. decreases as surfactant concentration increases.

![D.S.T. of N25S at different conc.](image)

Figure 4.5 Dynamic surface tension at different surfactant concentrations.

When the D.S.T. of the solutions of 0.01wt% N25-3S and 0.01wt%N25-7 are compared with that of the solutions containing 300ppm hardness, we saw that hardness speeds up the decrease of D.S.T. of the anionic surfactant to approximately that of the nonionic surfactants (see Figure 4.6). The latter was found to be almost independent of hardness.

![Dynamic surface tension](image)

Figure 4.6 Effect of hardness on dynamic surface tension
4.1.3a Film thinning behavior---at different surfactant concentrations

By producing horizontal thin films in Scheludko Cell, we observed the thinning process of films made by N25-3S solutions at different concentrations. Time recording is started at the moment thin film begins to form. Time code (00:00:00:00) shown on each film picture stands for hour:min:sec:frame. Time resolution is 33 milliseconds, i.e., there are 30 frames per second.

At 0.01wt% and as illustrated in Figure 4.7, asymmetric drainage of the dimple happens around 15 seconds after initial film formation. As channels disappeared with further drainage, part of the film became dark (Figure 4.7C), showing local thinning of the film. Film breaks at this stage.

![Figure 4.7 Consecutive thinning stages of film made by 0.01%N25-3S.](image)

(A) Asymmetric drainage of dimple
(B) Film contains channels formed after expulsion of the dimple.
(C) Film with locally thinner part. Film broke at this stage.
At 0.05 wt%, after asymmetric extrusion of the dimple and further thinning until channels disappear, an almost flat planar film forms which looks white under reflected light. Following that, step-wise thinning begins (Figure 4.8a). One or several dark spots (which are thinner than the remaining part of the film) appear and gradually increase in area. The dark area remains for several seconds in a new metastable state. Then even darker spots appear and after their expansion a subsequent metastable state is reached. Finally the film reaches a stable state and no more step-wise transitions occur (Figure 4.8b).

![Figure 4.8 Part of the thinning process of film made by 0.05 wt% N25-3S solution](image)

At 0.1 wt%, drainage is symmetric initially (figure 4.9A). Then a lens with a small finite contact angle forms which is separated from the meniscus by a uniform annular thin film (Figure 4.9 c&d). This process is complicated by the stepwise thinning of the annular film (Figure 4.9b). Finally, stable black film forms.
4.1.3b Film thinning behavior—at different hardness levels

Thin films made from 0.01wt% N25-3S solution containing hardness were studied. With 20ppm hardness, a planar white film forms after the quick asymmetric drainage of the dimple and channels. Upon further thinning, the film had heterogeneous thickness, but the heterogeneity was not remarkable (Figure 4.10a). Eventually, the heterogeneity became less distinguishable and finally, a not quite uniform common black film (with thicker periphery according to the shade of brightness of the film picture) formed (Figure 4.10b). Film is stable.
Figure 4.10 Film made from solution of 0.01wt%N25-3S + 20ppm hardness.

(a)  
(b) 

With 300ppm hardness, asymmetric drainage of dimple happens within seconds after dimple formation, much faster than for 0.01wt% N25-3S solution. After a planar white film is formed, further thinning starts around the periphery of the film (Figure 4.11a). Eventually, white spots appear as shown in Figure 4.11b. Some of the white spots left the film and flowed into meniscus, some disappeared before reaching the meniscus. Coalescence between them sometimes occurred. Finally, all white spots disappeared and a stable, black film formed.

Figure 4.11 Film made by solution of 0.01wt%N25-3S + 300ppm hardness.

(a)  
(b)
Hardness seems to be the reason of the occurrence of those white spots in Figure 4.11b, because no white spots were observed during drainage while hardness was absent. At 300ppm, the heterogeneity of film thickness after similar draining time was much more distinguishable (Figure 4.12a) than that at 20ppm (Figure 4.10a). The ‘white ridges’ we see in Figure 4.12a are more like liquid cylinders should they be imaged in 3-dimension. Those white ridges broke up into liquid pockets (Figure 4.12b), which were the origins of the white spots we noticed before.

Figure 4.12 Film produced from solution of 0.01wt%N25-3S + 300ppm

![image]

(a) ![image] (b)

At this hardness level, local thinning which looks like black spot occurred in a fairly thick film (Figure 4.13a). The black spot expanded as the film further thinned. Figure 4.13b was a stage of the thinning process where black spots and white ridges could be observed simultaneously. There might be a liquid rim formed around the slowly expanding black spot. But the white spots we saw developed mainly from the break up of the white ridges (Figure 4.13c).
Figure 4.13 Black spots and white ridges in film produced from 0.01\%N25-3S + 300ppmCa\textsuperscript{2+} solution

(a) (b) (c)

At much higher hardness level, e.g. 2000 or 3000ppm, black spots nucleated in the inhomogeneous film (Figure 4.14a). These black spots expanded faster than the black spot in figure 4.13a and coalesced with each other (Figure 4.14b), i.e., stratification seems pretty clearcut at these high concentrations of calcium. White ridges eventually formed but didn’t break up into individual liquid pockets (Figure 4.14c&d). Finally, uniform black film formed after the white ridge in Figure 4.14d was expelled from the film.

Figure 4.14 Film made from solution of 0.01\%N25-3S + 3000ppm hardness.

(a) (b)
The above information implies that the formation of white spots has a hydrodynamic origin – the break up of thick liquid ridges. The occurrence of this phenomenon has a dependence on the electrolyte concentration. At relatively low electrolyte concentrations, e.g. 20ppm hardness, there is no formation of thick liquid ridges that are vulnerable to hydrodynamic instability. At very high electrolyte concentrations, e.g. 3000ppm hardness, white ridges don’t break. This might be caused by the high rigidity of the film surfaces, as surfactant adsorption at the air-water surfaces could be very compact at such high concentration of counterions.

4.1.4 Vertical Foam Cell

Foam was generated on small scale in a vertical cell by injecting air into 0.01wt%N25-3S solution with/without hardness. Pictures of the foams taken after similar draining time, around 20 minutes, are quite different. Both foam lamellae and Plateau borders are much thinner with the presence of hardness, as shown in Figure 4.15.
Figure 4.15 Results of vertical foam cell
(a) Foam of 0.01% N25-3S + 300 ppm hardness (b) Foam of 0.01% N25-3S

Foam quality of the two illustrated foams was calculated. Here foam quality is defined as the volume fraction of liquid in total foam. From figure 4.16 we can see that the quality of foam in Figure 4.15a is only one half of that in Figure 4.15b. This is consistent with the foam appearance shown in Figure 4.15.

Figure 4.16

0.01% N25-3S

0 - 20
Foam Quality (%) 15
10
5
0
20
4

5 10 15 20 25 30 35
time (min.)

4.1.5 Discussion

4.1.5a Effect of surfactant concentration on foam behavior
Experimental results show that foamability increases as surfactant concentration increases. Foam formation involves rapid entrainment of air so that supply of surfactant may not be fast enough to ensure maintenance of equilibrium adsorption of surfactant. In these circumstances the dynamic air-water surface tension becomes relevant. Therefore foaminess was frequently related to dynamic surface tension (D.S.T.) in the literature [Garrett and Moore 1993, Tamura et al 1995, Arnaudov et al 2001]. Lower D.S.T. decreases energy needed to form bubbles. As we can see in figure 4.5, lower dynamic surface tension is observed at higher surfactant concentration. This is understandable considering the following relation: $\delta=\Gamma/C$. That is the diffusion distance of surfactant molecules to the air-water surface, $\delta$, is proportional to the surface saturation ($\Gamma$), which typically is nearly constant except at surfactant concentrations far below the CMC, but inversely proportion to the surfactant bulk concentration, C. So at higher surfactant concentration, surfactants don't have as far to go to reach the air-water surface. Also, as surfactant concentration increases, ionic strength increases and electrical repulsion between surfactant molecules decreases. This promotes surfactant adsorption at the surface and decreases D.S.T.

The process of film thinning changes as surfactant concentration changes. Asymmetric drainage and step-wise thinning (also called stratification) happen with 0.05wt%N25-3S solution. The stratification actually occurs by the repeated removal of successive layers of micelles [Nikolov & Wasan 1989]. These authors found that in cases where stratification happens, the height of each step is approximately equal to the mean distance between two ionic micelles in the solution. This distance is of the order of the diameter of a micelle together with the Debye atmosphere around it, suggesting that the
stratification is due to the presence of micellar structuring inside the film. Stepwise thinning behavior can readily be explained by the oscillatory form of $\Pi(h)$ isotherm, as shown in Figure 4.17. When $\Pi(h)$ is oscillating and the capillary pressure is held constant, an oscillating driving force develops to produce the observed stepwise thinning [Bergeron and Radke, 1992].

![Figure 4.17 Oscillatory form of $\Pi(h)$ isotherm](image)

At 0.01 wt% of N25-3S, which is near the CMC, the drainage is asymmetric but step-wise thinning doesn’t happen because there aren’t enough micelles to display micellar structuring effect. Thinning pattern at 0.1 wt% is different in two respects, symmetric drainage and formation of lens as shown in Figure 4.9. The transition from asymmetric to symmetric drainage implies a denser adsorption layer and higher surface viscosity. This may be because ionic strength increases as surfactant concentration increases. If more counter-ions adsorb at the air-water interfaces, electrical repulsion is less and closer packing of surfactant molecules would be expected. On the other hand, disjoining pressure is dominated by van der Waals attraction for high electrolyte concentration and as a result, a thin annular film forms that forces the dimple into a lens with a finite contact angle [Joye et al. 1992].

**4.1.5b Effect of hardness on foam stability and film drainage**
Individual foam film behavior in Sheludko cell may shed some light on why suitable amount hardness increased foam stability. Films made by 0.01wt% N25-3S broke without reaching a stable equilibrium thickness. But stable black films formed when hardness was added. As has been discussed in Chapter 2 (section 2.2.4), the adsorbed surfactants at air-water surfaces of a thin film may contribute to disjoining forces as stabilizing interactions. These could arise from overlapping double layers or steric factors due to interaction of bulky surfactant head groups. At sufficiently high adsorption levels of surfactants, the growth of perturbation at a particular critical thickness results not in foam film rupture but in thin black film. Addition of calcium ions promoted surfactant adsorption by reducing the electrical repulsion between adjacent ionic surfactant molecules at the air-water interface and therefore, enhanced the double layer repulsion that stabilizes thin films. So we saw foam stability increased as suitable amount hardness was added. But surfactant adsorption doesn’t increase unlimitedly as we keep increasing hardness level. The extra calcium ions in the film decrease surface potential and thus decrease double layer repulsion (Eq.2-4). This is why we saw that foam stability decreased when hardness level was very high, e.g. 2000ppm. Presumably, similar effects could be obtained with univalent electrolytes such as sodium chloride, but higher electrolyte concentrations would be required.

The effect of hardness on the shifts of disjoining pressure isotherm, e.g., from zero to 300ppm to 2000ppm can be qualitatively described as in Figure 4.18. That is, the maximum of repulsion increased initially due to promotion of surfactant adsorption but then began to decrease due to diminution of surface potential. The Debye length decreased as electrolyte concentration (Ca^{2+}) increased. The monotonic decrease of the
Debye length as the electrolyte concentration ($\text{Ca}^{2+}$) increases can be illustrated by an approximate calculation: In water at 25°C,

$$\kappa^{-1} = 0.178/\sqrt{C_b}$$

for 2:1 electrolytes like $\text{CaCl}_2$, ($C_b$ [mol/mL]).

and $\kappa^{-1} = 0.304/\sqrt{C_b}$ for 1:1 electrolytes like $\text{NaCl}$, ($C_b$ [mol/mL]).

Thus, for 0.01wt%N25-3S ($C_b = 2.3*10^{-4}$ M) with no hardness addition, Debye length is about 20nm. With 20ppm hardness as $\text{CaCO}_3$ ($C_b = 2*10^{-4}$ M), Debye length is about 13nm. With 300ppm hardness as $\text{CaCO}_3$ ($C_b = 3*10^{-3}$ M), Debye length is about 3.2nm. With the addition of 2000ppm hardness, Debye length is only 1.3nm.

Figure 4.18 Schematic presentation of the shifts of disjoining pressure isotherms as hardness level increases

Since hardness affects the disjoining pressure isotherm by shifting it to left (thinner thickness), the equilibrium thickness of the films is assumed to decrease as hardness level (electrolyte concentration) increases. Also, the presence of calcium ions screens the repulsion between ionic surfactant molecules. These effects are assumed to increase bulk fluidity and speed-up liquid drainage. With the general picture as aforementioned, film thinning process was different at different hardness levels, e.g., the
formation of white spots only occurs in certain range of electrolyte concentrations (CaCl$_2$).

Hédreul and Frens [2001] studied the formation of Newton Black Films (NBF) in single vertical SDS-stabilized films with varied electrolyte concentrations (NaCl). They found there was a distinct dependence on the electrolyte concentration of the probability that the NBF would 'nucleate' somewhere in the thicker film. In most cases, the common black film (CBF) would appear at the top of the film and the first spot of NBF would appear somewhere in that area. But in solutions with high electrolyte concentrations, the NBF would also nucleate in thicker films even before a discernible area of CBF had formed. They proposed that electrolyte (NaCl) addition changes the thickness of the CBF equilibrium film and also the barrier for the transition from CBF to NBF. In our experiments with 300ppm hardness or even higher levels, we saw black spots formed in films much thicker than CBF, presumably due to the same reason as they proposed. Because of the early appearance of local thinning in thick films, the heterogeneity of film thickness increases and induces formation of liquid ridges.

4.2 Experiments with Nonionic Surfactant N25-7

4.2.1 Foamability and Foam stability

Compared with the anionic surfactant N25-3S, N25-7 generally produces less stable foams, e.g., foam of the 0.1wt%N25-7 solution with initial height of 20cm decays more than 8cm after half an hour while foam of the
0.1wt%N25-3S solution almost doesn't decay after similar time. Even at 1wt%, foam made from N25-7 solution decays about 3cm after half an hour. Five concentrations of N25-7 were tested. Foamability is quite similar at 0.01wt%, 0.05wt% and 0.1wt% of surfactant, but increases substantially at 1.0wt%, as shown in Figure 4.19. The same trend is seen for foam stability.

With surfactant concentration being fixed at 0.1wt%, which is a representative of practical laundry application, the effect of hardness was tested at three hardness levels. Foam formation rate and foam stability with/without hardness are compared in Figure 4.20. Hardness seems to affect neither foamability nor foam stability.

Figure 4.20 Effect of hardness on foam stability and foam formation

4.2.2 Dynamic Surface Tension

Dynamic surface tensions at five surfactant concentrations of N25-7 were measured. As expected, somewhat lower surface tensions were obtained at higher surfactant levels (see Figure 4.21). As mentioned previously, dynamic surface tensions were unaffected by hardness.
D.S.T. of N25-7 at different concentration.

![Graph showing dynamic surface tension at different concentrations](image)

**Figure 4.21** Dynamic surface tension at different N25-7 concentrations

### 4.2.3 Thin Film Behavior

Thin films produced from solutions of 0.01wt%, 0.05wt% and 0.1wt% N25-7 were studied in Scheludko cell. The draining processes, which are quite similar at different surfactant concentrations, are slow but do exhibit asymmetric drainage. For films of size between 0.6mm-0.8mm, dimples were seen longer than 25 seconds before they were expelled from the film lamella. After dimple expulsion, the film contained several channels. As it gradually thinned, the channels disappeared and a plane parallel film formed. At low surfactant concentrations, e.g. 0.01wt% and 0.05wt%, the equilibrium film was a white planar film as shown in Figure 4.22. At higher surfactant concentration, e.g. 0.1wt%, slow drainage continued beyond the white planar film (Figure 4.23a), as shown in Figure 4.23b. It took several minutes to have distinguishable change in the film thickness, based

![Equilibrium films obtained from 0.01wt% and 0.05wt% N25-7 solutions](image)

**Figure 4.22** Equilibrium films obtained from 0.01wt% and 0.05wt% N25-7 solutions
on the brightness change of the film from white (bright) to gray. No white spots were observed during the draining process.

Figure 4.23 Film produced with 0.1wt%N25-7 solution

(a) (b)

The CMC of N25-7 is 0.0009wt%. Although the three studied surfactant concentrations are all above CMC, no stratification was observed. The reason may be that the micelles in 0.1%N25-7 are rod-like and polydisperse so that there is no micellar structuring effect. It’s reasonable that rod-like micelles tend to form in nonionic micellar surfactant solution because of relatively weaker repulsion between polar heads than for anionic surfactant.

Again, concentration of N25-7 was fixed at 0.1wt% to study the effect of hardness on film drainage. With the presence of 300ppm hardness, the asymmetric drainage of dimple was much faster (Figure 4.24a), happening within 1~2 seconds after its formation. The subsequent thinning process was also much faster. Within 1 minute, film patterns like those of Figure 4.24b were observed. White spots appeared thereafter. The white spots eventually either left the film during further drainage or disappeared before reaching film periphery. Finally a stable black film formed.
It appears that there are three origins of the white spots. Some come from the breakage of white ridges. In the specific case shown in Figure 4.25a, which is a schematic of the process video-taped in Figure 4.24 c,d&e, the breakage of the white liquid ridge in the upper part of Figure 4.24c produced a large spot and some smaller ones, showing no characteristic wavelength. Stratification phenomenon was seen in the process shown in
Figure 4.24 d & e, i.e., formation of black spots within large white spot in Figure 4.24d and then coalescence in Figure 4.24e, implying that the presence of calcium ions induced micellar structuring effect. Secondly, when the thinning pattern is like Figure 4.25b, liquid trapped in the middle of three black spots (thinner parts) turns into a white spot. Thirdly, some may come from the mechanism illustrated earlier in Figure 4.8 or Figure 4.9. That is liquid rim forms around an expanding black spot. It subsequently breaks apart into secondary fluid pockets which appear as white spots, as the thick rim is vulnerable to capillary instability [Bergeron et al., 1992].

![Diagram of white spots formation](image)

(a) White spots (b) White spot

Figure 4.25 Origin of white spots

### 4.2.4 Discussion

The relatively large equilibrium thickness of N25-7 stabilized films can be explained by the low concentration of ions in the solution (low ionic strength) and by the fact that there is a long-range electrostatic repulsion between the polar heads of surfactants that occupy the surfaces of the foam films. Generally, ions in nonionic surfactant solutions are generated only by dissociation of carbonic acid, which is formed as a result of CO₂ dissolution from the atmosphere. The ionic strength of such solutions is on the order of 10⁻⁵ M, which corresponds to a Debye screening length \( \kappa^{-1} \) of 100nm
[Marinova & Denkov, 2001]. This explains the equilibrium thickness of the foam films of the N25-7 solution. On the other hand, the ion concentration in a micellar solution of ionic surfactant like N25-3S can be estimated to be [Richetti & Kekicheff, 1992]:

\[ C_{\text{ION}} = 2\text{cmc} + \alpha(C_s - \text{cmc}) \]

Where \( C_s \) is the total surfactant concentration, \( \alpha \) is the degree of dissociation of the surfactant molecules in the micelles, and the free monomers are considered as completely dissociated. Thus the Debye screening length could be two orders of magnitude smaller than that of nonionic surfactant.

The role of the electrostatic force can be demonstrated by making films from N25-7 solution containing electrolyte, e.g., CaCl\(_2\). With the presence of hardness, as we can see in Figure 4.24, thinning process was faster and the equilibrium state was a thin black film instead of a thick white film as shown in Figure 4.22.

The observation that the equilibrium film thickness is thinner at higher concentration of N25-7, e.g. 0.1wt\%, may be caused by the impurity of the commercial surfactant mixture, which brought in some electrolytes. The results that hardness doesn't change foamability and foam stability of the nonionic surfactant (N25-7) are probably because electrolytes (calcium ions) have no significant effect on nonionic surfactant adsorption at the air-water surfaces.

4.3 Summary

Anionic surfactant N25-3S makes more stable foam than N25-7 in an open foam testing column, basically because the electric double layer repulsion is much stronger in anionic surfactant solutions than in nonionic surfactant solutions. Electrical effects also
explain why hardness has different effect on foam behavior of N25-3S and N25-7. Plausible suggestions of key mechanisms of interesting behaviors in thin film drainage have been made, but more extensive study is needed for completely understanding, e.g., quantitative information on film thickness as function of position and time; light scattering study of micelle size and shape as function of surfactant concentration and hardness.
Chapter 5 Mechanism for Defoaming Action in Aqueous systems by Oils and Calcium Soap

5.1 Introduction

Most previous research on foam stability has been directed toward understanding effects of chemically inert oils such as silicone oils, hydrophobic solids, and their mixtures which are added to aqueous solutions to prevent foam from forming and/or to destabilize any foam which does develop. Relatively little attention has been given to oils and solids consisting of fatty material such as liquid triglycerides (cooking oils), fats, body soils and solid food particles removed from dishes or fabrics and dispersed in the washing bath. Nor have effects on foam stability of time-dependent processes such as precipitation of calcium and magnesium soaps been studied systematically. However, knowledge involving questions of foam stability in the presence of oil and insoluble soaps is of practical importance, e.g., for laundering, personal cleaning, and the potential use of foam as a mobility control agent in alkaline/surfactant processes for improved oil recovery.

In many practical situations oils are contaminated with fatty acids. For example, cooking oils routinely contain long-chain fatty acids formed by hydrolysis of triglycerides. In hard water precipitation of calcium and magnesium soaps of these fatty acids may occur and destabilize the foam. This defoaming effect of calcium and magnesium soaps is well known but not well understood.

The objective of this chapter is to develop an improved understanding of how oily soils and soaps affect foam stability and especially, to explain the synergism between the oil and the insoluble soap particles. The investigation was conducted by following the
equilibrium and dynamic effects in systems containing a representative anionic surfactant N25-3S and a representative nonionic surfactant N25-7 and drops of triolein, hexadecane and their mixtures with oleic acid. These three oils are models of nonpolar lubricating oils, vegetable oils and nonpolar/polar sebum soil respectively. The mixture of hexadecane and oleic acid at weight ratio of 9 to 1 is denoted as C16/HO1, and the mixture of triolein and oleic acid at weight ratio of 9 to 1 is denoted as TO/HO1. During this work, foam stability has been determined by measuring the rate of collapse of a vertical foam column formed by mixing air with a surfactant solution at the base of the column. The results are supplemented by video-microscopy observations of symmetric air-water-air films and asymmetric oil-water-air films.

5.2 Effect of Pure Oils on Foam Stability

5.2.1 Foam Stability

To study the effect of oils on foams produced with solutions containing anionic surfactant N23-3S, surfactant concentration was fixed at 0.01wt%, which is near the CMC (critical micelle concentration). Liquid oils were added in increments to the aqueous solution after the initial study in the absence of oil. Foam heights after decaying 20 min are compared in Figure 5.1. In the absence of oil, foam height after 20 minutes was about 18cm. Figure 5.1 shows that triolein has almost no defoaming effect. Hexadecane has some, but it is not remarkable. The results also show that the defoaming effect is relatively insensitive to the oil-to-surfactant ratio.

Concentration of the nonionic surfactant N25-7 was fixed at 0.1wt%, which is a representative level for practical laundry applications. Oils were added in increments up to an oil-to-surfactant ratio of about one. Foam heights after 20 min are compared in
Figure 5.2. In the absence of oil, foam height after 20 minutes was about 15 cm. Triolein again showed no defoaming effect while hexadecane exhibited a much greater effect than it did with the anionic surfactant.

Figure 5.1 Effect of pure oils on the stability of foams with 0.01 wt% N25-3S

![Graph showing foam height after 20 min (cm) vs. oil to surfactant weight ratio for triolein and hexadecane.]

Figure 5.2 Effect of pure oils on the stability of foams with 0.1 wt% N25-7

![Graph showing foam height after 20 min (cm) vs. oil to surfactant wt. ratio for triolein and hexadecane.]

Plots of foam height versus time for the two surfactants' solutions with/without pre-emulsified hexadecane are given in Figure 5.3.
5.2.2 Individual Foam Films

The experiments with small horizontal foam films in the Sheludko cell with solutions containing 0.01wt% N25-3S and 0.02wt% oily additives (hexadecane or triolein) showed that the addition of the studied oils didn’t significantly change the film-thinning rate, while the movement of oil drops was clearly detectable under microscopy. No multiple stepwise transitions in the foam film thickness (stratification) were observed because the concentration of micelles was too low. Stratification was observed with a solution containing 0.05wt% N25-3S.

At 0.01wt% of N25-3S, most of the dozens of studied foam films were stable when the oily additive was hexadecane. Oil drops were either trapped at the periphery of the film without breaking the film (Figure 5.4a) or swept out of the film into the meniscus as the film thinned. Occasionally, oil bridge configurations formed and led to film rupture (Figure 5.4b). When the oily additive was triolein, the oil drops were always swept out of the film and didn’t affect film lifetime.
Figure 5.4 Typical cases in films made by 0.01%N25-3S solution containing hexadecane. (a) Captured oils drops stay in the periphery of the film. (b) Oil bridge cause film rupture.

Foam films made from solutions of 0.1wt% N25-7 were also studied. Although the surfactant concentration was well above the CMC (about 0.0009wt%), no stratification was observed, presumably because the micelles were rod-like and polydisperse so that there was no micellar structuring effect to induce stepwise transition in film thickness. The addition of 0.1wt% oils didn’t change the slow drainage process of this surfactant solution. With hexadecane as oily additive, most of the film samples broke before or around 2 minutes instead of lasting more than 6 minutes as in the oil-free system. With triolein as oily additive, however, film lifetime was not affected.

5.2.3 Vertical Foam Cell

After making foam in a thin vertical cell with solutions containing 0.01%N25-3S + 0.02wt% hexadecane/triolein, we observed the foam with video-microscopy. We saw oil drops come up through the plateau borders to the top of the foam (Figure 5.5a) or trapped in the nodes in the middle of the foam (Figure 5.5b). Such foam is fairly stable. We didn’t observe broken of film lamellae or plateau borders within 15min.
Figure 5.5 Foam in vertical cell of solution containing 0.01wt% N25-3S & 0.02wt% hexadecane

(a) 800µm  (b)

5.2.4 ESB Analysis

Entry, spreading and bridging coefficients were calculated with equilibrium interfacial tensions and compared with foam heights after 20 minutes to see whether the effectiveness of oils as antifoams was consistent with these coefficients. The measured interfacial tensions and foam heights are given in Table 5.1.

Table 5.1 Semi-quilibrium\(^a\) Entry, Spreading, Bridging coefficients and foam stability for solutions of 0.01wt% N25-3S and 0.1wt% N25-7 with pure oily

<table>
<thead>
<tr>
<th>Solution</th>
<th>oil</th>
<th>(\gamma_{AW})</th>
<th>(\gamma_{OW})</th>
<th>(\gamma_{AO})</th>
<th>E</th>
<th>B</th>
<th>(H_0) (cm)</th>
<th>(H_{20}) (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt% N25-3S</td>
<td>No oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>18.1</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>hexadecane</td>
<td>33.1</td>
<td>9.7</td>
<td>26.3</td>
<td>16.5</td>
<td>498</td>
<td>20</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>triolein</td>
<td>33.0</td>
<td>9.5</td>
<td>31.9</td>
<td>10.6</td>
<td>162</td>
<td>20</td>
<td>17.9</td>
</tr>
<tr>
<td>0.1wt% N25-7</td>
<td>No oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>14.9</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>hexadecane</td>
<td>29.7</td>
<td>1.7</td>
<td>26.3</td>
<td>5.1</td>
<td>193</td>
<td>20</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>triolein</td>
<td>29.5</td>
<td>8.4</td>
<td>31.9</td>
<td>6.0</td>
<td>-77</td>
<td>20</td>
<td>14.8</td>
</tr>
</tbody>
</table>

Note: \(^a\): definition see chapter 2.3.1. \(H_0\) is initial foam height, \(H_{20}\) is foam height after 20 minutes. The units of interfacial tensions are mN/m. For systems containing N25-3S, oil/surfactant = 1; for systems containing N25-7, oil/surfactant = 0.5. The \(\gamma_{AW}\) tensions are measured after equilibration with corresponding amounts of dispersed oil.
For N25-3S, this analysis shows that both hexadecane and triolein have large positive entry and bridging coefficients, and thus are expected to have significant destabilizing effects. But the observed effect was either slight (with hexadecane) or none (with triolein). This discrepancy occurs because the asymmetric oil-water-air films in anionic surfactant solutions are stabilized by repulsion due to the overlap of electrical double layers. The generalized entry coefficient \( E_g \) instead of the classical entry coefficient \( E \) should be used to predict entry behavior.

For N25-7, it was observed that hexadecane has a significant defoaming effect and triolein has no defoaming effect. This is consistent with ESB analysis. As Table 5.1 shows, hexadecane has large positive entry and bridging coefficients but triolein has a negative bridging coefficient, which indicates that oil-bridging is not destabilizing.

5.3. Effect of Oil Mixtures on Foam Stability

5.3.1 Foam Stability

The defoaming effect of mixtures of hexadecane/triolein with a small amount of oleic acid on stability of foams was investigated. Results with N25-3S at 0.01wt\% are illustrated in Figure 5.6 where foam heights after 10 minutes are compared. As we can see, oil mixtures themselves didn’t destabilize foam within 10 minutes. But when calcium and alkalinity (typically pH9 adjusted by NaOH) were present, foams became very unstable. Similar phenomenon was observed at different hardness levels studied from 50ppm to 300ppm.
Figure 5.6 Effect of oil mixtures on stability of foams with 0.01wt%N25-3S

![Graph showing effect of oil mixtures on stability of foams with 0.01wt%N25-3S](image)

For 0.1wt% N25-7, it's also true that the least stable foam occurred when both mixed oils and hardness were present at alkaline pH, as shown in Figure 5.7. Actually, when C16/HOI to surfactant ratio was increased to 1 in alkaline solution containing hardness, foam couldn't be built to 20cm high as usual. The maximum height reached was about 10cm.

Figure 5.7 Effect of oil mixtures on stability of foams with 0.1wt%N25-7

![Graph showing effect of oil mixtures on stability of foams with 0.1wt%N25-7](image)

The striking difference between the stable and the unstable foam is further illustrated in Figure 5.8, where foam height is shown as a function of time. For N25-3S,
0.01wt% C16/HOI had minimal destabilizing effect. But the effect was dramatically enhanced when calcium and alkalinity were present, and most of the foam was destroyed within several minutes after foam generation had ceased. For N25-7, C16/HOI destabilized foam over time but the effect was substantially enhanced when calcium and alkalinity were present. One can conclude that thicker foam lamellae or Plateau borders could be broken in that situation if drainage rates are comparable.

Figure 5.8 Effect of C16/HOI on decay behavior of foams with 0.01wt%N25-3S and 0.1wt%N25-7

Plot of foam height versus time

![Plot of foam height versus time](image)

The aforementioned large reduction in foam stability didn’t occur if only calcium or only alkalinity was present instead of both together.

5.3.2 Video-microscopy Contacting Experiment

Trying to understand what caused the diminution in foam stability, we first looked at the oil-water interfaces. A small drop of C16/HOI (diameter=160μm) was injected into the aqueous phase of 0.01wt%N25-3S with 300ppm Ca²⁺ present and pH adjusted to about 9 with sodium hydroxide. The initial state is shown by Figure 5.9a. A new phase formed at the oil-water interface several minutes after contacting. As time went
on, the interface became more rigid and was no longer smooth (Figure 5.9b). In order to check the rigidity of the interface, we rotated an oil drop at certain speed in a spinning drop tensiometer, and then suddenly reduced the speed. The interface crumpled (Figure 5.9c) as area decreased, indicating the rigidity of the interface. We conclude that calcium oleate, which has very low solubility in water with solubility product in the range of $10^{-15}$ [Irani & Callis, 1960], was formed at the oil-water interface due to the reaction between oleic acid and divalent calcium ions. Figure 5.10 shows a TO/HOl drop in the same solution as in Figure 5.9. Obviously, a new phase formed at the interface after several minutes (Figure 5.10a). Again, the spinning drop (Figure 5.10b) showed that the new phase was solid.

It's worth noting that these dynamic phenomena involving calcium soap formation didn’t occur in neutral solutions within the time scale we studied, which was about half an hour. This implies that alkaline pH is crucial to the speed and extent of oleic acid ionization.

Figure 5.9. Video-microscopy contacting experiments: a drop of C16/HOl mixture contacted the pH9solution containing 0.01wt% N25-3S and 300pphardness. (a) initial state (b) about 5 min later (c) a spinning drop
Figure 5.10. Video-microscopy contacting experiments: a drop of TO/HOl contacted the pH9 solution containing 0.01wt% N25-3S and 300ppm hardness. (a) about 5 min later (b) a spinning drop

So far what have been discussed are oil-water contacting phenomena in anionic surfactant (N25-3S) solutions. Similar phenomena were observed in corresponding experiments with 0.1wt%N25-7. That is, calcium soaps were formed at the oil-water interface, as shown in Figure 5.11 and Figure 5.12.

Figure 5.11 A drop of C16/HOl in pH9 solution containing 0.1wt%N25-7 & 300ppmCa^{2+}
Figure 5.12 A drop of TO/HOI in pH9 solution containing 0.1wt%N25-7 & 300ppmCa^{2+}

5.3.3 Horizontal Foam Films

Effect of formation of calcium soap at the oil-water interface on stability of foam films was checked by Sheludko cell. We studied tens of foam films produced from a solution containing 0.01wt%N25-3S, 300ppm hardness and 0.02wt% emulsified C16/HOI. We observed two types of behavior. Sometimes the individual foam films were very unstable, breaking within 1~2 second after their formation due to oil drops. Figures 5.13a & b are two examples. In Figure 5.13a, an oil drop carrying solid particles pierced the thinnest part of the foam film and ruptured it right away. In Figure 5.13b, the foam film broke immediately after the appearance of the so-called ‘fish eye’ configuration, which is an indication of oil bridging. Sometimes foam films were stable since oil drops were all swept out of the foam lamella into the meniscus. The relative frequencies of the unstable and stable films were about 30% and 70%.

Similar phenomena were observed with the nonionic surfactant. The pH9 solution containing 0.1wt%N25-7, 0.1wt% C16/HOI and 300ppm hardness produced unstable foam films. Thirteen out of fifteen samples studied broke within 1~3 seconds after the
dimple began to form and before its expulsion. Two of them broke after asymmetric expulsion of the dimple.

Figure 5.13 Foam films produced with pH9 solution of 0.01wt% N25-3S containing 0.01wt% C16/HOl and 300ppm Ca\(^{2+}\). (a) Particle with irregular shape pierced the periphery of the film and broke it. (b) Film broke because of oil bridging.

![Image of foam films](image_url)

5.3.4 Stability of Oil-water-air Asymmetric Films.

Having shown that the formation of solid calcium soap at the oil-water interface enhanced antifoaming effectiveness of oils, we propose that this is because soap particles, sitting at the oil-water interface, help destabilize the pseudoemulsion film and therefore, facilitate drop entry. To check this hypothesis, we have directly observed the entering characteristics for situations where no calcium soap was formed and where calcium soap was formed *in situ* by fatty acid reaction with calcium. The experiments involved an air-water interface older than 10 minutes, i.e., an interface at or near equilibrium.

5.3.4a Experiments with anionic surfactant N25-3S

When making a pseudoemulsion film by pressing a drop of C16/HOl (or n-hexadecane) from underneath the surface of 0.01wt%N25-3S solution (pH7), we saw that a dimple formed and drained asymmetrically, as shown in Figure 5.14a. Eventually, the
film thinned to a nearly parallel stage (Figure 5.14b) and remained stable for a long time. We didn’t see film rupture even at the highest accessible capillary pressure that our apparatus can achieve (around 120 Pa).

When TO/HOI (or triolein) was used in the above experiment, similar phenomena were observed except that drainage of the dimple was slower and symmetric.

Figure 5.14c illustrates the pseudoemulsion film formed by a drop of C16/HOI in pH9 solution containing 0.01 wt% N25-3S and 300 ppm calcium. Immediately after the film was formed, we saw a liquid dimple. As the film thinned asymmetrically, particles were seen in the film and left behind after dimple expulsion. Protrusion of the particles into the air-water surface became more obvious as the film became thinner but still exhibited channels and other nonuniformities. Such films ruptured before reaching a state with uniform thickness. Figure 5.14d shows an oil lens formed after the film in Figure 5.14c ruptured.

Figure 5.14 Pseudoemulsion films. (a) Asymmetric drainage of dimple (b) Stable film between oil phase (C16/HOI) and aqueous phase (0.01 wt% N25-3S) (c) Unstable film between oil phase (C16/HOI) and aqueous phase (0.01 wt% N25-3S +300 ppm Ca^{2+}, pH9). Interference fringes are last stages of dimple draining asymmetrically. Bright dots evidence the presence of solid particles in the film. (d) Oil lens formed after the oil drop entered the air-water surface.
In a pseudoemulsion film formed by a drop of TO/HOl in the same aqueous phase, the dimple drained asymmetrically and, again, particles were seen in the film and left behind after dimple expulsion, as shown in Figure 5.15a. However, the film was stable despite the presence of particles. Eventually, particles were swept out of the film. A stable, uniform thin film was the final state (Figure 5.15b).

Figure 5. 15. Asymmetrically draining stable pseudoemulsion film formed between oil phase (TO/HOl) and aqueous phase (0.01wt% N25-3S +300ppm Ca$^{2+}$, pH9). (a) Interference fringes are last stages of dimple draining asymmetrically. Bright dots evidence the presence of solid particles in the film. (b) Stable thin film in final state.
5.3.4b Experiments with nonionic surfactant N25-7

Parallel experiments were performed with the nonionic surfactant N25-7 at a concentration of 0.1wt%. Pseudoemulsion films formed by C16/HOl (or n-hexadecane) and TO/HOl (or triolein) in the neutral surfactant solution exhibited slow and symmetric drainage and finally reached a stable state. Since \( E > 0 \) for both pure oils and oil mixtures, according to calculation, the results suggest that an electrical contribution to disjoining pressure exists and \( E_g < 0 \). The existence of electrical effects in films stabilized by nonionic surfactants without added electrolytes is not unusual. For hexadecane and C16/HOl, significant foam breakage was seen. Apparently the pseudoemulsion films in these systems become unstable at higher capillary pressures than could be achieved with our apparatus.

When the aqueous phase was adjusted to pH9 and with 300ppm calcium present, films formed with C16/HOl were unstable. Similar to the case with the anionic surfactant, particles were seen in the film and ruptured the film by bridging. Emergence of the oil drop into the air-water surface was observed thereafter. Films formed with TO/HOl in the same aqueous phase, however, presented a different behavior. As shown in Figures 5.16a & b, dimples started with symmetric drainage but eventually approached one side of the film. As the film further thinned, water entered from the other side and later spread over the entire film (see Figures 5.16 b-d). Particles were seen in the thinner parts of the film (Figures 5.16 b& c).
Figure 5.16 Pseudoemulsion film formed by TO/HO1 in pH9 solution containing 0.1wt%N25-7 and 300ppm calcium. (a) A dimple (b) The dimple approached one side of the film and water entered from the other side of the film. (c-d) Water gradually spread over the entire film.

5.3.4c Experiments with preformed calcium soap particles

In above two sections calcium soaps were formed in situ by reaction of fatty acid in oil phase and calcium in aqueous phase. Such formed soap particles help destabilize pseudoemulsion films. To check such effect with that of the preformed calcium soap particles, we performed the following experiments. Calcium oleate particles were prepared by mixing the concentrated solutions of sodium oleate and calcium chloride. The precipitate was collected by vacuum filtration and dried at 45°C for at least 40 hours. The dry product was then ground into fine powders. We selected powders that went
through the 300µm screen but didn’t go through the 90µm screen. Because calcium oleate particles are polar and therefore tend to agglomerate, it’s possible that some particles have sizes smaller than 90µm. The powder and hexadecane were mixed at a weight ratio of 10 to 90 by vigorous hand shaking. Under microscope we can see particles have widely distributed sizes. Some are larger than 100µm and some are much smaller (see Figure 5.17).

Figure 5.17 calcium oleate particles dispersed in hexadecane

Pseudoemulsion films were made between the above described oil-solid mixture and 0.01wt%N25-3S solution. Figure 5.18 shows representative video frames of several such films we have studied. The pictures were taken right before their rupture. In Figure 5.17a & b, the particles are clearly visible. In Figure 5.17c, the particle could not be seen directly, but the fingering patterns imply the presence of solid particles in the film. This study confirms that preformed calcium soap particles help destabilize pseudoemulsion films, just as solid particles formed in situ do.
Figure 5.18 Pseudoemulsion films between hexadecane (containing 10wt% preformed calcium soap particles) and 0.01wt% N25-3S solution.

5.3.5 ESB Analysis

For systems where the combinations of oil mixtures, hardness and alkaline pH produced the least stable foams, entry, spreading and bridging coefficients were calculated based on the equilibrium tensions and compared with foam heights after 10 minutes and 20 minutes. The results are shown in Table 5.2. For solutions of each surfactant, C16/HOl has positive entry and bridging coefficients. Although the magnitudes of E and B are smaller than in Table 5.1 (mainly because $\gamma_{AW}$ is smaller), the positive values should ensure a good antifoam activity. The reason is that electrical double layer repulsion in the pseudoemulsion film need no longer be considered if soap particles effect oil entry, as explained in section 5.4 below. In fact, a large defoaming effect was observed. So the effectiveness of C16/HOl is consistent with entry/bridging coefficients.

For systems containing TO/HOl, however, we saw not only negative bridging coefficient B but also negative entry coefficient E. Both of these indicate stable foams, but the foams themselves were quite unstable. Failure of this observation to agree with
ESB analysis means either that a new antifoam mechanism is required or that consistency is masked because the non-equilibrium nature of the surfaces present in newly formed foams is not taken into account. We believe it is the latter effect, not the former, that influences the behavior. Indeed Garrett and Moore [1993] had found antifoam effects under dynamic conditions but not under equilibrium conditions with liquid paraffin/hydrophobed silica antifoam in certain sodium alkyl benzene sulphonate solutions which correlated with measurements of B under equilibrium and dynamic conditions.

Table 5.2 Semi-equilibrium Entry, Spreading, Bridging coefficients and foam stability for solutions of 0.01wt% N25-3S and 0.1wt% N25-7 with oil mixtures.

<table>
<thead>
<tr>
<th>Solution</th>
<th>oil</th>
<th>CaCl₂ (ppm)</th>
<th>γAw</th>
<th>γow</th>
<th>γ₀ₐ</th>
<th>E</th>
<th>B</th>
<th>H₀ (cm)</th>
<th>H₁₀ (cm)</th>
<th>H₂₀ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt% N25-3S, pH9</td>
<td>C16/HO1</td>
<td>300</td>
<td>30.1</td>
<td>0.1</td>
<td>26.5</td>
<td>3.7</td>
<td>204</td>
<td>20</td>
<td>4.0</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>TO/HO1</td>
<td>300</td>
<td>29.2</td>
<td>0.8</td>
<td>31.4</td>
<td>-1.4</td>
<td>-133</td>
<td>20</td>
<td>7.5</td>
<td>7.4</td>
</tr>
<tr>
<td>0.1wt% N25-7 pH9</td>
<td>C16/HO1</td>
<td>300</td>
<td>29.0</td>
<td>0.1</td>
<td>26.5</td>
<td>2.6</td>
<td>139</td>
<td>20</td>
<td>5.1</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>TO/HO1</td>
<td>300</td>
<td>29.3</td>
<td>1.6</td>
<td>31.4</td>
<td>-0.5</td>
<td>-125</td>
<td>20</td>
<td>7.2</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Notes same as for Table 5.1 except that H₁₀ is foam height after 10 minutes; C value is zero for foam system at equilibrium (refer to discussion on page 16-17).

Taking the anionic surfactant system, for example, we calculated the dynamic entry, spreading and bridging coefficients. The results are shown in Table 5.3. We found that because air-water surface tension decreases significantly with time (the change of oil-water interfacial tension was neglected since it's relatively small), entry/bridging coefficients were positive initially and later decreased to negative values. For the same reason spreading coefficient is positive initially, so that oil may spread at the air-water surface. If such spreading occurs, it will alter conditions for instability of
pseudoemulsion film, e.g. it reduces entry barrier of the antifoam globules and facilitates the subsequent bridging and rupture of the foam film, as discussed by Denkov [2002]. This implies that a clear distinction should be drawn between antifoam effects occurring when surface tensions haven’t reached equilibrium, e.g., during foam generation and shortly after foam generation has ceased, and those occurring when equilibrium has been reached.

Table 5. 3 Dynamic$^b$ and Semi-equilibrium$^a$ E, S, and B with N25-3S.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Oil</th>
<th>Semi-equilibrium</th>
<th>Defoaming effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%N25-3S, pH9,300ppmCa</td>
<td>TO/HOil</td>
<td>-1.4  -3.0  -133</td>
<td>none  large</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
E &= \gamma_{AW} + \gamma_{OW} - \gamma_{AO} \\
S &= \gamma_{AW} - \gamma_{OW} - \gamma_{AO} \\
B &= \gamma_{AW}^2 + \gamma_{OW}^2 - \gamma_{AO}^2
\end{align*}
\]

<table>
<thead>
<tr>
<th></th>
<th>Time</th>
<th>(\gamma_{AW})</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 min</td>
<td>33.8</td>
<td>2.8</td>
<td>1.3</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>4 min</td>
<td>31.5</td>
<td>0.5</td>
<td>-1.0</td>
<td>-18</td>
</tr>
<tr>
<td></td>
<td>8 min</td>
<td>29.7</td>
<td>-0.9</td>
<td>-2.5</td>
<td>-103</td>
</tr>
</tbody>
</table>

Note: $^a,b$ definition see chapter 2.3.1.

This explanation is consistent with experimental results. Taking 0.01wt% N25-3S solution containing TO/HOil + 300ppmCa$^{2+}$ + pH9 (the second entry of Table 5.2) for example, about 60 percent of the produced foam was destroyed within the initial eight minutes, and then the residual foam was quite stable. As indicated above, pseudoemulsion film observation of this system showed that the oil-water-air asymmetric films were stable when the air-water surface was near equilibrium. The quick decrease in foam height shortly after foam generation has ceased reflects the positive values of entry and bridging coefficients occurring in the foam when dynamic
surface tensions are high. The negative values for E and B measured under near equilibrium conditions, on the other hand, mean that the foam is stable a few minutes after foam generation has ceased.

The same is true for the nonionic surfactant solution with TO/HO1. Calculated values of E and B were positive during and shortly after foam formation but negative at equilibrium, as shown in Table 5.4. Foam breakage was observed mainly during the first few minutes after the foam was generated.

The dynamic entry, spreading and bridging coefficients in Table 5.3 and Table 5.4 were calculated with surface and interfacial tensions measured by the spinning drop tensiometer. In such measurements, the areas of the air-water or oil-water interfaces were different than those in the foaming equipment. Moreover, the oil-to-surfactant ratio was about 20 times higher in the spinning drop measurement than in the foam column. So the correspondence between E, S, B values and the time scale in Tables 5.3 & 5.4 may not be that in the real foam. But the trend that E, S, B change within a few minutes from positive to negative values is consistent with the foam stability results.

Table 5.4 Dynamic\(^b\) and Semi-equilibrium\(^a\) E, S, and B with N25-7

<table>
<thead>
<tr>
<th>Solution</th>
<th>Oil</th>
<th>Equilibrium</th>
<th>Defoaming effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 wt% N25-7, pH9, 300 ppm Ca</td>
<td>TO/HO1</td>
<td>E</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.5</td>
<td>-3.7</td>
</tr>
</tbody>
</table>

\[
E = \gamma_{AW} + \gamma_{OW} - \gamma_{AO}
\]

<table>
<thead>
<tr>
<th>Time</th>
<th>(\gamma_{AW})</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/7 min</td>
<td>33.1</td>
<td>3.3</td>
<td>0.1</td>
<td>112</td>
</tr>
</tbody>
</table>

\[
S = \gamma_{AW} - \gamma_{OW} - \gamma_{AO}
\]

<table>
<thead>
<tr>
<th>Time</th>
<th>(\gamma_{AW})</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/3 min</td>
<td>30.9</td>
<td>2.1</td>
<td>-1.1</td>
<td>34</td>
</tr>
</tbody>
</table>

\[
B = \gamma_{AW}^2 + \gamma_{OW}^2 - \gamma_{AO}^2
\]

<table>
<thead>
<tr>
<th>Time</th>
<th>(\gamma_{AW})</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 min</td>
<td>29.7</td>
<td>-0.1</td>
<td>-3.3</td>
<td>-101</td>
</tr>
</tbody>
</table>

Note: \(^a\)\(^b\) definition see chapter 2.3.1.
5.3.6 Synergism between Oil Drops and Insoluble Soap Particles

So far it has been demonstrated that alkaline solutions of N25-3S or N25-7 containing both calcium and oil mixtures with oleic acid produce unstable foams. Since it has been shown earlier that the oils themselves are not always effective defoamers, one might argue that the large diminution in foam stability was caused by the presence of calcium soap alone and the oil actually did nothing, as the defoaming effect of calcium/magnesium soaps is well known (see Chapter 9). In order to distinguish the effect of oil and soap, we compared foam stability of three systems. In all systems, 0.01wt%N25-3S and 300ppm calcium were present. System I contained 0.01wt% pure hexadecane. System II contained no oil but 0.0005wt% sodium oleate. System III was a combination containing both sodium oleate and hexadecane. As may be seen from Figure 5.19, hexadecane had minimal defoaming effect. Calcium soap destabilized foam to some extent. But the combination of oil and soap indeed enhanced the defoaming effectiveness significantly. For systems II and III where reduction of foam stability was substantial, foam appearances were different. Regarding the initially produced foams, foam of system III (with oil) consisted of large air bubbles, some with diameters in the range of centimeters. Foam of system II (oil-free) consisted of only fine bubbles with diameters in the range of 1 millimeter. Coalescence of air bubbles was observed during foam formation process for the solution with oil but not for the solution free of oil. Regarding the foam decay process, foam collapse occurred simultaneously at different heights within the foam of system III (with oil) and hence, led to “discontinuous foam” (Figure 5.20). For foam of system II (oil-free), however, decay proceeded from the top and
occurred only when foam lamellae became sufficiently thin after a certain time of drainage.

The above information proves the functionality of oils in decreasing foam stability. That they are much more powerful as defoamers in the presence of calcium soap is a synergistic effect.

Figure 5.19 Synergistic effect between oil drops and soap particles on foam stability

![Foams of solutions containing 0.01wt%N25-3S, 300ppmCa$^{2+}$ and other additives](image)

Figure 5.20 Foam of solution containing oil (system III). For explanation, see text.

5.4 Mechanism
It's interesting that small oil drops sometimes cause film rupture and sometimes not. It's worth an attempt to look at the effect of disjoining pressure $\Pi$ and not simply entry coefficient $E$, which does not account for capillary pressure and surface forces like overlap of the electrical double layers.

Consider a spherical drop or particle in a film at equilibrium (Figure 5.21a), for example. The disjoining isotherm is qualitatively sketched as Figure 5.21c. It corresponds to $E > 0$, i.e., water does not spread between the sphere and air. At point 1, the film thickness of the uniform portion of the film is $h_1$, where $\Pi_1(h_1) = P_c$, i.e., the capillary pressure of the meniscus. At point 2, the disjoining pressure $\Pi_2$ in the pseudoemulsion film must exceed $\Pi_1$ by $2\gamma_{AW}/R_{oil}$, according to Young-Laplace equation, and $h_2 < h_1$. If $\Pi_2$ exceeds $\Pi^*$ at the maximum of the disjoining pressure isotherm, equilibrium cannot exist and the film will break. But if the electrical double layer repulsion provides additional stability and the capillary pressure in the asymmetric film is not large enough to overcome the entry barrier, that is if $\Pi_2 = \Pi_1 + 2\gamma_{AW}/R_{oil} < \Pi^*$, this configuration is stable and drop entry cannot occur. This is presumably what happens in anionic surfactant solutions where the classical entry and bridging coefficients are positive but antifoam activities are poor.

Suppose now that we have a rough sphere or a drop with small solid particles at the oil-water interfaces, as observed in the videomicroscopy experiments and sketched in Figure 5.21c. The equilibrium disjoining pressure at point 3, $\Pi_3$, must exceed $\Pi_1$ by $2\gamma_{AW}/R_{particle}$. $\Pi_3$ can be much larger than $\Pi_2$ because $R_{particle}$ is much smaller than $R_{oil}$. So $\Pi_3$ is more likely to exceed $\Pi^*$, and hence emergence of the particle into the air-water interface is more likely to happen. Such an argument involving local curvature can be
made although \( \Pi^* \) in the configuration of Figure 5.21a will be different from that in Figure 5.21b because the former is related to the oil-water-air asymmetric film while the latter is related to the solid-water-air asymmetric film. Even for the nonionic surfactant system, however, both the solid-water and air-water surfaces should be charged in the presence of calcium and oleate ions, so that the basic shape of the \( \Pi-h \) curve should be as shown in Figure 5.21c. This mechanism also works for an oil drop trapped in Plateau borders since in some cases that may be where the instability occurs. And it’s not necessary for the solid particle to be spherical. It could have various shapes. The key point is that the portion of the solid approaching the air-water surface, which could even be some kind of long projection or asperity, have a rounded tip which resembles a sphere and causes a high local curvature of the pseudoemulsion film.

Figure 5.21 Schematic presentation of a drop (or particle) in foam film.
(a) A drop with smooth surface (b) Drop with rough surface
(c) The disjoining pressure isotherm.

\[
\Pi_2 = \Pi_1 + 2\gamma_{AW}/R_{oil} < \Pi^* \\
\Pi_3 = \Pi_1 + 2\gamma_{AW}/R_{particle} > \Pi^*
\]

Point 1: \( h_1 \)  Point 2: \( h_2 \)

Point 1: \( h_1 \)  Point 3

The process following entry of the solid particle has been discussed by Garrett [1993], who showed that the following condition must be satisfied for coincidence of three phase contact lines to occur (see Figure 5.22):
\[ \theta_{AW} > 180^\circ - \theta_{OW} \quad [5] \]

After the particle bridges the pseudoemulsion film, whether or not the oil drop will enter the air-water surface is determined by the classical entry coefficient, since \( E \) equals \( E_g \) at the three phase contact line [Bergeron et al., 1993]. That is, electrical repulsion in the pseudoemulsion film is no longer a barrier to drop entry. At equilibrium, entry of the oil drop should occur only when \( E > 0 \). This condition is consistent with our experimental results for the pseudoemulsion films. As indicated in Table 5.2, C16/HOl has positive equilibrium entry coefficient, and indeed emergence of oil drops into the air-water surface was observed when the entry process was facilitated by calcium oleate particles. But no entry of TO/HOl drops was observed since the equilibrium entry coefficient of TO/HOl is negative and, in fact, the experiment involved an air-water interface at (or near) equilibrium.

Figure 5.22 Bridging of water-oil-air asymmetric film by spherical particle

![Diagram of bridging](image)

5.5 Summary

For foams made with 0.1 wt\% of the nonionic surfactant N25-7, measurement of the various tensions showed that the conventional ESB approach correctly predicted the
defoaming characteristics of these oils for the nonionic surfactant. For foams made with 0.01 wt\% of the anionic surfactant N25-3S, ESB analysis yielded positive values of E and B for both n-hexadecane and triolein. However, neither oil caused substantial reductions in foam stability. This discrepancy reflects the stability of the oil-water-air asymmetric film due to the electrical contribution to disjoining pressure in the “pseudoemulsion” film of surfactant solution. This contribution caused entry to the air-water surface to be more difficult than predicted by the usual equation for E (Eq. [1]).

When drops of triolein/oleic acid (TO/HOI) or n-hexadecane/oleic acid (C16/HOI) mixtures were dispersed in solutions of the same surfactants containing small amounts of calcium ions under mildly alkaline conditions (pH9), a large defoaming effect was observed. Results from several types of experiments indicate that solid calcium oleate particles form and collect at the drop surfaces. A mechanism has been proposed in which these small particles facilitate drop entry to the air-water surface, enabling the well known bridging instability of foam films or Plateau borders to occur. With this mechanism electrical disjoining pressure in the oil-water-air pseudoemulsion film can no longer prevent foam instability. For C16/HOI drops, calculated spreading and bridging coefficients for both surfactants are consistent with the observed defoaming effect. Results with TO/HOI, however, are consistent with entry/bridging coefficients only taking account of the decrease in $\gamma_{Aw}$ and $\gamma_{OW}$ with time, so that E>0 initially but later decreases to values near zero or slightly negative. Experiments demonstrated that most of the defoaming action occurred during or soon after foam generation.
Chapter 6 Effect of Fatty Acid and Sodium Soap on Foam behavior

In Chapter 5 the effect of nonpolar oils and their mixtures with an organic acid on foam stability was determined for conditions where both alkalinity and hardness were present and insoluble calcium soap formed. This chapter presents related results on the effect of these oils on foam stability for alkaline solutions of the same surfactants in the absence of hardness. Chapter 7 considers neutral surfactant solutions with hardness. In neither case are insoluble calcium soaps formed. The combined results of chapters 5-7 provide a comprehensive picture of how oils influence foam stability in model systems representative of those used in many cleaning applications.

6.1 Introduction

Systems containing surfactants and oil mixtures of nonpolar/polar compounds are frequently met in daily life. In practical washing situations, for instance, removal of oily soils which are mixtures of nonpolar compounds such as hydrocarbons or triglycerides and polar compounds such as long-chain alcohols or fatty acids is of great interest. Polar compounds produce large reductions in PIT (phase inversion temperature), so that excellent removal of these mixed soils can frequently be achieved at temperatures below the surfactant cloud point. In contrast, for nonpolar soils the maximum removal of hydrocarbons occurred near PIT which is well above the surfactant cloud point [Raney et al., 1987; Raney and Miller, 1987]. In enhanced oil recovery, alkaline solutions are injected into the reservoir to react with the naturally occurring acids in the crude oil to produce ionized form of the acids, commonly called soap. These soaps reduce interfacial
tension between the crude oil and floodwater, lowering the capillary forces and facilitating oil recovery.

Such alkali/acidic oil systems have been studied for years. Harkins and Zollman [1926] measured very low interfacial tensions between sodium oleate solutions and benzene, under both equilibrium and non-equilibrium conditions. They found that an equimolar mixture of sodium oleate and oleic acid produced extremely low interfacial tensions. Danielli [1937] supported the notion that the lowering of interfacial tension must be due to the ionization of the acid groups at the interface. Qutubuddin et al. [1984] determined microemulsion phase behavior for a system with oleic acid. They found that changes in pH affect the degree of ionization and hence the phase behavior. An increase in the degree of ionization produces a more hydrophilic surfactant film. Rudin and Wasan [1992], using oleic acid in decane as a model oil to mimic the crude oil, showed that interfacial tension goes through an ultralow minimum as a function of initial pH at constant ionic strength. Unionized acid is shown to be present in the system at alkali concentrations where interfacial tension is ultralow, suggesting that the unionized acid adsorbs onto the interface together with the ionized acid, resulting in ultralow transient and equilibrium interfacial tension.

Chen et al. [1998] studied the solubilization of the mixtures of triolein or hydrocarbon with fatty acid in nonionic surfactant solutions. They found that rapid initial solubilization accompanied by vigorous Marangoni flow occurs when drops of triolein/oleic acid are injected into nonionic surfactant solution. This behavior continues until most of the oleic acid has been solubilized, after which the solubilization rate becomes that seen for pure triolein. Similar behavior was seen for n-hexadecane/oleic
acid and triolein/oleyl alcohol drops. They proposed that the presence of oleic acid in the surfactant film at the oil-water interface reduces interfacial tension, and perhaps also generates a local interfacial tension gradient driving flow from the oil phase into micelles which have a higher tension and are temporarily attached to the drop. When the contact was conducted at pH9 or pH10, spontaneously-generated convection and rapid initial solubilization of triolein occurred for only a few seconds, possibly because conversion of acid to soap increased interfacial tension, eliminating the local Marangoni flow from drop to micelle.

Studies of foam properties of such alkali/acidic oil systems have been relatively rare. In this chapter we describe a study on foams using the mixtures of triolein or hexadecane and oleic acid as model oils and 0.01wt% N25-3S or 0.1wt% N25-7 as foaming agent. Interesting dynamic phenomena were observed at the oil-water interface, in foam films, in pseudoemulsion films and on foam stability at alkaline pH (typically pH9). All these dynamic effects originate from the fact that alkalinity stimulates ionization of fatty acid into soap and hence, affects oil-water and air-water interfacial properties. However, diversities exist since triolein and hexadecane have substantial differences in properties such as bulk viscosity, surface tension, etc. In the following discussion, the mixture of triolein and oleic acid at a weight ratio of 9 to 1 is denoted as TO/HOl, while the mixture of hexadecane and oleic acid at a weight ratio of 9 to 1 is denoted as C16/HOl. As indicated previously, none of the experiments discussed in this chapter has hardness, and there is no formation of insoluble soap.

6.2 Horizontal Contacting Experiment

6.2.1 Experiments in Absence of N25-3S or N25-7
The dynamic process that occurs when a drop of C16/HO1 contacts water, which is made pH9 by adding sodium hydroxide, is shown in Figure 6.1. The original drop size is about 130μm. Spontaneous convection was observed the moment the oil drop contacted the aqueous solution (Figure 6.1a). Small droplets formed and diffused away from the mother drop into surrounding solution (Figure 6.1b). After about 3 min the original drop started deforming rapidly, perhaps due to a strong interfacial turbulence and the convection flow inside it (Figure 6.1c). After several seconds of such behavior, the mother drop broke into several drops covered by small droplets and separated by regimes containing small droplets (Figure 6.1d)

Figure 6.1 A C16/HO1 drop in pH9 DI water. The original drop size is about 130μm.
When a drop of TO/HOl of similar size contacted DI water at pH9, similar phenomena were observed except that the original drop didn’t break up. Eventually spontaneous convection and emulsification slowed down, leaving thousands of tiny droplets in the solution. At the end, the size of the original drop decreased a little since most of the fatty acid had diffused out of the oil drop.

6.2.2 Experiments in the Presence of N25-3S or N25-7

When a drop of C16/HOl was injected into a pH9 solution of 0.01wt% N25-3S, this surfactant suppressed the strong spontaneous convection and emulsification. Small droplets formed at the oil-water interface (Figure 6.2). The oscillation of these drops was visible, but there was no observation of their detaching into the solution, nor of their moving around along the interface. The number of newly formed small drops increased slowly as time elapsed. Since the oil-water interfacial tension of this system is very low, less than 0.006mN/m, the system is presumably in a three-phase region. These small drops are assumed to be bulk microemulsion phase.

Figure 6.2 A C16/HOl drop in pH9 solution of 0.01wt%N25-3S. Drop size is around 130μm.
When a drop of TO/HO1 was injected into the pH9 solution of 0.01 wt% N25-3S, convection at the interface was observed at the moment the oil contacted the solution. Many tiny drops formed and moved around quickly along the oil surface. Such convection stopped eventually as time elapsed. More and more droplets gradually formed and slowly gathered together at the oil-water interface, as shown in Figure 6.3.

Figure 6.3 A TO/HO1 drop in pH9 solution of 0.01 wt%N25-3S. Drop size is about 120μm

Experiments with the nonionic surfactant N25-7 gave similar results. Figure 6.4 shows the results when a drop of C16/HO1 contacted the pH9 solution of 0.1 wt%N25-7. Upon contact, the injected drop kept moving around quickly. Gradually the movement slowed, and tiny droplets emulsified at the oil-water interface. These droplets initially traveled fast along the interface, but later the motion slowed and stopped.
6.2.3 Discussion of Contacting Results

It's not surprising that Marangoni convection exists for situations where a mixture of a nonpolar oil and a fatty acid contacts an alkaline surfactant solution, as evidenced by former studies [Raney 1985; Rudin & Wasan 1993; Chen et al. 1998]. The spontaneous emulsification in the aqueous phase as described above appears to be caused by localized interfacial tension lowering, due to the unequal formation of soap at different points in the interface. In the absence of N25-3S or N25-7, the mass transfer of fatty acid from oil phase to the interface and of soap from interface to aqueous phase were fast, so strong interfacial turbulence and convection in oil phase were observed. Since sodium soap is quite hydrophilic, microemulsion droplets stabilized by soap tend to be dispersed in the aqueous phase. Interfacial turbulence might have sped the diffusion. In the presence of N25-3S or N25-7, flow along the interface produced by mass transfer built up a gradient in surfactant concentration with opposed the flow, so interfacial turbulence was suppressed.
6.3 Horizontal Foam Films

Foam films produced from alkaline (pH9 by NaOH) solution containing 0.01wt% N25-3S and 0.02wt% C16/HO1 were studied. Results are shown in Figure 6.5. Asymmetric drainage of the dimple happened very quickly within 1 ~2 seconds after its formation. Later, smaller new dimples formed (Figure 6.5a). Interestingly, when such a dimple reached the film periphery, it moved back and forth but could not get out. The subsequent thinning process was slow and more like axisymmetric drainage (Figure 6.5b). This behavior implies that the film became more rigid (higher surface viscosity) due to the ionization of fatty acid, i.e. the formation of sodium soap. Very likely, the film surfaces have mixed adsorption of Neodol®, soap and acid.

Figure 6.5 Consecutive stages of the drainage of a film produced from pH9 solution containing 0.01wt% N25-3S and 0.02wt% C16/HO1

Foam films produced from pH9 solution containing 0.1wt%N25-7 and 0.1wt% emulsified C16/HO1 were also studied. This solution contains five fold as much oil as the anionic surfactant solution, so the outcome of forming soap is more striking. Two samples of the studied films are shown in Figures 6.6 a & b. These films were stable and exhibited symmetric drainage, implying fairly viscous film surfaces.
Figure 6.6 Films produced from pH 9 solution containing 0.1wt%N25-7 and 0.1wt% C16/HOl.

(a) ![Image](image1.png)  (b) ![Image](image2.png)

Of interest is that when the solution is loaded to the Scheludko cell and left stationary for a while without forming a film, it looks like Figure 6.7a under reflected light. The solution seems to be in three-phase region. The phase between water and oil, which looks white under the reflected monochromatic light, should be the microemulsion phase. Films produced from such solution, as shown in Figure 6.7b, are quite unstable and break within seconds. It seems that microemulsion phase coalesces into large drops under stagnant condition, which are then able to bridge the film. But this solution doesn’t produce unstable foam in foam testing experiment. A possible reason may be that there are no large microemulsion drops under the dynamic condition in foam testing column.

Figure 6.7 (a) pH 9 solution containing 0.1wt%N25-7 and 0.1wt% C16/HOl under reflected light. (b) Unstable thin film produced with such solution.

(a) ![Image](image3.png)  (b) ![Image](image4.png)
6.4 Oil-water-air Asymmetric Films

We have shown in Chapter 5.3.4a that when making a pseudoemulsion film by pressing a drop of C16/HO1 against the surface of 0.01wt%N25-3S at pH7, dimple forms and drains asymmetrically. After about 3 min, the film thins to a parallel stage and remains stable under capillary pressures lower than or near 120 Pa. Pseudoemulsion film between TO/HO1 and the same solution presents similar phenomena except that drainage of the dimple is slower and symmetric. Those studies were performed at neutral pH. Here in this section, films between the same oil and aqueous are studied at alkaline pH.

Figure 6.8 is a time sequence of an asymmetric film formed between a drop of C16/HO1 and pH9 solution of 0.01wt%N25-3S. The drainage of such film is very slow. Dimple never completely flowed into meniscus although initial drainage was asymmetric. That is, the dimple in second frame is the same as that in the first frame but more than 4 minutes later. As we can see from Figure 6.8c, the film was still of non-uniform thickness (with dimples and channels inside) after draining for 8 minutes. Such film is stable. No drop entry was observed over a time frame of half an hour.

Figure 6.8 Consecutive stages of the drainage of a pseudoemulsion film formed between a drop of C16/HO1 and pH 9 solution of 0.01wt%N25-3S
Figure 6.9 is the thinning process of a pseudoemulsion film formed from a TO/HOl drop approaching the surface of the pH9 solution of 0.01wt%N25-3S. A dimple was initially formed in the center. It drained slowly and symmetrically (Figure 6.9a). Then one or two spherical interferences were observed near the peripheral of the film (Figure 6.9b). The number and size of these interferences increased rapidly within one minute (Figure 6.9c). As these interferences coalesced with each other, a quick flow in the film was observed, starting from the lower right corner of the film toward the center, and the dimple was expelled from the other side (Figure 6.9d-f). After dimple expulsion, the film was of uniform thickness and remained stable for a long time. Based on a contacting experiment which showed that drops of a third phase (presumably L₃) form at the oil-water interface, it's quite possible that the spherical interferences in Figure 6.9 b&c were caused by these drops. Drops were at the interface to start with, and they became visible as the drainage proceeded.

Figure 6.9 Consecutive thinning process of a pseudoemulsion film formed by a drop of TO/HOl in pH 9 solution of 0.01wt% N25-3S.
It's interesting to relate the thinning behavior of pseudoemulsion films with the contacting results introduced before. Droplets at the interface between TO/HO1 and pH9 surfactant solution are mobile in contacting experiment, here we saw a flow in the pseudoemulsion film (Figure 6.9d-f). Droplets at the interface between C16/HO1 and pH9 surfactant solution don’t travel around, and here we observed only slow drainage of the film.

6.5 Foam Stability and ESB Analysis

Effect of the oil mixtures on foam stability of 0.01wt%N25-3S and 0.1wt%N25-7 was studied at both neutral and alkaline pH. Results with C16/HO1 are shown in Figure 6.10. The corresponding entry, spreading and bridging coefficients (ESB analysis) are shown in Table 6.1. Results with TO/HO1 are as shown in Figure 6.11 while the corresponding ESB calculation is shown in Table 6.2.

At neutral pH for N25-3S, both C16/HO1 and TO/HO1 have positive entry and bridging coefficients, but defoaming effectiveness is either slight or absent. This discrepancy can be understood considering that the asymmetric oil-water-air films in
anionic surfactant solutions are stabilized by repulsion due to the overlap of electrical double layers. The generalized entry coefficient $E_g$, instead of the classical entry coefficient $E$, should be used to predict entry behavior. At neutral pH for N25-7, C16/HO1 has a significant defoaming effect and TO/HO1 has no defoaming effect. This is consistent with ESB analysis since C16/HO1 has large positive entry and bridging coefficients, but TO/HO1 has a negative bridging coefficient which indicates that oil-bridging is not destabilizing.

At alkaline pH, results with nonionic surfactant N25-7 are understandable by the basic ESB analysis. Electrical repulsion and negative $E_g$ should be invoked to explain foam stability results with anionic surfactant N25-3S. For N25-3S with C16/HO1, foam was somewhat more stable at alkaline pH. The reasons may be first, formation of soap increases surface viscosity and slows liquid drainage in foam column. Results of both foam film and pseudoemulsion film studies give evidence that ionization of oleic acid leads to more rigid surfaces and decreases the rate of film drainage. Second, total moles of surfactants increased (per Table 6.3), and surfactant films now contain some sodium oleate. The air-water surface tensions, $\gamma_{AW}$, and oil-water interfacial tensions, $\gamma_{OW}$, are therefore lower than those at pH7 (see Tables 6.1&2). For N25-7 with C16/HO1, effect of going from pH7 to pH9 is significant only at times shorter than 20 min. Since foam height at long times is about the same for pH 7 and 9, it may be that drainage rate is reason for the difference.

The decrease in air-water surface tension and oil-water interfacial tension leads to smaller entry and bridging coefficients, and actually changes their sign from positive to negative in case of TO/HO1.
Table 6.1 Semi-equilibrium<sup>a</sup> Entry, Spreading, Bridging coefficients for solutions of 0.01wt% N25-3S and 0.1wt% N25-7 with C16/HOI.

<table>
<thead>
<tr>
<th>Solution</th>
<th>oil</th>
<th>pH</th>
<th>$\gamma_{AW}$</th>
<th>$\gamma_{ow}$</th>
<th>$\gamma_{AO}$</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%</td>
<td>C16/HOI</td>
<td>7</td>
<td>33.0</td>
<td>3.7</td>
<td>26.5</td>
<td>10.4</td>
<td>3.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>414</td>
</tr>
<tr>
<td>N25-3S</td>
<td>C16/HOI</td>
<td>9</td>
<td>30.5</td>
<td>0.006</td>
<td>26.5</td>
<td>4.0</td>
<td>4.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>228</td>
</tr>
<tr>
<td>0.1wt%</td>
<td>C16/HOI</td>
<td>7</td>
<td>29.6</td>
<td>0.085</td>
<td>26.5</td>
<td>3.2</td>
<td>3.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>174</td>
</tr>
<tr>
<td>N25-7</td>
<td>C16/HOI</td>
<td>9</td>
<td>28.8</td>
<td>0.024</td>
<td>26.5</td>
<td>2.3</td>
<td>2.3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>127</td>
</tr>
</tbody>
</table>

Note: <sup>a</sup> definition see chapter 2.3.1. <sup>c</sup> value is zero for foam system at equilibrium. The units of interfacial tensions are mN/m. The $\gamma_{AW}$ tensions are measured after equilibration with corresponding amounts of dispersed oil. For systems containing N25-3S, oil/surfactant = 1; for systems containing N25-7, oil/surfactant = 0.5.
Table 6.2 Semi-equilibrium Entry, Spreading, Bridging coefficients for solutions of 0.01wt% N25-3S and 0.1wt% N25-7 with TO/HOl.

<table>
<thead>
<tr>
<th>Solution</th>
<th>oil</th>
<th>pH</th>
<th>$\gamma_{AW}$</th>
<th>$\gamma_{OW}$</th>
<th>$\gamma_{AO}$</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%</td>
<td>TO/HOl</td>
<td>7</td>
<td>33.0</td>
<td>6.5</td>
<td>31.4</td>
<td>8.1</td>
<td>-4.9</td>
<td>145</td>
</tr>
<tr>
<td>N25-3S</td>
<td>TO/HOl</td>
<td>9</td>
<td>29.9</td>
<td>0.17</td>
<td>31.4</td>
<td>-1.3</td>
<td>-1.7</td>
<td>-92</td>
</tr>
<tr>
<td>0.1wt%</td>
<td>TO/HOl</td>
<td>7</td>
<td>29.5</td>
<td>2.01</td>
<td>31.4</td>
<td>0.11</td>
<td>-3.9</td>
<td>-112</td>
</tr>
<tr>
<td>N25-7</td>
<td>TO/HOl</td>
<td>9</td>
<td>28.1</td>
<td>0.88</td>
<td>31.4</td>
<td>-2.4^e</td>
<td>-4.2</td>
<td>-196</td>
</tr>
</tbody>
</table>

Note same as for Table 6.1

Table 6.3 Anionic surfactant concentration in aqueous system containing emulsified oil mixtures.

<table>
<thead>
<tr>
<th>System (wt%)</th>
<th>Pre-added conc. (mmol/l)</th>
<th>Titration results of total surfactant conc. (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N25-3S</td>
<td>oleic acid</td>
</tr>
<tr>
<td>0.01%N25-3S + 0.02%C16/HOl</td>
<td>0.229</td>
<td>0.071</td>
</tr>
<tr>
<td>0.01%N25-3S + 0.06%C16/HOl</td>
<td>0.229</td>
<td>0.212</td>
</tr>
<tr>
<td>0.01%N25-3S + 0.02%TO/HOl</td>
<td>0.229</td>
<td>0.071</td>
</tr>
<tr>
<td>0.01%N25-3S + 0.06%C16/HOl</td>
<td>0.229</td>
<td>0.212</td>
</tr>
</tbody>
</table>

A summary of the experimental results of this chapter is given in Appendix IV. Besides, the stability of foam of 0.01wt%N25-3S has been compared with that of 0.01wt%NaOl (at pH9). As shown in Figure 6.12, the latter is less stable. Foam of the mixture of N25-3S and NaOl, e.g. 0.008%N25-3S + 0.01wt%NaOl, appears to be a little more stable than that of N25-3S alone, at least before 30 minutes. This may be related to more rigid film surfaces and decrease in film drainage. But this tiny difference in foam stability could also be within experimental error.
6.6 Summary

Foam behavior with oil mixtures (C16/HO1 and TO/HO1) seems to be basically the same as for pure hexadecane or triolein in neutral pH solutions without hardness. For ionic surfactant $E > 0$, and one needs to invoke negative $E_g$ to explain foam stability. For nonionic surfactant simple ESB analysis works. Raising pH from 7 to 9 seems to have minimal effect on foam stability (with marginal stabilizing effect in some cases), although it does cause $\gamma_{aw}$ and $\gamma_{ow}$ to decrease and hence also the values of entry/bridging coefficients.
Chapter 7 Effect of Hardness in the Presence of Oils on Foam Stability

7.1 Introduction

Electrolytes, in general, do not influence significantly either the foaming power or foam stability of nonionic foaming systems [Schoff, 1988]. However, the addition of a simple electrolyte to an anionic foaming system may have a significant effect on its stability.

Under certain conditions, electrolytes stabilize the foam generated by anionic surfactants. Such an effect has been attributed to the cationic-anionic-type interaction, resulting in decreases in head group repulsion at the interface [Lai and Dixit, 1996]. Camp and Durham [1955] systematically investigated the effect of simple and polyvalent electrolytes on the foam stability of sodium laurate solution. They conclude that electrolytes exert their foam-stabilizing action by influencing the rate of attainment of surface tension equilibrium.

Electrolytes can also destabilize the foam by screening the repulsive forces between the ionic head groups, which leads to reduced repulsion between the surfactant layers or the opposing film interfaces, which in turn leads to faster film drainage and lower maximum in disjoining pressure curve [Bendure, 1975]. Furthermore, electrolytes also destabilize the foam by forming insoluble complexes between the cation and anionic moiety of the surfactant [Peacock and Matijevic, 1980; Baviere et al., 1983; Kumar and Bhat, 1987].

In Chapter 4 we’ve studied how hardness (mainly CaCl₂) influences foams of N25-3S solution in the absence of oily additives. It was observed that hardness speeds up
liquid drainage and decreases equilibrium film thickness. Foam stability is first enhanced and then decreased as the divalent electrolyte concentration increases. In this chapter, effect of hardness on foams of 0.01wt% N25-3S is investigated in the presence of oily additives. Substantial influences of hardness on the defoaming effectiveness of emulsified oils, on pseudoemulsion film properties and on phase behavior are discussed. All the studies were performed at neutral pH. So formation of insoluble calcium soap is negligible.

7.2 Experimental Results

7.2.1 Foam Stability

Effect of oily additives on foam stability was tested at different hardness levels. Results with C16/HO1 are illustrated in Figure 7.1, which shows foam decay as a function of time. Surfactant concentration was fixed at 0.01wt%. The oil-to-surfactant weight ratio was fixed at 2.

Figure 7.1 Effect of C16/HO1 on foam stability at different hardness concentrations

0.01wt%N25-3S, pH7

![Graph showing foam height (cm) over time (min) for different conditions]
In absence of hardness, C16/HOI showed certain defoaming effect, i.e., foam was somewhat less stable than that without oily additive. With the addition of 300ppm hardness, foam destruction pattern in the presence of C16/HOI was stepwise. That is, foam was destroyed in steps of 5 - 6cm, separated by a relatively long period, 8 or 15 minutes, with negligible foam destruction. A similar phenomenon was observed and addressed by Arnaudov et al. [2001]. Such a collective destruction of many bubbles in a single step can be explained by the mechanism of “rupture of Plateau borders by oil drops”. The drops are expelled from the foam films into the neighboring Plateau borders in the early stages of foam evolution. The liquid drainage leads to a gradual narrowing of the Plateau borders and to an increase of the capillary pressure compressing the trapped drops. When the compressing capillary pressure exceeds a certain critical value, which depends on the stability of the asymmetric oil-water-air film, the oil drops enter the surface of the Plateau border and rupture the neighboring foam films. It’s assumed that the entry of one of the drops trapped in the upper layer of the foam column would trigger an avalanche of film ruptures and drop entry events, so that the top portion of the foam column, where films are thinnest, is destroyed. Visual observation confirmed this rapid destruction of the upper layer of foam in each step.

Step-wise foam destruction by C16/HOI was clearly observed when 300ppm hardness was present but not when hardness was absent. This is probably related to different rates of liquid drainage, since it’s less likely that defoaming mechanism changes as 300ppm hardness was applied. For both cases, with or without 300ppm hardness, most oil drops were expelled from the foam films in the early stages of foam evolution and destabilized Plateau borders later on. With 300ppm hardness added, the thinning process
of foam lamellae and the narrowing of Plateau borders are speeded up. Also, the gradient of film thickness down the foam column is presumably less at 300ppm than at zero hardness. Thus, when rupture of one or several Plateau borders in the upper layer of the foam column triggers an avalanche of film ruptures, a larger portion of foam is vulnerable to such perturbation at 300ppm hardness than in absence of hardness. Therefore, the decrease in foam height at one step is large enough to be clearly observed at 300ppm hardness, but too small to be remarkable in absence of hardness. Clearly, stepwise foam destruction would not happen if most oil droplets are able to rupture foam lamellae and when foam is highly unstable.

When hardness level was increased to 2000ppm, foam with oily additives was very unstable, i.e., 85% foam disappeared within 5 minutes after foam generation ceased. Dramatic coalescence of air bubbles was observed during foam generation. At the end of foam generation, foam column consisted of bubbles with an average diameter in the range of 1cm. The freshly produced foams of the other three studied systems, however, consisted of only millimeter-sized air bubbles.

The results with TO/HOI are illustrated in Figure 7.2. It shows that, without hardness or with an addition of 300ppm hardness, foams produced in the presence of 0.02wt% TO/HOI are stable, perhaps even a little bit more stable than without any oil. But at high concentration of hardness, i.e. 2000ppm, the produced foam is very unstable. Again, dramatic coalescence of air bubbles was observed during foam generation. Most of the foam (90%) disappeared within 15 minutes after foam generation has ceased.
7.2.2 Video-microscopy Contacting Experiment

When small oil drops (diameter =60–120μm) of C16/HOI were injected into the neutral surfactant solution of 0.01wt%N25-3S containing zero or 300ppm hardness, no dynamic interfacial phenomena were observed. But at very high hardness level drops of new phase were observed at the oil-water interface. Figure 7.3 is a drop of C16/HOI (70μm) in 0.01wt% solution of N25-3S plus 2000ppm hardness. When the drop initially contacted the solution, its surface was smooth. Within seconds, small drops appeared at the oil surface. As time elapsed, more drops appeared and grew larger gradually. The oil-water interface looks very flexible since its fluctuation was noticeable and the oil drop had irregular shape (Figure 7.3a). Eventually, the oil drop rounded into a sphere. Because the interfacial tension of this system is very low, around 0.004mN/m, the newly formed phase is presumably a microemulsion. The same contacting experiments with small drops of TO/HOI, however, show that there is no formation of the middle phase at the oil-water
interface. Even at this high hardness no indication of formation of solid CaCO₃ was seen in either experiment.

(a)  (b)

Figure 7.3 a drop of C16/HOI in the 0.01wt% solution of N25-3S containing 2000ppm hardness

7.2.3 Horizontal Foam Films

In the absence of hardness, experiments in Sheludko cell with solutions containing 0.01wt%N25-3S and 0.02wt% oily additives (C16/HOI or TO/HOI) show that the addition of the studied oils didn’t change significantly the film-thinning rate. When the oily additive was C16/HOI, most of the dozens of studied foam films were stable. Generally oil drops were swept out of the film into the meniscus as the film thinned. Sometimes several oil drops were trapped at the periphery of the film but didn’t break the film. Occasionally, oil bridge configurations formed and led to film rupture. When the oily additive was TO/HOI, the oil drops were always swept out of the film and didn’t affect film lifetime.

With 300ppm hardness, the addition of 0.02wt% oils, either TO/HOI or C16/HOI, didn’t change the quick asymmetric drainage and the film lifetime. The main stages of
foam film thinning were quite similar to those in the absence of oils except that one could now see oil drops moving around as a result of strong convection during the initial stage of the drainage. After the dimple was expelled and channels disappeared, oil drops were all swept out of the film. The final state was a stable common black film.

With 2000ppm hardness, the addition of 0.02wt% TO/HOI almost doesn’t affect film lifetime. The addition of 0.02wt% C16/HOI, however, causes substantial diminution of foam film stability. The average lifetime of the 30 studied films was less than 1 minute. Most of them broke within 30 seconds, though the reason of film rupture was not clearly evidenced by the microscopy observation.

7.2.4 Oil-water-air Asymmetric Films

In this section the stability of pseudoemulsion film was studied as a function of hardness concentrations. As described in Chapter 5.3.4a, when making a pseudoemulsion film by pressing a drop of C16/HOI from underneath the surface of 0.01wt%N25-3S solution (pH7), we saw that a dimple formed and drained asymmetrically. Eventually, the film thinned to a nearly parallel stage and remained stable for a long time (Figure 5.14b). We didn’t see film rupture even at the highest accessible capillary pressure that our apparatus can achieve (around 120 Pa). Pseudoemulsion film between TO/HOI and the same surfactant solution exhibits similar behavior, except that the drainage is symmetric and slower.

With addition of 300ppm hardness in the aqueous phase, pseudoemulsion film formed between C16/HOI drop and the surface of the 0.01wt%N25-3S solution drains asymmetrically. A brief description of the main stages of film thinning is shown in Figure 7.4. The dimple was initially formed in the center of the film, and eventually left the film
from one side. After the dimple expulsion, the film is of uniform thickness and very bright. Based on the brightness of the interference, one can tell that this film (in Figure 7.4e) is thinner than that in Figure 5.14b. That is, the presence of hardness decreases the equilibrium thickness of the pseudoemulsion film. Perhaps because thinner film is more vulnerable to perturbation, this bright thin film couldn't remain stable. Film rupture and oil drop entry were later on observed. Among the several samples we studied, half of them broke at the last step of dimple expulsion before reaching a uniform thickness (the stage as shown in Figure 7.4d).

Figure 7.4 Thinning process of a pseudoemulsion film formed by a drop of C16/HOl in solution containing 0.01 wt% N25-3S and 300pp hardness. About 5sec (a), 46sec (b), 1min30min(c), 2min 22sec(d), 3min(e) after the film was formed.
Films between TO/HOI drops and the same solution as above go through symmetric drainage and eventually reach a stable state, as shown in Figure 7.5. The final bright thin films remain stable for a long time at a constant uniform thickness. No drop entry was observed.

Figure 7.5 Thinning process of a pseudoemulsion film formed by a drop of TO/HOI in solution containing 0.01wt% N25-3S and 300ppm hardness. About 15sec(a), 59sec(b), 2min14sec(c) and 3min33sec(d) after it’s formed.

With 2000ppm hardness in the aqueous phase, a typical film formed with C16/HOI drop is shown in Figure 7.6. About 3 minutes after the film was formed, a small area of oil surface emerged into the air-water surface (the bright area in Figure 7.6a). The subsequent expansion of the oil lens was relatively slow. It took around 50 seconds for the film to be completely replaced by the oil surface. After that, the oil lens continued to
spread over the air-water surface and moved around as an oil lens. Such drop entry behavior is quite different from that seen for unstable pseudoemulsion films in other systems. In those cases the rupture of the films and drop entry happened instantly within one second, but here the entry process took about one minute. It is conjectured that this drop entry behavior was triggered by the micro-emulsion drops formed at the oil-water interface. To further justify this assumption, pseudoemulsion film between a drop of pure hexadecane and the same surfactant solution as above were studied. There was no formation of microemulsion in this case. And such films indeed behaved differently. Firstly films with pure hexadecane are relatively more stable than those with C16/HO1, forming bright parallel thin films after an asymmetric drainage for about 3 min. Secondly, when the thin films break later on, drop entry happens instantly within one second.

Figure 7.6 Rupture of a pseudoemulsion film formed by a drop of C16/HO1 in solution containing 0.01wt% N25-3S and 2000ppm hardness. Around 1min33sec(a), 2min 5sec(b), 3min19sec(c) after the film was formed.
With 2000ppm hardness in the aqueous phase, the thinning process of films with TO/HOI drops is shown in Figure 7.7. After film formation, a strict symmetric drainage follows. Within one minute, the dimple shrank into a small lens separated from the meniscus by a mostly uniform thin film (Figure 7.7 a&b). Interestingly, small amount liquid moved into the film from the meniscus and formed many isolated dimples. These dimples moved toward the initial dimple in the center of the film and eventually gathered together (Figure 7.7 c&d). Film was stable.

Figure 7.7 Thinning process of a pseudoemulsion film formed by a drop of TO/HOI in solution containing 0.01wt% N25-3S and 2000ppm hardness.
Results discussed above show that, within the hardness levels studied from 0ppm to 2000ppm, pseudoemulsion films with C16/HO1 presented asymmetric drainage while films with TO/HO1 presented symmetric drainage. This behavior is similar to that of pure hexadecane and triolein for the same conditions, implying that oleic acid doesn’t significantly influence film thinning at neutral pH.

7.3 Discussion

Entry, spreading, and bridging coefficients of the tested systems were calculated and given in Table 7.1. Foam stability is then compared with E, S and B, and with the stability of pseudoemulsion films. For a summary of all the experimental results presented in this chapter, please refer to Appendix V.

C16/HO1 has certain defoaming effect at all the studied hardness levels (Figure 7.1). This result is consistent with the ESB analysis since C16/HO1 has positive entry/bridging coefficients. The defoaming effectiveness of C16/HO1 increases as hardness level increases, which is consistent with the stability of the pseudoemulsion films. As evidenced by experimental results, pseudoemulsion films become less stable as hardness increases.

TO/HO1 has no defoaming effect at low hardness concentrations such as 300ppm. This is also consistent with ESB analysis since entry/bridging coefficients are negative under this situation. In the absence of hardness, TO/HO1 has positive E and B but has no defoaming effects. This is because the pseudoemulsion films in anionic surfactant solutions are stabilized by repulsion due to overlap of electrical double layers, as discussed earlier in Chapter 5. With 2000ppm hardness, TO/HO1 has negative E, S and B but presented significant defoaming effect. To understand this, time-dependent changes
in E, S, B need to be taken into account. There is no doubt of the non-equilibrium nature of
the surfaces present during foam formation and in newly formed foams. For this specific
system, as the air-water surface tension decreases from near 70mN/m to about 28mN/m,
entry and bridging coefficients go through a change from positive to near zero to
negative. During the initial transient period when E & B are positive, since the electrical
repulsion in the pseudoemulsion film is significantly weakened by copious hardness,
TO/HO1 is able to destroy foam. One may ask why TO/HO1 doesn’t defoam at 300ppm
hardness when such transient change of E, B from positive to negative should also exist.
The reason should be that the electrolyte concentration is not enough to sufficiently
reduce the electrical repulsion, so that drop entry is prevented by an entry barrier even
though E is positive initially. The negative E with TO/HO1 at equilibrium does explain
why drop entry didn’t happen in Scheludco cell and in pseudoemulsion film testing cell
where the experiments involve air-water surfaces at or near equilibrium.

Table 7.1 Semi-equilibrium* Entry, Spreading, Bridging coefficients and foam
stability for C16/HO1 and TO/HO1

<table>
<thead>
<tr>
<th>Solution</th>
<th>oil</th>
<th>Hardness (ppm)</th>
<th>$\gamma_{AW}$</th>
<th>$\gamma_{OW}$</th>
<th>E</th>
<th>S</th>
<th>B</th>
<th>$H_0$</th>
<th>$H_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%</td>
<td>No oil</td>
<td>0</td>
<td>32.0</td>
<td>3.7</td>
<td>10</td>
<td>3.0e</td>
<td>414</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>N25-3S</td>
<td>C16/ HO1</td>
<td>0</td>
<td>33.2</td>
<td>1.0</td>
<td>3.0e</td>
<td>414</td>
<td>20</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C16/ HO1</td>
<td>300</td>
<td>29.7</td>
<td>0.08</td>
<td>3.3</td>
<td>3.1e</td>
<td>180</td>
<td>20</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>C16/ HO1</td>
<td>2000</td>
<td>28.0</td>
<td>0.003</td>
<td>1.5</td>
<td>1.5e</td>
<td>82</td>
<td>20</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>TO/HO1</td>
<td>0</td>
<td>33.1</td>
<td>6.5</td>
<td>8.2</td>
<td>-4.8</td>
<td>152</td>
<td>20</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>TO/HO1</td>
<td>300</td>
<td>29.5</td>
<td>0.27</td>
<td>-1.6e</td>
<td>-2.2</td>
<td>-116</td>
<td>20</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>TO/HO1</td>
<td>2000</td>
<td>27.9</td>
<td>0.21</td>
<td>-3.3e</td>
<td>-3.7</td>
<td>-207</td>
<td>20</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Note: * definition see chapter 2.3.1; e value is zero for foam system at equilibrium;
$H_0$ is initial foam height (cm). $H_{20}$ is foam height (cm) after 20 min. Surface
tension of C16/HO1 is 26.5 mN/m. Surface tension of TO/HO1 is 31.4mN/m.
Surfactant solution is at neutral pH. Oil to surfactant ratio is 2 in foam column.
In case of C16/HO1, the very unstable foam at 2000ppm hardness is not only because that the double layer repulsion in the pseudoemulsion film is weakened, but also related to the formation of a separate microemulsion phase. This effect can be further illustrated by comparing the defoaming effect of C16/HO1 and pure hexadecane under same situations. Foam testing results are as shown in Figure 7.8, the corresponding entry, spreading and bridging coefficients calculated are given in Table 7.2. As we can see, both hexadecane and C16/HO1 destabilize foam at 0.01wt% of N25-3S, with C16/HO1 having more effect. When surfactant concentration is increased to 0.05wt%, hexadecane cannot destabilize foam any more although E and B are positive. This is presumably because $E_g$ is now negative since electrical repulsion in pseudoemulsion film is stronger as surfactant adsorption at the film surfaces increases. C16/HO1, however, still destabilizes foam. A separate microemulsion phase forms in the system of C16/HO1 but not in the system of pure hexadecane. This should be the reason that causes the difference in foam stability. It’s possible that microemulsion droplets caused bridging of pseudoemulsion film. It’s also possible that dissolving of surfactants into the micro-emulsion phase would make surface adsorption of surfactants more difficult.

In Chapter 6 it was also observed that droplets of ME or L₃ phase formed at oil-water interface, i.e. C16/HO1 or TO/HO1 in pH9 solution of N25-3S. However, pseudoemulsion films with these systems were stable. Drop entry was not observed even with C16/HO1. This is presumably because electrical repulsion in pseudoemulsion film is so strong (since there is no hardness) that ME droplets, although having higher curvature than oil drops, cannot enter the air-water interface.
Figure 7.8 Comparison of the defoaming stability of hexadecane and C16/HOI at high hardness

Table 7.2 Semi-equilibrium Entry, Spreading, Bridging coefficients for C16/HOI and hexadecane.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Oil</th>
<th>$\gamma_{AW}$ (mN/m)</th>
<th>$\gamma_{ow}$ (mN/m)</th>
<th>$\gamma_{OA}$ (mN/m)</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt% N25-3S</td>
<td>C16/HOI</td>
<td>28.0</td>
<td>0.005</td>
<td>26.5</td>
<td>1.5</td>
<td>1.5</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>hexadecane</td>
<td>27.8</td>
<td>0.9</td>
<td>26.3</td>
<td>2.4</td>
<td>0.6</td>
<td>82</td>
</tr>
<tr>
<td>0.05wt% N25-3S</td>
<td>C16/HOI</td>
<td>26.9</td>
<td>0.003</td>
<td>26.5</td>
<td>0.4</td>
<td>0.4</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>hexadecane</td>
<td>26.3</td>
<td>0.57</td>
<td>26.3</td>
<td>0.6</td>
<td>-0.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Note: Surfactant solutions contain 2000ppm hardness and at neutral pH. $\gamma_{AW}$ were measured after being equilibrated with corresponding amount of oils.

7.4 Summary

Effect of hardness (mainly CaCl$_2$) on foams from N25-3S solutions was studied with the presence of oils. It was found that hardness increases thinning speed and decreases equilibrium thickness of the pseudoemulsion (oil-water-air) films, just as it does with the symmetric (air-water-air) foam films. Antifoam effectiveness of the oily additives such as hexadecane, triolein and their mixtures with small amount of oleic acid
is negligible in the absence of hardness (presumably at low hardness also), but very significant at high hardness level, e.g. 2000ppm, reflecting that antifoam ability of these oils is dominated by the stability of the pseudoemulsion film. At neutral pH, increasing hardness reduces electrical repulsion in pseudoemulsion film and makes foam less stable. Results with C16/HOI are consistent with the measured equilibrium entry/bridging coefficients. Results with TO/HOI are consistent with semi-equilibrium entry/bridging coefficients at low hardness concentrations, but not consistent at high hardness concentrations. For the latter case, time-dependent changes in E, S, B need to be considered. In case of C16/HOI, formation of a separate microemulsion phase further decreases foam stability.
Chapter 8 Foam Boosting Study

8.1 Introduction

Results presented in Chapter 5 show that foam is unstable in the presence of oil mixtures (hexadecane/triolein with oleic acid), hardness and alkalinity where insoluble soaps are formed. Those in Chapter 7 with foams from 0.01wt% solution of N25-3S show that foam is unstable in the presence of oils and high hardness at neutral pH. However, stable foams are sometimes desirable under the above two situations, e.g. in hand dishwashing, in ground water remediation and enhanced oil recovery processes where foam is used for mobility control. Therefore, interest in this chapter is to enhance foam stability by adding so-called ‘foam boosters’.

We studied and compared the foam boosting effect of two types of additives. One is a fatty alcohol, lauric alcohol (n-dodecanol), denoted as LA from now on. Some papers attribute foam boosting effect of long chain alcohol to slower film thinning and water drainage from the foam, which is due to the effect of alcohol on the surface viscosity [Brown et al., 1953; Miles et al., 1945]. Schick and Fowkes [1957] reported the critical micelle concentration lowering effect of LA on sodium lauryl sulfate solution and correlated it to foam stabilizing effect.

The other additive we studied is an amine oxide, N,N-dimethylmyristal amine oxide, denoted as C\textsubscript{14}DMAO later on. Its structure is given here.

\[
\text{CH}_3 \quad \text{C}_{14}\text{H}_{29} - \text{N} \rightarrow \text{O} \quad \text{CH}_3
\]

Amine oxides have long been known to have surface active and germicidal characteristics [Guenther and Saftien, 1939] and are widely used in shampoos and light-duty liquid detergents.

8.2 Experimental Results with Lauric Alcohol (LA)
8.2.1 Foam Stability

Foam stability was tested in the presence of oil mixtures, either C16/HOI or TO/HOI, under two different conditions. One is at pH9 and medium hardness, therefore calcium soap forms in situ. The other is at high hardness but neutral pH, therefore formation of calcium soap is negligible. With the concentration of N25-3S being kept at 0.01wt%, effect of LA on foam stability was studied at three concentrations, 0.0001wt% (1ppm), 0.001wt% (10ppm) and 0.005wt% (50ppm). Solutions of 0.01wt%N25-3S plus 1ppm and 10ppm LA were prepared by diluting the solutions of 5wt%N25-3S + 0.05wt%LA and 1wt%N25-3S + 0.1wt%LA respectively. LA has very limited solubility in water, but does have much better solubility in micellar solutions of the anionic surfactant. The 5%N25-3S+0.05%LA solution is isotropic and stable. The 1%N25-3S+0.1%LA solution, however, tends to separate into turbid lower layer and clearer upper layer after standing for a while. Magnetic stirring was applied to achieve uniform mixing before each use. The diluted solutions were clear and stable.

Foam stability of solutions containing C16/HOI, calcium soap and different amounts of LA is shown in Figure 8.1. The corresponding ESB calculation is given in Table 8.1. In Table 8.1 $\gamma_{AW}$ was measured with solutions free of oil; $E^I$, $S^I$ and $B^I$ were then calculated with it. $\gamma_{AW}$ was also measured after the solution equilibrated with 0.01-0.02wt% C16/HOI; E, S and B were then calculated. Since there are oils present during foam testing, the latter should be more appropriate to be used for analysis. The presence of oil could affect a) partitioning of LA and N25-3S between aqueous and oil phases; b) formation of soluble/insoluble soap; c) consumption of calcium ion due to formation of insoluble soap. These factors may account for the fact that $\gamma_{AW}$, E and B are
larger than $\gamma_{AW}^l$, $E^l$ and $B^l$. $E$, $S$ and $B$ have been defined as semi-equilibrium coefficients in chapter 2.3.1. For an overall discussion of their significance, refer to pages 16-17.

Figure 8.1 shows that even a tiny amount LA significantly enhanced foam stability. As more LA was used, foam stability was further increased. The equilibrium $E$, $S$ and $B$ of the studied system decrease as the concentration of LA increases, going through a sign change from positive to negative.

Figure 8.1 Foam stability of solutions containing C16/HO1, calcium soap and different amount of LA

![Graph showing foam height over time for different LA concentrations](image)

Table 8.1 Entry, Spreading, Bridging coefficients for C16/HO1 with calcium soap and LA

<table>
<thead>
<tr>
<th>Systems</th>
<th>$\gamma_{AW}^l$</th>
<th>$\gamma_{AW}$</th>
<th>$\gamma_{OW}$</th>
<th>$E^l$</th>
<th>$E$</th>
<th>$S^l$</th>
<th>$S$</th>
<th>$B^l$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%N25-3S, 0.01wt%C16/HO1, 300ppm hardness, pH9 plus:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0wt%LA</td>
<td>27.5</td>
<td>30.1</td>
<td>0.1</td>
<td>1.1</td>
<td>3.7</td>
<td>0.9</td>
<td>3.5</td>
<td>54</td>
<td>204</td>
</tr>
<tr>
<td>0.0001wt%LA</td>
<td>24.9</td>
<td>29.8</td>
<td>0.03</td>
<td>-1.6</td>
<td>3.3</td>
<td>-1.6</td>
<td>3.3</td>
<td>-82</td>
<td>186</td>
</tr>
<tr>
<td>0.001wt%LA</td>
<td>23.0</td>
<td>27.6</td>
<td>0.03</td>
<td>-3.5</td>
<td>1.1</td>
<td>-3.5</td>
<td>1.1</td>
<td>-173</td>
<td>59</td>
</tr>
<tr>
<td>0.005wt%LA</td>
<td>20.7</td>
<td>21.6</td>
<td>0.011</td>
<td>-5.8</td>
<td>-4.9</td>
<td>-5.8</td>
<td>-4.9</td>
<td>-274</td>
<td>-236</td>
</tr>
</tbody>
</table>

Note: Oil surface tension $\gamma_{OA}$ is 26.5mN/m. $^c$ value is zero at equilibrium per discussion on page 16-17
The different appearances of foams are compared in Figure 8.2. Figure 8.2a is foam of the pH9 solution containing 0.01wt%N25-3S, 300ppm hardness and 0.005wt% LA, without oil. Figure 8.2b is foam of the same solution as that in Figure 8.2a but in the presence of 0.01wt%C16/HO1. Figure 8.2c is foam of the solution similar to that in Figure 8.2b except that it's in the absence of LA. Foams in Figure 8.2a & b are both stable. Compared with foam in Figure 8.2a, foam in Figure 8.2b consists of larger air bubbles. This implies that oil drops caused bubble coalescence during foam generation but lost influence shortly after foam generation has ceased. Compared with the foam in Figure 8.2c, foam in Figure 8.2b consists of bubbles with narrower size distribution. Foam in Figure 8.2c is unstable, consistent with E, S, B values above.

Figure 8.2 Comparison of different foam appearance. Solution descriptions see text.

Following are foam testing results at high hardness and neutral pH, with negligible calcium soap present. Figure 8.3 is the result with C16/HO1. Table 8.2 gives the corresponding entry, spreading and bridging coefficients. It shows that addition of
1ppm LA had very little effect on foam stability while 10ppm and 50ppm LA enhanced foam stability significantly. Again, E, S and B of the studied system decrease as the concentration of LA increases, going through a sign change from positive to zero at equilibrium.

Figure 8.3 Foam stability of solutions containing C16/HOI, high hardness and different amount of LA

0.01wt% N25-3S, 0.01wt% C16/HOI
2000ppm hardness, pH7 plus

![Graph showing foam stability over time with various concentrations of LA](image)

Table 8.2 Semi-equilibrium$^a$ Entry, Spreading, Bridging coefficients ($\gamma_{AW}$ measured with solution equilibrated with 0.01–0.02wt% C16/HOI)

<table>
<thead>
<tr>
<th>Systems</th>
<th>$\gamma_{AW}$</th>
<th>$\gamma_{OW}$</th>
<th>$\gamma_{OA}$</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt% N25-3S, 0.01wt% C16/HOI, 2000ppm hardness, pH7 plus:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0wt% LA</td>
<td>28.0</td>
<td>0.005</td>
<td>26.5</td>
<td>1.5</td>
<td>1.5$^c$</td>
<td>82</td>
</tr>
<tr>
<td>0.0001wt% LA</td>
<td>28.0</td>
<td>0.005</td>
<td>26.5</td>
<td>1.5</td>
<td>1.5$^c$</td>
<td>82</td>
</tr>
<tr>
<td>0.001wt% LA</td>
<td>26.3</td>
<td>0.004</td>
<td>26.5</td>
<td>-0.2</td>
<td>-0.2</td>
<td>-11</td>
</tr>
<tr>
<td>0.005wt% LA</td>
<td>22.1</td>
<td>0.003</td>
<td>26.5</td>
<td>-4.4$^c$</td>
<td>-4.4</td>
<td>-214</td>
</tr>
</tbody>
</table>

Note: $^a$ definition see chapter 2.3.1; $^c$ value is zero for foam system at equilibrium per discussion on page 16-17.

Results with TO/HOI are given in Figure 8.4 and Table 8.3. It shows again that addition of 1ppm LA had very little effect on foam stability while 10ppm and 50ppm LA enhanced foam stability significantly. The equilibrium E, S and B of the studied system
are all negative. So the transient effect, i.e. E, S, B are initially positive but are negative when air-water surface reaches equilibrium, should be invoked to understand the unstable foams in absence or at very low concentration of LA.

Figure 8.4 Foam stability of solutions containing TO/HOI, high hardness and different amount of LA

![Graph showing foam stability](image)

Table 8.3 Semi-equilibrium Entry, Spreading, Bridging coefficients ($\gamma_{AW}$ measured with solution equilibrated with 0.01~0.02wt% TO/HOI)

<table>
<thead>
<tr>
<th>Systems</th>
<th>$\gamma_{AW}$</th>
<th>$\gamma_{OW}$</th>
<th>$\gamma_{OA}$</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%N25-3S, 0.01wt%TO/HOI, 2000ppm hardness, pH7 plus:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0wt%LA</td>
<td>27.9</td>
<td>0.36</td>
<td>31.4</td>
<td>-3.1°</td>
<td>-3.9</td>
<td>-207</td>
</tr>
<tr>
<td>0.0001wt% LA</td>
<td>28.2</td>
<td>0.08</td>
<td>31.4</td>
<td>-3.1°</td>
<td>-3.3</td>
<td>-191</td>
</tr>
<tr>
<td>0.001wt% LA</td>
<td>25.0</td>
<td>0.09</td>
<td>31.4</td>
<td>-6.3°</td>
<td>-6.5</td>
<td>-361</td>
</tr>
<tr>
<td>0.005wt% LA</td>
<td>21.1</td>
<td>0.78</td>
<td>31.4</td>
<td>-4.6°</td>
<td>-6.2</td>
<td>-256</td>
</tr>
</tbody>
</table>

Note: same as Table 8.2

8.2.2 Dynamic and Equilibrium Surface Tension

Dynamic surface tensions (D.S.T.) were measured by the method of maximum bubble pressure. The equipment gives measurement from 30 mill-second to 1 minute. All tensions for time longer than 1 minute were measured by the spinning drop tensiometer.
Results show that addition of LA decreases both the equilibrium surface tension (E.S.T) and dynamic surface tension (D.S.T) significantly. Typical results at neutral pH are as follow:

\[0.01\text{wt\%N25-3S} + 2000\text{ppmCa (pH7)}\]

<table>
<thead>
<tr>
<th></th>
<th>1 min</th>
<th>2 min</th>
<th>7 min</th>
<th>12 min</th>
<th>20 min</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>34.6</td>
<td>28.1</td>
<td>26.77</td>
<td>26.47</td>
<td>26.4</td>
<td>26.4</td>
</tr>
</tbody>
</table>

\[0.01\text{wt\%N25-3S} + 0.005\text{\%dodecanol} + 2000\text{ppmCa(pH7)}\]

<table>
<thead>
<tr>
<th></th>
<th>1 min</th>
<th>2 min</th>
<th>4 min</th>
<th>10 min</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>29.7</td>
<td>23.9</td>
<td>20.9</td>
<td>20.6</td>
<td>20.6</td>
</tr>
</tbody>
</table>

Typical results at pH9 are given in Figure 8.5.

![Figure 8.5 S. T. of pH9 solutions containing 0.01wt\% N25-3S, 300ppmCa, and dodecanol](image)

8.2.3 Pseudoemulsion Films

Millimeter-sized pseudoemulsion films were studied. Films between C16/HO1 and solutions containing 0.01%N25-3S, 300ppm hardness and 0.0001~0.005% LA are difficult to observe. Due to low interfacial tensions, a pendant drop cannot stay at the tip of the capillary (d = 1mm) being used. When the oil drop detaches from the capillary, it moves around and makes focusing very difficult. Films formed with TO/HO1 don’t have
this problem and all the studied films are stable. With 0.0001% or 0.001% LA, the drainage is asymmetric and formation of calcium soap particles can be seen, as shown in Figure 8.6. With 0.005%LA, drainage is very slow. During a long time, e.g. 8min, the film contains several dimples with different sizes, probably associated with calcium soap particles, as shown in Figure 8.7.

Figure 8.6 Pseudoemulsion film between TO/HO1 and 0.01%N25-3S + 0.001%LA + 300ppmCa, pH9 solution

Figure 8.7 A pseudoemulsion film (d = 820μm) between TO/HO1 and pH9 solution containing 0.01%N25-3S, 0.005%LA and 300ppm hardness.
8.3 Experiments with Amine Oxide (C\textsubscript{14}DMAO).

8.3.1 Foam Stability

8.3.1a Results with C16/HOI

Foam testing results at pH9 and the corresponding ESB calculations are given in Figure 8.8 and Table 8.4. At alkaline pH and in the presence of insoluble soap, addition of even 0.01wt\% C\textsubscript{14}DMAO didn’t enhance foam stability. The entry/bridging coefficients are positive for all of the three test concentrations of C\textsubscript{14}DMAO.

![Figure 8.8 pH9 solution of 0.01%N25-3S containing 300ppmCa,0.01%C16/HOI and C\textsubscript{14}DMAO](image)

Table 8.4 Semi-equilibrium\textsuperscript{a} Entry, Spreading, Bridging coefficients (\(\gamma_{AW}\) measured with solution equilibrated with 0.01~0.02wt\% C16/HOI)

<table>
<thead>
<tr>
<th>Systems</th>
<th>(\gamma_{AW})</th>
<th>(\gamma_{OW})</th>
<th>(\gamma_{OA})</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%N25-3S, 0.01wt%C16/HOI, 300ppm hardness, pH9 plus:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0wt%C\textsubscript{14}DMAO</td>
<td>30.1</td>
<td>0.1</td>
<td>26.5</td>
<td>3.7</td>
<td>3.5\textsuperscript{e}</td>
<td>204</td>
</tr>
<tr>
<td>0.0001wt% C\textsubscript{14}DMAO</td>
<td>30.5</td>
<td>0.03</td>
<td>26.5</td>
<td>4.0</td>
<td>4.0\textsuperscript{e}</td>
<td>228</td>
</tr>
<tr>
<td>0.001wt% C\textsubscript{14}DMAO</td>
<td>30.3</td>
<td>0.03</td>
<td>26.5</td>
<td>3.8</td>
<td>3.8\textsuperscript{e}</td>
<td>216</td>
</tr>
<tr>
<td>0.005wt% C\textsubscript{14}DMAO</td>
<td>26.9</td>
<td>0.2</td>
<td>26.5</td>
<td>0.6</td>
<td>0.2</td>
<td>21.4</td>
</tr>
</tbody>
</table>

Note: same as Table 8.2
Foam testing results at neutral pH with high hardness are given in Figure 8.9. Table 8.5 gives the corresponding ESB calculations. At such high hardness, addition of 0.005wt% C$_{14}$DMAO produced noticeable foam stabilizing efficacy but the effect at low concentrations is negligible. The entry, spreading and bridging coefficients decrease as the concentration of C$_{14}$DMAO increases, but foams were still not very stable even if $E = 0$ at equilibrium.

![Figure 8.9](image)

Table 8.5 Semi-equilibrium* Entry, Spreading, Bridging coefficients ($\gamma_{AW}$ measured with solution equilibrated with 0.01–0.02wt% C$_{16}$/HOI)

<table>
<thead>
<tr>
<th>Systems</th>
<th>$\gamma_{AW}$</th>
<th>$\gamma_{OW}$</th>
<th>$\gamma_{OA}$</th>
<th>$E$</th>
<th>$S$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%N25-3S, 0.01wt%C$_{16}$/HOI, 2000ppm hardness, pH7 plus:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0wt%C$_{14}$DMAO</td>
<td>28.0</td>
<td>0.005</td>
<td>26.5</td>
<td>1.5</td>
<td>1.5&lt;sup&gt;e&lt;/sup&gt;</td>
<td>82</td>
</tr>
<tr>
<td>0.0001wt% C$_{14}$DMAO</td>
<td>27.0</td>
<td>0.005</td>
<td>26.5</td>
<td>0.5</td>
<td>0.5&lt;sup&gt;e&lt;/sup&gt;</td>
<td>26.7</td>
</tr>
<tr>
<td>0.001wt% C$_{14}$DMAO</td>
<td>26.5</td>
<td>0.002</td>
<td>26.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.005wt% C$_{14}$DMAO</td>
<td>24.7</td>
<td>0.17</td>
<td>26.5</td>
<td>-1.6&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-1.8</td>
<td>-92</td>
</tr>
</tbody>
</table>

Note: same as Table 8.2

8.3.1b Results with TO/HOI

At pH9 and in the presence of insoluble soap, foam stability enhancement is significant when the concentration of C$_{14}$DMAO is as high as 0.005wt% (Figure 8.10).
Semi-equilibrium $E$, $S$ and $B$ are negative for all the tested concentrations, as given in Table 8.6. At neutral pH and high hardness, $C_{14}$DMAO starts to exhibit foam-stabilizing effect at a lower concentration, although the efficacy is modest, as shown in Figure 8.11. Semi-equilibrium $E$, $S$ and $B$ are negative for all the tested concentrations, as given in Table 8.7.

![Figure 8.10](image)

Table 8.6 Semi-equilibrium Entry, Spreading, Bridging coefficients ($\gamma_{AW}$ measured with solution equilibrated with 0.01–0.02wt% TO/ HOI)

<table>
<thead>
<tr>
<th>Systems</th>
<th>$\gamma_{AW}$</th>
<th>$\gamma_{OW}$</th>
<th>$\gamma_{OA}$</th>
<th>$E$</th>
<th>$S$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%N25-3S, 0.01wt%TO/HOI, 300ppm hardness, pH9 plus:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0wt%$C_{14}$DMAO</td>
<td>29.2</td>
<td>0.8</td>
<td>31.4</td>
<td>-1.4(^e)</td>
<td>-3</td>
<td>-133</td>
</tr>
<tr>
<td>0.0001wt% $C_{14}$DMAO</td>
<td>29.8</td>
<td>0.11</td>
<td>31.4</td>
<td>-1.5(^e)</td>
<td>-1.7</td>
<td>-98</td>
</tr>
<tr>
<td>0.001wt% $C_{14}$DMAO</td>
<td>30.4</td>
<td>0.14</td>
<td>31.4</td>
<td>-0.9</td>
<td>-1.1</td>
<td>-62</td>
</tr>
<tr>
<td>0.005wt% $C_{14}$DMAO</td>
<td>26.5</td>
<td>0.26</td>
<td>31.4</td>
<td>-4.5(^e)</td>
<td>-5.3</td>
<td>-284</td>
</tr>
</tbody>
</table>

Note: same as Table 8.2
Figure 8.11 

0.01wt% N25-3S, 0.01wt% TO/HOI
2000ppm hardness, pH7 plus

Table 8.7 Semi-equilibrium* Entry, Spreading, Bridging coefficients ($\gamma_{aw}$ measured with solution equilibrated with 0.01–0.02wt% TO/HOI)

<table>
<thead>
<tr>
<th>Systems</th>
<th>$\gamma_{aw}$</th>
<th>$\gamma_{ow}$</th>
<th>$\gamma_{oa}$</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%N25-3S, 0.01wt%TO/HOI, 2000ppm hardness, pH7 plus:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0wt%C_{14}DMAO</td>
<td>27.9</td>
<td>0.36</td>
<td>31.4</td>
<td>-3.1e</td>
<td>-3.9</td>
<td>-207</td>
</tr>
<tr>
<td>0.0001wt% C_{14}DMAO</td>
<td>26.6</td>
<td>0.18</td>
<td>31.4</td>
<td>-4.6e</td>
<td>-5.0</td>
<td>-278</td>
</tr>
<tr>
<td>0.001wt% C_{14}DMAO</td>
<td>24.6</td>
<td>0.19</td>
<td>31.4</td>
<td>-6.6e</td>
<td>-7.0</td>
<td>-381</td>
</tr>
<tr>
<td>0.005wt% C_{14}DMAO</td>
<td>24.0</td>
<td>3.0</td>
<td>31.4</td>
<td>-4.4e</td>
<td>-10.4</td>
<td>-4.1</td>
</tr>
</tbody>
</table>

Note: same as Table 8.2

8.3.2 Pseudoemulsion Films

Pseudoemulsion films between C16/HOI and pH9 solutions containing 0.01%N25-3S, 300ppm hardness and 0.0001–0.005% C_{14}DMAO are unstable. As shown in Figure 8.12 for example, film rupture started at the ‘broken point’. Oil surface emerged into the air-water surface and formed an oil lens several seconds later. Films between C16/HOI and the neutral solutions containing 2000ppm hardness are difficult to track due to low interfacial tensions.
Figure 8.12 A pseudoemulsion film between C16/HOI and pH9 solution containing 0.01%N25-3S, 0.005%C_{14}DMAO and 300ppm hardness.

Pseudoemulsion films between TO/HOI and pH9 solutions containing 0.01%N25-3S, 300ppm hardness and different amounts of C_{14}DMAO are always stable. As shown earlier in Figure 5.15, drainage is asymmetric in the absence of C_{14}DMAO. In contrast, drainage is symmetric with 0.0001% C_{14}DMAO. As film thickness decreases to a certain state, indicated by the change of the area outside the dimple from bright to dark (Figure 8.13 a&b), several thinner spots nucleate in the area outside the dimple which quickly grow as white film (Figure 8.13 c&d). This is clearly step-wise thinning (stratification) in the planar area of the pseudoemulsion film.

Figure 8.13 A pseudoemulsion film (d = 800\mu m) between TO/HOI and pH9 solution containing 0.01%N25-3S, 0.0001wt%C_{14}DMAO and 300ppm hardness.
With 0.001% C$_{14}$DMAO (10ppm), drainage exhibits a very different pattern. As shown in Figure 8.14, the shrinking dimple and non-uniform thickness around it form a 'sunflower'. As the film drains symmetrically, a planar area develops outside the dimple (Figure 8.14a). This area turns into a white rim about 40 seconds later (Figure 8.14b). Shortly after that the rim goes through an instability and develops into the fingering pattern (Figure 8.14 c&d). This finger pattern eventually goes away as excess water drains into meniscus. The dimple shrinks fast while the rim and fingers develop, i.e., as the instability grows. When the number of fingers begins to decrease and after fingers disappear, the size of the dimple changes extremely slowly. This phenomenon is reproducible.
Figure 8.14 A pseudoemulsion film (d = 780μm) between TO/HO1 and pH9 solution containing 0.01%N25-3S, 0.001wt%C_{14}DMAO and 300ppm hardness.

With 0.005% C_{14}DMAO, as shown in Figure 8.15, drainage is very slow and symmetric. The dimple is large and flat.

Figure 8.15 A pseudoemulsion film (d = 770μm) between TO/HO1 and pH9 solution containing 0.01%N25-3S, 0.005wt%C_{14}DMAO and 300ppm hardness.
8.4 Discussion

8.4.1 Foam-stabilizer Efficacy

A summary of the different experimental results for this chapter is given in Appendix VI and VII.

For a brief summary of the foam-stabilizer efficacy of lauric alcohol (LA) and C_{14}DMAO in situations involving oily additives and insoluble calcium soap or at high hardness, the experimental results show that LA is much more effective than C_{14}DMAO as a foam booster at comparable doses. The effectiveness of LA is good both with calcium soap at pH9 and high hardness without calcium soap.

Foam boosting effect of long chain alcohol is sometimes attributed to slowing down film thinning and water drainage from the foam, which is due to the effect of alcohol on the surface viscosity. In the present study of horizontal foam films in Scheludko cell, noticeable decrease in the rate of foam film drainage hasn’t been observed. Liquid drainage is asymmetric in the presence of 0.001wt% - 0.005wt% LA, as in the absence of LA. In the study of pseudoemulsion films with TO/HO1, an obvious slowdown of liquid drainage was observed. Drainage information for pseudoemulsion films with C16/HO1 is missing due to experimental difficulties caused by low interfacial tensions.

Basheva et al. [2001] studied the boosting effect of LA on foams of sodium dodecyl polyoxyethylene-3 sulfate (SDP3S), which is an anionic surfactant similar to our N25-3S. Total surfactant concentration in their system is 500 times of ours with 3% of that being LA. They found that adding LA leads to a very high barrier to entry of the oil drops and thereby stabilizes foam. The high entry barrier, these authors remark, is
probably related to a very strong attraction between the molecules of SDP3S and LA in the adsorption layers. That is, the higher entry barrier is a consequence of a more cohesive monolayer. In their study with systems containing silicone oil, the equilibrium entry, spreading and bridging coefficients are positive. That the oil cannot enter the air-water surface to destabilize foam must be due to a negative $E_g$. In our study with C16/HO1 and TO/HO1, the results show that LA significantly decreases surface tensions of the surfactant solutions. As LA concentration increases, Semi-equilibrium E and B decrease and even change sign from positive to negative for some systems. Therefore we sometimes have negative entry/bridging coefficients, especially for the case of TO/HO1 which has a fairly high surface tension. This implies that drop entry is impossible at near equilibrium state. Moreover, dynamic surface tensions decrease faster in the presence of LA. Although some air bubbles coalesce during foam generation implying that both E B and are positive at early stage, the shift of E from positive to negative is now faster compared to that in the absence of LA. That is, in a shorter period of time after new air-water surfaces are created, drop entry becomes energetically unfavorable. In this way defoaming effect of oils is weakened and foam stability increases. In short, all of the foam stability results discussed above are consistent with ESB approach if time dependent changes in E, S, B are included for C16/HO1 and TO/HO1, and if generalized entry coefficient $E_g$ is also included to account for strong entry barrier in pseudoemulsion films for silicone oil.

Matson [1963] investigated and compared the foam-stabilizing efficacy of fatty amine oxides to that of alkanolamides in light-duty and heavy-duty detergents. Amine oxide was found to be a much more effective foam stabilizer than amides for the
detergents studied, particularly at low hardness. In shampoo applications, amine oxides are often preferred to amides as foam stabilizers. This is particularly true for acid shampoos, because amides are unstable below pH 5.5 while amine oxides are quite stable at low pH as 3.5 [Lai and Dixit, 1996]. Our study here shows that amine oxide is not very effective as foam stabilizer at alkaline pH and at high hardness. This appears to be a supplement to the former studies.

Independent investigations on the mechanism by which amine oxides operate as foam stabilizers by Kolp et al. [1963] and Rosen et al. [1964] led to the same conclusions that interaction occurs between the protonated amine oxide cation, RN(CH₃)₂OH⁺, and the surfactant anion, yielding a product that has been isolated, RN(CH₃)₂OH⁺O₂SR, in which cation and anion are strongly hydrogen-bonded via the H⁺ of the cation. This compound is much more surface active than either the amine oxide or the anionic surfactant and adsorbs strongly at the air-water interface to form a closely packed film. In our study with alkaline systems, this process is suppressed since formation of the protonated amine oxide cation is not favored.

An important consideration in selecting an effective foam additive is the compatibility between the hydrophobes of the foaming surfactants and those of the additives. In general, a compound having hydrocarbon chain with length comparable to the hydrocarbon length of the surfactant functions as an effective foam stabilizer. In this respect both LA and C₁₄DMAO can be good candidates, since the foaming surfactant, N25-3S, has a straight hydrocarbon chain between 12 and 15.

Another consideration is that the effectiveness of these additives is dependent upon their surface activity and how easily they can be incorporated into the foam films.
The complexing ability of the additive with the surfactant in the foam film also plays an important role in stabilizing foam, as is the case with amine oxides added to an anionic surfactant system. Here we compared the influence of C$_{14}$DMAO and LA on surface and interfacial tensions of the studied systems. Results are given in Table 8.8. Obviously, LA is more effective in decreasing air-water surface tensions than C$_{14}$DMAO at comparable doses, especially at alkaline pH. One possible reason may be that LA forms a more compact mixing adsorption layer with N25-3S than C$_{14}$DMAO does, since the former is straight chain alcohol but the latter has two methyl groups at the hydrophilic head and therefore a larger area/molecule. Furthermore, the complexing ability of C$_{14}$DMAO with the N25-3S is restrained at alkaline pH. The influences of these two additives on interfacial tensions are not linear and depend on compositions of both aqueous and oleic phases.

<table>
<thead>
<tr>
<th>Aqueous system</th>
<th>wt% of booster</th>
<th>$\gamma_{AW}$</th>
<th>$\gamma_{OW(\text{C16/HOI})}$</th>
<th>$\gamma_{OW(\text{TO/HOI})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01%N253S, 300ppmCa, pH9</td>
<td>0</td>
<td>27.5</td>
<td>0.1</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>25.9</td>
<td>0.1</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>24.8</td>
<td>0.03</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>24.3</td>
<td>0.03</td>
<td>0.17</td>
</tr>
<tr>
<td>0.01%N253S, 2000ppmCa, pH7</td>
<td>0</td>
<td>26.4</td>
<td>0.005</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>25.5</td>
<td>0.004</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>24.5</td>
<td>0.004</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>23.9</td>
<td>0.003</td>
<td>0.99</td>
</tr>
</tbody>
</table>

(\(\gamma_{AW}\) were measured with solutions free of oils)
8.4.2 Comments on Drainage of Pseudoemulsion Films

When a dimple forms in pseudoemulsion film, it's proposed that the oil-water (OW) is more easily deformable than the air-water (AW) interface. Here is the argument. Suppose a dimple forms as sketched in Figure 8.16b. Assume lubrication theory applies during drainage but film is thick enough that disjoining pressure effects are negligible.

Let \( P_f \) equal local pressure at some point in the film. Then

\[
P_f - P_A = \gamma_{AW}(2H)_{AW} \tag{1}
\]

\[
P_f - P_O = \gamma_{OW}(2H)_{OW} \tag{2}
\]

\( H \) is the mean curvature. \( 2H \) is the sum of the reciprocal radii of curvature of the interface as measured in any two perpendicular planes containing the local normal to the interface.

Subtracting (2) from (1) leads to

\[
P_O - P_A = \gamma_{AW}(2H)_{AW} - \gamma_{OW}(2H)_{OW} = (P_O - P_W) - (P_A - P_W)
\]

Here \( P_W \) = Pressure of bulk water \( \approx P_A \) since air-water surface is flat away from the drop.

And \( P_O - P_W = 2\gamma_{OW} / R \)

Hence

\[
2\gamma_{OW} / R = \gamma_{AW}(2H)_{AW} - \gamma_{OW}(2H)_{OW} \tag{3}
\]

In our study \( \gamma_{AW} \) is usually in the range of 25 ~ 30mN/m and \( \gamma_{OW} \leq 1 \) mN/m. So \( (2H)_{AW} \) is smaller in magnitude than \( (2H)_{OW} \) from equation (3), i.e. the air-water surface is pretty flat compared with the oil-water interface.
Figure 8.16 Schematic of thick rim formation process in pseudoemulsion film.

Now let's look at the drainage of pseudoemulsion films between TO/HOI and pH9 solution of 0.01wt%N25-3S plus 300ppm hardness and C14DMAO. At 0.0001wt% C14DMAO video shows clear nucleation and growth of a thin white film (stratification) outside the dimple (Figure 8.13). One can see this white film at 0.001wt% C14DMAO near the periphery of the film and outside the “fingering” pattern (Figure 8.14). The expansion of the white film, from periphery into the film, tends to produce a thick rim. Shrinkage of dimple may also help to build up a thicker rim outside the dimple. An illustration of the proposed process of forming thicker rim is given in Figure 8.16. That is (a) an oil drop approaches the air-water surface; (b) a dimple is formed; (c) an annular planar film forms outside the dimple (corresponding to Figure 8.14a); (d) Local thinner area forms along the periphery since liquid drains faster there than in the planar film. Expansion of the thinner area and shrinkage of dimple produce a thick rim (corresponding to Figure 8.14b). It looks like the thinner region expanded non-uniformly inward, then the rim broke up due to some instability and formed the “fingering pattern” (Figure 8.14 c&d).
8.5 Summary

Effect of two potential boosters, dodecanol (LA) and C₁₄DMAO, on foam stability for two situations where foam was highly unstable was investigated for both C₁₆/HOI and TO/HOI with N25-3S. One of the two conditions is pH9 solution of 0.01wt%N25-3S plus 300ppm hardness, with the presence of calcium soap. The other is 0.01wt%N25-3S plus 2000ppm hardness at neutral pH, with negligible calcium soap present. Microemulsion forms with C₁₆/HOI in such solution. Results for C₁₆/HOI with both boosters are consistent with ESB analysis, except for 0.005wt% C₁₄DMAO where foam is unstable even though E is negative (-1.6mN/m). More such occasions occur for TO/HOI due to its high surface tenison, i.e. foam is unstable even though E is negative. For these cases time-dependent changes of E from positive to negative due to decrease of $\gamma_{AW}$ must be invoked. This way foam results can be understood by entry/bridging coefficients. Under the two investigated conditions, LA is better stabilizer than C₁₄DMAO because it causes larger decrease in $\gamma_{AW}$. LA at high concentration may also decrease $E_g$ due to formation of a less mobile and compact film, so there could be a steric contribution to disjoining pressure. This proposition might be tested by the film trapping technique (FTT) developed by Hadjiiski et al. [1996].
Chapter 9 Defoaming Effect of Calcium Soap

9.1 Introduction

It has been illustrated in Chapter 5 that the combination of oil and calcium soap produces a synergistic effect facilitating the bridging instability of foam films or Plateau borders and producing a substantial antifoam effect. It's well-known that insoluble soaps alone destabilize foam [Peper 1958; Ferch and Leonhart 1993]. This chapter will focus on foam properties of solutions containing calcium soap but free of oils. Calcium soap is formed by adding sodium oleate to surfactant solutions with dissolved calcium chloride and pH adjusted to 9 by sodium hydroxide. Alkalinity is applied to limit the hydrolysis of oleate into oleic acid, which would otherwise be significant in micellar surfactant solutions due to easy incorporation of oleic acid into micelles.

It's found that the calcium soap has a significant destabilizing effect, even when no oil is present. It is greatest when many solid particles form which may themselves cause a bridging instability. But even when the solutions are transparent, the foam is somewhat less stable than in the absence of calcium and oleate. Moreover, intriguing aging results are observed, i.e., foam produced with solution that has been allowed to stand for hours was more stable than that produced with freshly mixed solution.

9.2 Experimental Results

9.2.1 Turbidity

Most calcium soaps have low solubility in water, e.g., the solubility product of calcium oleate is ten to the power of \(-15.4\) at \(295\,\text{K}\) and zero ionic strength [Irani & Callis 1960]. So when sodium oleate is added to an alkaline aqueous phase containing hardness, turbidity of the solution is expected to increase. Accordingly, a series of turbidity studies
was carried out by measuring the transmittance as a function of aging time, hardness level, surfactant concentration etc. Zero turbidity is considered as 100% transmittance. The sodium oleate used in this study had purity higher than 99%. Samples were blanketeted by nitrogen during aging. The transmittance of fresh de-ionized water was taken as 100%T and was used for calibration.

First, we kept surfactant (N25-3S) concentration at 0.01 wt%, which is near CMC in absence of hardness, and changed concentrations of hardness and sodium oleate. The results are given in Table 9.1(a), (b) and (c) respectively. Regarding the stoichiometry of calcium oleate, CaO\(_2\), calcium is in excess for all the compositions studied. Here, fresh solution means that the measurement was made within 30 minutes after the samples were prepared. It is also worth clarification that calcium and oleate incorporated in micelles must be excluded in the calculation to see if solubility product of calcium oleate is exceeded.

Clearly, turbidity increases with aging time except for the first solution of Table 9.1(b). This shows that calcium oleate solid particles are growing. Based on the data of fresh solutions, we can see that hardness had less effect on turbidity than sodium oleate since it was in excess. With the same amount of sodium oleate, solution containing 300ppm hardness is less turbid than that with 20ppm hardness, presumably because there are more micelles to incorporate oleate as CMC is lowered by hardness. But this trend doesn’t continue linearly as hardness level is further increased.

<table>
<thead>
<tr>
<th>Time</th>
<th>T%</th>
<th>NaO(_2): 0.0004%</th>
<th>0.0008%</th>
<th>0.001%</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh</td>
<td>98.3</td>
<td>95.7</td>
<td>93.1</td>
<td></td>
</tr>
<tr>
<td>4hrs</td>
<td>97.5</td>
<td>91.6</td>
<td>90.0</td>
<td></td>
</tr>
<tr>
<td>74hrs</td>
<td>96.6</td>
<td>89.9</td>
<td>88.4</td>
<td></td>
</tr>
<tr>
<td>98hrs</td>
<td>96.4</td>
<td>89.8</td>
<td>88.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 9.1 (a)
Secondly, the effect of surfactant concentration on turbidity was studied by increasing the concentration of N25-3S from 0.01wt% to 0.02wt% to 0.05wt%. Results are shown in Table 9.1(d) & (e). As concentration of N25-3S increases, turbidity decreases, indicating fewer particles were formed because more oleate and calcium were incorporated in micelles.
Turbidity of solutions with 0.1wt%N25-7 was also studied. With hardness fixed at 300ppm, we scanned the concentration of sodium oleate, as shown in Table 9.2. The solutions are quite clear up to 0.002%NaO1. Beyond that point, transmittance decreases fast.

**Table 9.2**

<table>
<thead>
<tr>
<th>T%</th>
<th>NaO1: 0.001%</th>
<th>0.002%</th>
<th>0.003%</th>
<th>0.004%</th>
<th>0.005%</th>
<th>0.01%</th>
<th>0.05%</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh</td>
<td>99.9</td>
<td>99.6</td>
<td>99.4</td>
<td>91.4</td>
<td>88.7</td>
<td>69.5</td>
<td>13.7</td>
</tr>
<tr>
<td>4hrs</td>
<td>99.9</td>
<td>99.7</td>
<td>2hrs: 95.0</td>
<td>83.0</td>
<td>7hrs: 59.3</td>
<td>34.6</td>
<td>1.30</td>
</tr>
<tr>
<td>23hrs</td>
<td>99.9</td>
<td>99.3</td>
<td>25hrs: 92.2</td>
<td>77.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29hrs</td>
<td>99.9</td>
<td>99.5</td>
<td>34hrs: 93.1</td>
<td>79.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 9.2.2 Foam Stability - Experiments with Fresh Solutions

A series of fresh pH9 solutions containing 0.01wt%N25-3S and different amounts of sodium oleate and hardness were tested for foam stability. Figure 9.1 illustrates the results at 300ppm hardness. As we can see, foam stability decreased as the amount of sodium oleate increased. The lower the concentration of sodium oleate, the longer the delay before the occurrence of foam decay, and the larger the final stable foam height. Substantial decrease in foam stability is found up to 0.005%NaO1 with little additional effect if sodium oleate concentration increases beyond that point. Solutions containing 0.0004wt% and 0.0008wt% sodium oleate were visually transparent, although transmittance is less than 100% as shown in Table 9.1(b). No particles were observed in Scheludko cell when making thin films with these solutions. With 0.001% NaO1,
particles were sometimes seen in Scheludko cell. When concentration of sodium oleate increased to 0.005% and 0.01%, solutions were quite turbid.

The results of foam stability at other hardness levels are given in Table 9.3. Similar trend as for 300ppm was observed for other calcium concentrations. As with turbidity, foam stability is relatively insensitive to hardness because calcium is in excess.

Figure 9.1 Foam stability with 0.01% N25-3S at different amounts of sodium oleate

0.01%N25-3S, 300ppmCa\(^{2+}\), pH9

![Foam stability graph](image)

Without any sodium oleate, it was observed that alkaline pH influences the stability of foam with 0.01% N25-3S, 300ppm hardness solution. As shown in Figure 9.2, foam is less stable at pH9 than at neutral pH for freshly mixed solution. The difference in stability occurs after 10 minutes when the dry foam consists very thin film lamellae. It’s found that pH of the initially alkaline solution decreased as the solution aged. When the solution was tested again after about 43 hours, pH was around 7.5 and foam stability was similar to that of the freshly mixed solution at neutral pH. On the contrary, pH didn’t change in the absence of N25-3S. That is, a pH9 water solution with 300ppm hardness stayed at pH9 after aging. So some component in this commercial surfactant seems to slowly consume the hydroxide ions.
Figure 9.2 Effect of pH on foam stability with 0.01%N25-3S and 300ppm hardness

![Graph showing foam height over time for fresh pH7 and pH9 solutions, and pH9 solution aged 43 hours.]

Table 9.3 Defoaming effect of calcium soap at different hardness level

<table>
<thead>
<tr>
<th>Hardness (Ca^{2+} wt%)</th>
<th>N25-3S (wt%)</th>
<th>NaOl (wt%)</th>
<th>H_0</th>
<th>H_{10}</th>
<th>H_{20}</th>
</tr>
</thead>
<tbody>
<tr>
<td>20ppm</td>
<td>0.01</td>
<td>0.0004</td>
<td>20</td>
<td>13.0</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0008</td>
<td>20</td>
<td>10.0</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001</td>
<td>20</td>
<td>8.3</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.002</td>
<td>20</td>
<td>7.0</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.003</td>
<td>20</td>
<td>5.9</td>
<td>5.2</td>
</tr>
<tr>
<td>50ppm</td>
<td>0.01</td>
<td>0.0004</td>
<td>20</td>
<td>14.0</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0008</td>
<td>20</td>
<td>8.0</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001</td>
<td>20</td>
<td>6.7</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.003</td>
<td>20</td>
<td>4.8</td>
<td>4.5</td>
</tr>
<tr>
<td>100ppm</td>
<td>0.01</td>
<td>0.0004</td>
<td>20</td>
<td>17.0</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001</td>
<td>20</td>
<td>6.8</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>20</td>
<td>9.0</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0004</td>
<td>20</td>
<td>16.8</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0008</td>
<td>20</td>
<td>13.4</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001</td>
<td>20</td>
<td>7.1</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.002</td>
<td>20</td>
<td>5.6</td>
<td>5.5</td>
</tr>
<tr>
<td>300ppm</td>
<td>0.01</td>
<td>0.01</td>
<td>20</td>
<td>19.8</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.01</td>
<td>20</td>
<td>18.6</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>20</td>
<td>18.7</td>
<td>14.4</td>
</tr>
<tr>
<td>0ppm</td>
<td>0.01</td>
<td>0.01</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: All solutions were tested at pH9. Calcium is in excess for all the solutions since the molar ratio of [Ca^{2+}] to [Ol] is larger than two. H_{10} is foam height after 10min (cm); H_{20} is foam height after 20min (cm);
Similar experiments were performed with 0.02wt% surfactant concentration, as shown in Figure 9.3. We can see the same trend of foam height versus time as in Figure 9.1. Again, as concentration of sodium oleate increased, substantial decrease in foam height was seen up to 0.003%, with little additional effect beyond that point.

Figure 9.3 Foam stability with 0.02%N25-3S at different amounts of sodium oleate

$0.02\% \text{N}25-3\text{S}, 300\, \text{ppm} \text{Ca}^{2+}, \text{pH}9$

For nonionic surfactant N25-7, surfactant concentration was kept at 0.1wt%. Foam stability of pH9 solution containing 300ppm hardness and different amounts of sodium oleate was tested. The results are shown in Figure 9.4. No significant effect on foam stability was seen up to 0.002wt% NaOl. At this concentration the solution has virtually 100% transmittance per Table 9.2. Decrease in foam stability was noticeable with 0.003%NaOl, which made the solution a little bluish. At higher concentrations of sodium oleate, which make the solutions turbid, foam stability was further decreased.
9.2.3 Foam Stability - Aging Study

In turbidity study we saw turbidity changed with time for solutions containing calcium soap particles. Now, we look at how aging affects foam stability. During aging process, the solutions were blanketed with nitrogen and well covered.

With concentration of the anionic surfactant N25-3S being fixed at 0.01wt% and hardness at 300ppm, foam stability was tested at several concentrations of sodium oleate. Figure 9.5 shows results at 0.0004% and 0.01% NaOl. Figure 9.6 shows result at 0.001%NaOl. We can see that, compared with the fresh solutions, foam stability increased after aging. The change was significant with 0.0004% and 0.01% NaOl, while even larger at intermediate concentration of 0.001%NaOl. Solution with 0.0004% NaOl looks transparent even after aging (refer to Table 9.1(c)). Solution with 0.01%NaOl was quite turbid from the beginning, obviously with substantial amount of insoluble soap particles. Solution with 0.001%NaOl looks bluish, indicating the existence of solid
particles, but they must be small. pH value of these solutions decreased after aging from 9 to about 7.5.

Figure 9.5 Comparison of foam stability between fresh and aged solutions

0.01%N25-3S, 300ppm Ca²⁺

Figure 9.6 Comparison of foam stability between fresh and aged solutions

0.01%N25-3S, 300ppm Ca²⁺, pH9

As a comparison, solutions containing both oils and calcium soap were also tested after aging. The studied systems were pH9 solution of 0.01wt%N25-3S plus 300ppm hardness and 0.01% oil mixture, C16/HO1 or TO/HO1. As discussed in Chapter 5, calcium soaps form *in situ* at the oil-water interface in these systems. In the presence of oils, Figure 9.7 shows that foams were still quite unstable after aging. Foams of fresh
and aged alkaline solutions containing 0.009 wt% cetane + 0.001 wt% NaOl + 300 ppm hardness were also tested. Both of them were quite unstable and behaved similarly to the foams containing C16/HOl.

Figure 9.7 Comparison of foam stability between fresh and aged solutions of N23-3S in the presence of oil

0.01 wt% N25-3S, 300 ppm, pH9

Same experiments were performed with 0.1 wt% N25-7. As shown in Figure 9.8, foam of oil-free solution became more stable after aging 60 hours. But when oil mixture was present, foam was even less stable than that of the freshly mixed solution.

Figure 9.8 Comparison of foam stability between fresh and aged solutions of N25-7 in the presence of oil

0.1 wt% N25-7, 300 ppm, pH9
9.2.4 Dynamic and Equilibrium Surface Tension

Dynamic surface tensions were measured by maximum bubble pressure method. Figure 9.9 shows the results with the anionic surfactant N25-3S, and Figure 9.10 shows those with the nonionic surfactant N25-7. Table 9.4 summarizes the equilibrium surface tensions (E.S.T.) measured with spinning drop tensiometer for a time longer than 20 minutes.

Figure 9.9 Dynamic surface tensions with N25-3S and soap

![Dynamic Surface Tension Graph]

Compared with the dynamic surface tension of 0.01wt% N25-3S + 300ppm hardness solution, 0.001wt%NaOl additive increases dynamic surface tension by around 2mN/m at short bubble life time, e.g., less than 1100 milliseconds. At longer bubble lifetime, dynamic surface tension is the same as that without soap additive. With 0.005wt%NaOl, dynamic surface tension is always slightly above that of the solution with no soap additive within the measurable timescale of 1 minute. For freshly mixed solutions, data in Table 9.4 show that soap additive also slightly increased the equilibrium surface tensions of the studied systems. For aged solutions, however, surface tensions approach the value for the solution without any oleate.
Table 9.4 Equilibrium surface tension of solutions containing soap and hardness

<table>
<thead>
<tr>
<th>E.S.T. (mN/m) of</th>
<th>0.01wt%N25-3S, 300ppm hardness, pH9 plus</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0%NaOl</td>
<td>0.001%NaOl</td>
<td>0.005%NaOl</td>
<td>0.05%NaOl</td>
</tr>
<tr>
<td>freshly mixed solution</td>
<td>27.5</td>
<td>27.8</td>
<td>28.8</td>
<td>30.1</td>
</tr>
<tr>
<td>aged 40 hours</td>
<td>27.5</td>
<td>27.6</td>
<td>27.9</td>
<td></td>
</tr>
<tr>
<td>aged 140 hours</td>
<td>27.4</td>
<td>27.7</td>
<td>27.5</td>
<td></td>
</tr>
<tr>
<td>0.1wt%N25-7, 300ppm hardness, pH9 plus</td>
<td>27.1</td>
<td>27.2</td>
<td>27.5</td>
<td>50.9</td>
</tr>
</tbody>
</table>

For N25-7, increase in dynamic surface tension is noticeable only with substantial amount of soap additive, i.e. ≥ 0.05%. The equilibrium surface tension increases as concentration of sodium oleate increases, but the change is tiny.

Figure 9.10 Dynamic surface tensions with N25-7 and soap

9.2.5 Individual Foam Film

Thin films made by alkaline solutions containing N25-3S, NaOl and calcium chloride were studied in Scheludko cell. Film size is between 0.6mm~1mm. It was
pointed out in Chapter 4 that, for films produced from 0.01%N25-3S + 300ppm Ca\(^{2+}\) solution, asymmetric drainage of the dimple takes place within 1~2 seconds after the film is formed. Channels disappear and a white planar film forms at around 1 minute. And as drainage goes on continuously, a uniform stable black film forms at around 3 minutes. In the following discussion, we’ll take this process as a reference for comparison.

9.2.5a pH9 solution of 0.01%N25-3S + 0.001%NaOl + 300ppm Ca\(^{2+}\)

Ten thin film samples were studied. Eight of them behaved similarly to the film with no sodium oleate additive. Two of them showed a different thinning pattern. That is, after the initial asymmetric dimple drainage (within two seconds), a new dimple-like pattern formed, as shown in Figure 9.11a. The film appeared to have good fluidity, but drainage was slow and it didn’t form a white planar film (Figure 9.11b). A uniform black film finally formed after approximately 3 minutes. A particle was observed in the middle of the newly formed dimple.

Figure 9.11 Foam film with pH9 solution containing 0.01%N25-3S, 0.001%NaOl, 300ppm Ca\(^{2+}\)
9.2.5b pH9 solution of 0.01%N25-3S + 0.005%NaOl + 300ppm Ca^{2+}

At a higher concentration of sodium oleate, quick initial asymmetric dimple drainage was again observed. However, at around 1 minute the white film was not uniform (Figure 9.12 a&b); at around three minutes, the black film was not uniform either (Figure 9.12c&d).

Figure 9.12 Foam film with pH9 solution containing 0.01%N25-3S, 0.005%NaOl and 300ppm Ca^{2+}

When this same solution was tested after aging 40 hours, the phenomenon described above was not observed. The thinning process was the same as for solutions without any oleate (Figure 4.10). Although the presence of solid soap particles in the solution was obvious, particles were all expelled and not able to stay in the film during drainage.
9.2.5c pH9 solution of 0.01%N25-3S + 0.01%NaOl + 300ppm Ca^{2+}

By making thin films with this solution containing even more sodium oleate, we saw both stable films and less stable films with similar frequency. After the initial quick asymmetric dimple drainage, a new dimple formed and it was still there after 1 minute, as shown in Figure 9.13a. Some films broke after several minutes. For example, Figure 9.13b was such a film right before it broke. Some films lasted longer than 8 minutes, as seen in Figure 9.13c. Many particles were seen in all these studied films.

Figure 9.13 Foam film with pH9 solution containing 0.01%N25-3S, 0.01%NaOl, 300ppm Ca^{2+}

(a)  (b)  (c)

Again, when this same solution was tested after aging 40 hours, phenomenon described above was not observed. All the particles were expelled during film drainage, with the thinning process the same as that for solutions without any oleate (Figure 4.10).

9.2.5d pH9 solution of 0.01%N25-3S + 0.04%NaOl + 300ppm Ca^{2+}

For freshly mixed solutions, more particles were seen in foam film as more sodium oleate was added. With 0.04wt% NaOl, as shown in Figure 9.14, quick asymmetric drainage was not observed. Film broke before 3 minutes, presumably by the
bridging of the particles. Figure 9.14b is a film right before it broke. Aged solutions were not tested at this concentration.

Figure 9.14 Foam film with pH9 solution containing 0.01%N25-3S, 0.04%NaO1, 300ppm Ca$^{2+}$

9.3 Discussion

9.3.1 Effect of Alkalinity on Foam Stability in the Presence of Calcium

As shown in Figure 9.2, foam of 0.01%N25-3S + 300ppm hardness (mainly CaCl$_2$) is very stable at neutral pH but is less stable at alkaline pH. This phenomenon was also observed at other hardness levels, e.g. 50ppm. A possible reason may be related to the work of Rutland and Pugh [1997]. They made measurements with surface forces apparatus of forces between negatively charged mica plates separated by alkaline aqueous solutions. When the only counterion in solution was Na$^+$, there was a strong short-range repulsion, i.e. hydration force. But when calcium was present at pH9, they say that substantial Ca(OH)$^+$ was specifically adsorbed at the negatively charged surfaces and hydration forces were found to be minimal. This is because Ca(OH)$^+$ was less strongly bound with water of hydration than Na$^+$ and Ca$^{2+}$. For the latter ions the water of hydration strongly bound, limited how close they could approach the solid surfaces. The
relevance of our case to their study is 1) the two surfaces of foam film are negatively charged due to presence of anionic surfactants; 2) Na\(^{+}\), Ca\(^{2+}\) and Ca(OH)\(^{+}\) and are the only cations present; 3) a strong short-range repulsion helps stabilize thin film; 4) instability of foam at alkaline pH occurs only when foam lamellae become very thin. Thus, the decrease of foam stability as pH changes from 7 to 9 may be related to Rutland and Pugh’s finding. As the solution ages, pH decreases, i.e. concentration of OH\(^{-}\) decreases with the result that concentration of Ca(OH)\(^{+}\) also decreases. This is presumably why foam stability returns to that for solutions formed at neutral pH.

### 9.3.2 Defoaming by Calcium Soap

When calcium soaps are formed by mixing sodium oleate and oil-free surfactant solution containing hardness, foams are less stable than in the absence of oleate. At low concentration of sodium oleate with few particles, e.g. 0.0004%NaOl, foam has quite uniform bubble size distribution and decays from the top. Also, the height of residual relatively stable foam decreases as NaOl concentration increases. Based on these observations, one possible defoaming mechanism is that calcium soap molecules in the surfactant films decrease the first repulsion maximum of the disjoining isotherm curve and therefore produce less stable thin films. In Sheludko cell, the black film seems stable. This may be just because that the capillary pressure the Sheludko cell can provide, which is around 22 Pa, is too small to cause film rupture. Larger capillary pressure can occur in real foam columns, e.g. capillary pressure in the Plateau border at 10cm foam height is around 980 Pa. At high concentrations of sodium oleate, e.g. 0.005%, coalescence of air bubbles was observed during foam generation, and film breakage was observed
throughout the foam. This seems to imply that the bridging mechanism by solid particles became important.

For solutions containing nonionic surfactant N25-7, no significant effect on foam stability was seen except when substantial amounts of calcium soap were present, e.g. 0.003%NaOl. For higher concentrations of sodium oleate where solid calcium oleate did form, making the solutions turbid, the particles decreased foam stability, presumably by a bridging mechanism.

The aging study with N25-3S indicates that defoaming effect of calcium soap is not simply related to particle size. The loss of defoaming efficacy for some systems after aging implies that other factors, such as the air-water surface properties, the extent of precipitation, the position where solid particles crystallize and grow, etc. might play important roles.

Peper [1958] proposed that rapid defoaming of detergent solutions by soap or fatty acid occurs when conditions are favorable for the formation of a solid film by the action of calcium ion. The author advanced a hypothesis: the surfaces of the foam bubbles are heterogeneous and consist of a continuous film of adsorbed detergent in which there are islands of solid calcium soap film. He suggested that these islands make the film unstable because of their inflexible, brittle nature.

In our study with freshly mixed solutions, we saw small increases in dynamic and equilibrium surface tensions in the presence of calcium soap. Thin film study by Scheludko cell with fresh solutions shows the presence of particles in some studied films. And more particles were seen as more sodium oleate was added. In the studies with aged solutions, however, surface tension and film thinning process were found to be the same
as that for solution without any soap additive. Although soap particles were apparently present in the aged solutions, they had minimal influence on surface properties, and had difficulty entering the air-water surface at early stage of film drainage (or foam decay).

It’s intriguing that the aged oil-free solutions containing calcium soaps produce more stable foam than the freshly prepared solutions. And this aging effect is significant at some concentrations of oleate but is less significant at others. While a complete understanding is still lacking, a conjecture is proposed here: when making foam with freshly mixed solutions, some oleate or molecular calcium oleate will adsorb at the surfaces of foam films since precipitation is not complete. The possible implications of adsorption of soap at the film surfaces could be 1) calcium soap particles nucleate and grow at the air-water surface (proposed by Raghavachari et al. [2002]). This will greatly facilitate the subsequent bridging if it’s the mechanism of instability. 2) It will change surface properties and disjoining pressure in thin foam film. Since foam stabilized by sodium oleate is less stable than that stabilized by N25-3S (Figure 6.12), it may well be that the presence of soap at film surfaces reduces the disjoining pressure in thin foam films. When making foam with the aged solutions, adsorption of soap at film surfaces would be negligible since most oleate is in precipitate.

As indicated by Scheludko cell study, calcium soap particles have difficulty entering air-water surface during fast foam film drainage. So it seems likely that their defoaming efficacy occurs when they are trapped and compressed in Plateau borders. One requirement for particles to destabilize the Plateau borders is that they are compressed by the walls of Plateau borders and finally enter the air-water surface. So it’s necessary to have a look at the thickness of Plateau border. The radius of the sphere that
fits the cross section of the Plateau border can be estimated from the following equation [Basheva 2000]:

\[ R_D = \left( \frac{2\sqrt{3}}{3} - 1 \right) R_P \approx 0.155 R_P \]  \hspace{1cm} (Eq. 9-1)

where \( R_P = \frac{\gamma_{AW}}{P_c} \) is the radius of curvature of the air-water interface at the Plateau border (Figure 9.15). Equation 9.1 is obtained by assuming that the contact angle of foam film meniscus is equal to zero; positive values of the contact angle correspond to a narrower Plateau channel, i.e., to a smaller \( R_D \). If one introduces \( \gamma_{AW} = 30 \text{mN/m} \) and \( P_c \approx 1000 \text{Pa} \), which is about the capillary pressure at 10cm height, one finds \( R_D \approx 5 \mu \text{m} \). Since most soap particles are smaller than 0.5 micrometer (because they pass through 0.5\( \mu \text{m} \) filter), it’s not likely that one soap particle could bridge and break the Plateau border. So if there are many particles in the solution and many of them are trapped in each Plateau border, defoaming efficacy might be significant. If there are not many particles, defoaming efficacy would not be significant.

This conjecture is based on experimental results with the anionic surfactant N25-3S. It includes two mechanisms. One involves disjoining pressure in the film and surface nucleation of soap particle, the other involves particles in Plateau borders. It’s suggested that the former is more important at low NaOIl contents and the latter at high NaOIl contents. Obviously, this phenomenon needs further study for a conclusive explanation.

The increase in foam stability after aging was not observed when oils were present. As discussed in Chapter 5, the defoaming mechanism when both oil and insoluble soap are present is a synergism between smaller soap particles and larger oil...
drops. Oil is the main specie that bridges and destabilizes foam, and soap particles help destabilize pseudoemulsion film by providing local high curvature. This mechanism is not expected to change after solution ages.

9.4 Precipitation of Calcium Soap in Micellar Solution of N25-3S

In surfactant micellar solutions, precipitation of calcium soap is a more complex process than that in the absence of micelles. Since some calcium and oleate are incorporated in micelles, concentrations of molecularly dissolved calcium and oleate are less than what was added. This effect should be taken into account in the calculation to see if solubility product of calcium oleate is exceeded. In this section, a simplified approach is applied to model such systems. The purpose is to find the precipitation boundary of calcium oleate, i.e., the amount of sodium oleate a solution with given N25-3S and CaCl₂ can take before calcium oleate starts to precipitate. The idea is when one knows the amount of free calcium (i.e. calcium not bound with micelles) and the solubility product of calcium oleate, one knows the concentration of free oleate (i.e. oleate monomer not incorporated in mixed micelles) at the precipitation boundary. Furthermore, if the thermodynamic equilibrium between monomers and mixed micelles is known, one knows the composition of mixed micelles and therefore the amount of oleate in micelles. The sum of concentrations of oleate as monomer and in micelles is the precipitation boundary at that given concentration of N25-3S and hardness. On the other hand, precipitation boundary can be found experimentally, which is the boundary between the isotropic region (100%Transmittance) and the region with turbidity. The calculated precipitation boundary is then compared with the experimentally found one.
So the first step is to estimate the association of calcium with surfactant micelles. An electrostatic model of Hirasaki and Lawson [1986] is utilized here. That is, the association of calcium with micelles having sulfate anionic groups can be described by electrostatics alone. To justify the model, data obtained with Ultrafiltration (UF) membranes that separate free electrolyte solution from micelles are interpreted. The experimental method of ultrafiltration was introduced in Chapter 3.3.8. Filtrations were performed at several levels of surfactant and electrolyte concentrations.

Table 9.5 contains retentate and filtrate compositions for solutions of N25-3S without other added electrolyte. During each filtration, samples of filtrate were successively collected every 12 minutes and analyzed for surfactant. The composition of the retentate was determined by material balance. Note that the filtrate surfactant concentrations are higher than the measured CMC (0.21mM). This happens presumably because UF membranes were not fine enough to exclude all micelles. The data show that at about 4 to 10 times of CMC, there was an increase in filtrate concentration with time. One possible contribution to this result may be that the micelles become more hydrophilic as total surfactant concentration increases (because we have a mixture of components). Concentration of monomeric surfactant in retentate, as well as in filtrate, increases as micelle concentration builds up in the retentate since the initial concentration of micelles was not high. Another observation is that filtrate surfactant concentration increases as initial surfactant concentration increases, especially at low concentrations such as 4 to 50 fold of CMC. The data also imply that filtrate surfactant concentration remains stable (or decreases slightly) as total surfactant concentration further increases.
Table 9.5 Filtration data of N25-3S at different concentrations

<table>
<thead>
<tr>
<th>System</th>
<th>Retentate Concentration</th>
<th>Filtrate Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N25-3S (mmol/l)</td>
<td>N25-3S (mmol/l)</td>
</tr>
<tr>
<td>0.98mM N25-3S</td>
<td>1.05</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>1.238</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>1.405</td>
<td>0.42</td>
</tr>
<tr>
<td>1.94mM N25-3S</td>
<td>2.143</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>2.415</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>3.096</td>
<td>0.67</td>
</tr>
<tr>
<td>9.70mM N25-3S</td>
<td>11.31</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>13.23</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>17.11</td>
<td>0.97</td>
</tr>
<tr>
<td>19.33mM N25-3S</td>
<td>22.88</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>27.75</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>35.68</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Filter: 3,000 MWCO cellulose membrane, 48 psi nitrogen pressure. Samples were collected at 12min, 24min, 36min since filtration started.

Table 9.6 presents filtration data for solutions containing N25-3S or N25-7 and hardness (CaCl₂). Anionic surfactant and calcium in filtrate were analysed by titration. Their concentrations in retentate were calculated by mass balance. The table shows that considerable calcium/surfactant association occurred with the anionic surfactant N25-3S, but none occurred with the nonionic surfactant N25-7. As concentration of N25-3S increased, more calcium ions were associated with micelles. Comparing data at the same concentration of N25-3S but different levels of hardness, one can see that filtrate surfactant concentration decreases as hardness increases. This is expected since CMC of anionic surfactant decreases as electrolyte concentrations increases. Also, micelles should be larger in the presence of calcium ions, and possibly fewer micelles can pass through the membranes. The actual CMC of N25-3S versus concentrations of calcium was not measured. But based on the average of filtrate surfactant concentration over time, a value of 0.15mM was chosen and used later as approximation of CMC at hardness in the range of 300 ~ 500ppm.
Table 9.6 Filtration data of N25-3S and N25-7 at different hardness levels

<table>
<thead>
<tr>
<th>System</th>
<th>Retentate Concentration</th>
<th>Filtrate Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N25-3S (mmol/l)</td>
<td>hardness (ppm)</td>
</tr>
<tr>
<td>1mM N25-3S</td>
<td>1.05</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>1.238</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>1.405</td>
<td>0.42</td>
</tr>
<tr>
<td>1mM N25-3S + 100ppm Ca</td>
<td>1.146</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>2.083</td>
<td>0.22</td>
</tr>
<tr>
<td>1mM N25-3S + 300ppm Ca</td>
<td>1.52</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>1.86</td>
<td>0.14</td>
</tr>
<tr>
<td>1mM N25-3S + 500ppmCa</td>
<td>1.085</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>1.242</td>
<td>0.11</td>
</tr>
<tr>
<td>2mM N25-3S + 500ppmCa</td>
<td>2.96</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>3.289</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>3.911</td>
<td>0.19</td>
</tr>
<tr>
<td>0.1wt%N25-7 + 500ppmCa</td>
<td>502</td>
<td>496</td>
</tr>
<tr>
<td></td>
<td>503</td>
<td>502</td>
</tr>
<tr>
<td></td>
<td>504</td>
<td>498</td>
</tr>
</tbody>
</table>

Filter: 3,000 MWCO cellulose membrane, 48psi nitrogen pressure.

Models of the electrical double layer used in Hirasaki and Lawson [1986]'s work are as shown in Figure 9.16. The Stern model assumes the ionic charge of the hydrophilic group extends a distance up to $\delta_S$ from the hydrocarbon/water surface of the micelle into the electrolyte solution, which is referred to as the Stern layer and simplified to be a region of constant electrical potential. The rest of the charge is located at the boundary between the Stern layer and the Gouy-Chapman layer. The Donnan model assumes that the potential is uniform in the region of Donnan equilibrium, $\delta_D$, and the potential is zero outside this region. This thickness, $\delta_D$, is the sum of the thickness of the Stern layer and the Debye-Huckel thickness of the double layer, $\delta_{DH}$. Two parameters estimated for these electrostatic models are the length of the hydrophilic group and the specific areas of the surfactants on the surfaces of micelles.
The potential of the Stern layer, $\psi_0$, is determined by solving the following equation:

$$
(9.0 \times 10^3) e^2 \left[ \frac{z}{A} + N_A \delta_s \sum_i z_i C_i^0 \exp(-z_i \psi_0) \right]^2 = \frac{N_A eKT}{2\pi} \sum_i C_i^0 \left[ \exp(-z_i \psi_0) - 1 \right] \quad \text{(Eq. 9-2)}
$$

$\psi_0 = \frac{e \psi}{K T}$ is the dimensionless form of $\psi$, which is electrical potential in Volt. The left side of Eq. 9-2 is the square of the net surface-charge density of the Stern layer. The charge caused by the ionic charge of the hydrophilic group is $ez_s / A$ and the other contribution results from the counter-ions and the co-ions in the Stern layer. The right side of the equation is the contribution caused by the diffuse double layer. The concentration, $C_i^0$, is the electrolyte concentration at zero electrolyte potential; in this case, it is the electrolyte concentration in the bulk far from the interface. In the experiments, it is the filtrate concentration.

The surface excess concentration is defined as:

$$
\Gamma_i = \int_0^\infty [C_i(x) - C_i^0] dx
$$
The excess concentration can be expressed per unit volume of the solution containing the micelles if the specific area, A, of the surfactant is known:

\[ C_i^E = N_A A C_s \Gamma_i \]

This excess concentration is compared with the measured excess concentration

\[ C_i^E = C_i^T - C_i^0 \]

The fraction of the excess ions caused by calcium, \( f_{Ca^{2+}} \), is expressed as the fraction of the total excess electrolyte ions that are calcium:

\[ f_{Ca^{2+}} = \frac{z_{Ca^{2+}} C_{Ca^{2+}}^E}{\sum_{i \in s} z_i C_i^E} \]

In Donnan model, the potential, \( \psi_D \), is determined by solving the following equation:

\[ \frac{z_i}{A \delta_D} + N_A \sum_i z_i C_i^0 \exp(-z_i \psi_D) = 0 \quad \text{(Eq. 9-3)} \]

Again, \( \psi_D \) is the dimensionless potential. The first item on left side of Eq. 9-3 is the surface charge, the second term is the bulk charge. The condition of electroneutrality must be satisfied in the region of in the region of Donnan equilibrium, \( \delta_D \).

The excess concentration of the ions with the Donnan model is:

\[ C_i^E = N_A \delta_D A C_s \{ \exp(-z_i \psi_D) - 1 \} C_i^0 \quad \text{(Eq. 9-4)} \]

Eq. 9-4 represents the equilibrium between the excess concentration, \( C_i^E \), and the concentration far away from the interface, \( C_i^0 \). That is the equilibrium relationship between the associated ions and the free ions with the Donnan equilibrium model.

Parameters used in calculations are: A - Specific area of surfactant (N25-3S) on the surface of micelles, \( 50 \times 10^{-20} \text{m}^2 \), which corresponds to a value between that of a
spherical micelle and a cylindrical micelle; \( \delta_S \) - length of the hydrophilic group (thickness of Stern layer). A value of \( 15 \times 10^{-10} \text{m} \) is used for N25-3S. Other nomenclatures are given in Appendix VII.

Some experimental data and calculations are given in Table 9.7, which presents four levels of N25-3S and two levels of calcium concentration studied. In Figure 9.17 Donnan potential, \( \psi_D \), is compared with the potential from Stern model, \( \psi_0 \), for all the experiments listed in Table 9.7. It shows that, at the studied electrolyte strengths, Donnan potentials are somewhat smaller than the potentials from the Stern model, but both have plausible values.

Figure 9.17  \hspace{1cm} \text{Comparison of Donnan potential and Stern layer potential}
<table>
<thead>
<tr>
<th>Initial mixture</th>
<th>Filtrate</th>
<th>Potential dimensionless</th>
<th>Excess concentration of Ca$^{2+}$</th>
<th>% of Ca binding</th>
<th>$f_{Ca^{2+}}$</th>
</tr>
</thead>
</table>
| 0.05wt%N25-3S + 500ppm hardness | Cs =1.2mM  
Ca$_2$ =5mM  
Cl$^-$ =10mM | Cs = 0.15mM  
Ca$_2$ = 4.46mM  
Cl$^-$ =10.02mM | $\psi_0 = -2.2372$  
$\psi_o = -2.6492$ | Exp:0.54mM  
Cal: 0.5857mM (DN)  
0.6894mM (Stn) | 10.8  
Exp:1.0  
Cal: 0.976(DN)  
0.975(Stn) |
| 0.1wt%N25-3S + 500ppm hardness | Cs =2.1mM  
Ca$_2$ =5mM  
Cl$^-$ =10mM | Cs = 0.17mM  
Ca$_2$ = 4.07mM  
Cl$^-$ =10.02mM | $\psi_0 = -2.2730$  
$\psi_o = -2.6899$ | Exp:0.93mM  
Cal: 1.0468mM (DN)  
1.2324mM (Stn) | 18.6  
Exp:0.9550  
Cal: 0.9651(DN)  
0.9646(Stn) |
| 0.5wt%N25-3S + 500ppm hardness | Cs =10.6  
Ca$_2$ =5mM  
Cl$^-$ =10mM | Cs = 0.285mM  
Ca$_2$ = 1.07mM  
Cl$^-$ =10.7mM | $\psi_0 = -2.8189$  
$\psi_o = -3.2962$ | Exp:3.93mM  
Cal: 4.275mM (DN)  
5.077mM (Stn) | 78.6  
Exp:0.7629  
Cal: 0.8063(DN)  
0.8274(Stn) |
| 1wt%N25-3S + 500ppm hardness | Cs =20.96  
Ca$_2$ =5mM  
Cl$^-$ =10mM | Cs = 0.46mM  
Ca$_2$ = 0.28mM  
Cl$^-$ =10.4mM | $\psi_0 = -3.3201$  
$\psi_o = -3.8497$ | Exp:4.72mM  
Cal: 6.120mM (DN)  
7.668mM(Stn) | 94.4  
Exp:0.4605  
Cal: 0.5852(DN)  
0.6410(Stn) |
| 0.05wt%N25-3S + 1000ppm hardness | Cs =1.17  
Ca$_2$ =10mM  
Cl$^-$ =20mM | Cs = 0.115mM  
Ca$_2$ = 9.20mM  
Cl$^-$ =20.06mM | $\psi_0 = -1.9815$  
$\psi_o = -2.2830$ | Exp:0.80mM  
Cal: 0.8259mM (DN)  
0.9247mM(Stn) | 8  
Exp:0.8913  
Cal: 0.9715(DN)  
0.9682(Stn) |
| 0.1wt%N25-3S + 1000ppm hardness | Cs =2.18m  
Ca$_2$ =10mM  
Cl$^-$ =20mM | Cs = 0.14mM  
Ca$_2$ = 9.0mM  
Cl$^-$ =20.09mM | $\psi_0 = -1.9899$  
$\psi_o = -2.2979$ | Exp:1.0mM  
Cal: 1.055mM (DN)  
1.182mM(Stn) | 10  
Exp:0.9809  
Cal: 0.9683(DN)  
0.9650(Stn) |
| 0.5wt%N25-3S + 1000ppm hardness | Cs =11mM  
Ca$_2$ =10mM  
Cl$^-$ =20mM | Cs = 0.19mM  
Ca$_2$ = 5.28mM  
Cl$^-$ =20.2mM | $\psi_0 = -2.1969$  
$\psi_o = -2.5318$ | Exp:4.72mM  
Cal: 4.931mM (DN)  
5.5397mM(Stn) | 47.2  
Exp:0.8776  
Cal: 0.8968(DN)  
0.8986 (Stn) |
| 1wt%N25-3S + 1000ppm hardness | Cs =21.3m  
Ca$_2$ =10mM  
Cl$^-$ =20mM | Cs = 0.26mM  
Ca$_2$ = 2.29mM  
Cl$^-$ =20.2mM | $\psi_0 = -2.5212$  
$\psi_o = -2.8904$ | Exp:7.71mM  
Cal: 8.284mM (DN)  
9.378mM(Stn) | 77.1  
Exp:0.7229  
Cal: 0.7782(DN)  
0.7916 (Stn) |
| 5wt%N25-3S + 2500ppm hardness | Cs =0.1M  
Ca$_2$ =25mM  
Cl$^-$ =50mM | Cs = 0.50mM  
Ca$_2$ = 3.0mM  
Cl$^-$ =58mM | $\psi_0 = -2.3003$  
$\psi_o = -2.5445$ | Exp:22.0mM  
Cal: 24.636mM (DN)  
26.516mM(Stn) | 88  
Exp:0.4446  
Cal: 0.4964(DN)  
0.533(Stn) |

Note: % of Ca binding is the percentage of total calcium associated with micelles
With hardness fixed at 500ppm or 1000ppm, Donnan (and Stern) potentials increase as the surfactant concentrations increase, and so does the percentage of the calcium bound with the micelles, as shown in Figure 9.18 a & b. At same concentration of surfactant, both potentials and calcium binding decrease as hardness level increases. These are expected results as counter-ion concentration increases.

Figure 9.18 Donnan potential and calcium binding as a function of surfactant concentration

The measured and predicted values of $f_{\text{Ca}^{2+}}$ are compared in Figure 9.19. Agreement is found with the measured values less than the predicted values except for the two points that are close to 1.
Interpretation of data obtained with ultrafiltration shows consistency with Hirasaki and Lawson's work that the association of calcium with micelles of N25-3S can be described by the Donnan model or Stern model. Our interest here is looking for precipitation boundary of calcium oleate for systems where the molar concentration of oleate is much less than that of N25-3S and calcium. Owing to low solubility product of calcium oleate, monomer concentration of oleate ion is likely to be very low for most significant amounts of calcium in bulk solution. Therefore, there should be very little oleate in the micelles, and their behavior should be similar to N25-3S micelles. So we suppose that binding of calcium with micelles in the presence of small amount sodium oleate and alkalinity can be estimated by the same model as for a solution without sodium oleate. That is, if the measured concentration of free calcium ions, $C_{Ca}^{0}$, is not available, it can be estimated from the model of Hirasaki and Lawson [1986]. Also, we suppose ideal mixing of N25-3S and oleate in micelles, as has been found to be reasonable for other mixtures of anionic surfactants. Thus, with a solubility product of calcium oleate as $K_{sp} = 10^{-15}$ [Irani and Callis, 1960], the monomer concentration of oleate, $C_{Or}^{0}$, is calculated by $C_{Or}^{0} = \sqrt{K_{sp} / C_{Ca}^{0}}$. With CMC of NaOl at pH9 as 0.052mM [Theander and Pugh, 2001], the composition of oleate in the mixed micelle is calculated by $x = C_{Or}^{0} / C_{Ol}^{cmc}$. The concentration of N25-3S in micelles is the difference between total surfactant concentration, $C_{S}^{T}$, and monomer concentration, $C_{S}^{0}$, the later is based on surfactant concentration is filtrate at the same total calcium concentration. These micelles are expected to contain oleate in the amount $C_{Or}^{m} = x(C_{S}^{T} - C_{S}^{0})$. Therefore, the precipitation boundary is $C_{Or}^{m} + C_{Or}^{0}$. 
Precipitation boundary calculated this way was compared with that found experimentally. Results with surfactant concentration at or below 0.05wt% are given in Figure 9.20. As we can see, the calculated boundary matches well with the experimentally found one, and the effect of micelles must certainly be included. Figure 9.20 is based on experiments and calculations in Table 9.8. It's clear from the sixth column in Table 9.8 that percentage of oleate in mixed micelles was as low as 1%. This justifies our assumption that there should be very little oleate in the micelles, and their behavior should be similar to N25-3S micelles. Actually, calcium binding was compared between solutions containing 0.05%N25-3S and 300ppm hardness with/without 0.0003%NaO1. No difference in calcium binding was found. Experimentally, precipitation boundary was found by adding NaO1 into pH9 solution containing N25-3S and calcium. The point where transmittance starts to deviate from 100% is taken as precipitation boundary, as shown in Table 9.9. Transmittance was read within 30 minutes after the solution was mixed.

Figure 9.20 Precipitation boundary of calcium oleate in micellar solution of N25-3S

![Graph showing precipitation boundary](image-url)
Table 9.8 Calculation of precipitation boundary at 300ppm hardness (CaCl₂)

<table>
<thead>
<tr>
<th>Conc. of N25-3S (wt%)</th>
<th>Conc. of N25-3S (mM)</th>
<th>Conc. of free Ca²⁺ (mM)¹</th>
<th>Conc. of mono.Ol²⁺ mM×10⁴</th>
<th>molar% of Ol⁻ in micelle</th>
<th>Conc. of Ol⁻ in micelle(µM)</th>
<th>calculated boundary wt%×10⁵</th>
<th>experiment boundary wt%×10⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>3.00</td>
<td>5.77</td>
<td>0.0</td>
<td>0.0</td>
<td>1.76</td>
<td>-</td>
</tr>
<tr>
<td>0.01</td>
<td>0.22</td>
<td>2.87</td>
<td>5.90</td>
<td>1.13</td>
<td>0.79</td>
<td>4.22</td>
<td>9</td>
</tr>
<tr>
<td>0.02</td>
<td>0.44</td>
<td>2.79</td>
<td>5.99</td>
<td>1.15</td>
<td>3.34</td>
<td>12.0</td>
<td>15</td>
</tr>
<tr>
<td>0.03</td>
<td>0.66</td>
<td>2.73</td>
<td>6.05</td>
<td>1.16</td>
<td>5.94</td>
<td>19.9</td>
<td>22</td>
</tr>
<tr>
<td>0.04</td>
<td>0.88</td>
<td>2.59</td>
<td>6.21</td>
<td>1.19</td>
<td>8.72</td>
<td>28.5</td>
<td>30</td>
</tr>
<tr>
<td>0.05</td>
<td>1.10</td>
<td>2.47</td>
<td>6.36</td>
<td>1.22</td>
<td>12.85</td>
<td>41.1</td>
<td>42</td>
</tr>
</tbody>
</table>

Note: conc. of mono. is monomeric concentration; ¹ obtained by direct measurement of filtrate composition; 0.15mM was used as CMC of N25-3S at 300ppm hardness per Table 9.6.

Table 9.9 Transmittance measurements

<table>
<thead>
<tr>
<th>wt% of N25-3S</th>
<th>wt% of NaOl</th>
<th>Transmittance</th>
<th>wt% of N25-3S</th>
<th>wt% of NaOl</th>
<th>Transmittance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.00006</td>
<td>100%</td>
<td>0.03</td>
<td>0.00020</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>0.00009</td>
<td>99.9%</td>
<td></td>
<td>0.00023</td>
<td>99.8%</td>
</tr>
<tr>
<td></td>
<td>0.00012</td>
<td>99.7%</td>
<td></td>
<td>0.00026</td>
<td>99.5%</td>
</tr>
<tr>
<td>0.02</td>
<td>0.0001</td>
<td>100%</td>
<td>0.04</td>
<td>0.00027</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>0.00015</td>
<td>99.9%</td>
<td></td>
<td>0.00030</td>
<td>99.9%</td>
</tr>
<tr>
<td></td>
<td>0.0002</td>
<td>99.6%</td>
<td></td>
<td>0.00033</td>
<td>99.6%</td>
</tr>
</tbody>
</table>

For other situations where assumptions made for this model are reasonable such as low concentration of NaOl at hardness less than 300ppm, a frequently occurring situation in laundry applications, this model can be used to predict the amount of N25-3S needed to prevent calcium oleate from precipitating. For a constant value of NaOl at 0.0005wt% for instance, the amount of N25-3S needed decreases as hardness decreases, as shown in Figure 9.21 which was based on model calculation instead of experimental
measurement. Also, this same method could be used to get precipitate boundary (or at least turbidity boundary) for other anionic surfactants.

Figure 9.21 Plot of calcium versus N25-3S for a constant value of NaOl at precipitation boundary

![Graph showing calcium versus N25-3S for a constant value of NaOl at precipitation boundary.]

However, the experiment could not be performed with higher concentration of N25-3S, because significant solid particles precipitate from the solution before adding any sodium oleate. At concentrations of 0.1wt% or higher, a solution of N25-3S with high hardness was found to be isotropic and stable. But when a small amount sodium hydroxide was applied to adjust pH to 9, the solution became turbid. The higher the surfactant concentration, the faster the precipitation starts. At this moment, it’s not clear what caused such precipitation.

9.5 Summary

It was illustrated in this chapter that calcium soap, without dispersed oil, can decrease foam stability. For anionic surfactant N25-3S, the foams were generally less
stable than without calcium soap, even in some cases where soap particles were so small that the solutions appeared to be transparent or slightly bluish. For higher concentrations of sodium oleate where solid soap particles precipitated in bulk solution causing them to appear turbid, the particles decreased foam stability presumably by bridging mechanism. For nonionic surfactant N25-7, no significant effect on foam stability was seen until many soap particles started to precipitate in bulk solution.

For solutions containing calcium soap particles, not only is turbidity a function of aging time, but also the foam stability changes after aging, e.g. the fresh solution produced unstable foam while the aged solution produced much more stable foam. It was found that, with freshly mixed solutions, soap particles were frequently observed in Scheludko cell, and soap additives affected surface tension and disjoining pressure of foam films. But these influences were lost when the solutions were aged, i.e., when precipitation of calcium soap was complete.

A simplified model was presented to find the precipitation boundary of calcium oleate in micellar solution of anionic surfactant (N25-3S). This model assumes ideal mixing of N25-3S and oleate in micelles; micelles in small amount of sodium oleate behave similarly to N25-3S micelles; and calcium binding with micelle can be described by electrostatic approach. It's demonstrated that predictions of this model gave reasonable agreement with the measured precipitation boundary.
Chapter 10 Conclusions and Future studies

10.1 Conclusion for This Thesis Work

10.1.1 ESB Theory

A systematic study of foam stability in the presence of oils was conducted for an anionic (N25-3S) and a nonionic (N25-7) surfactant under neutral and alkaline conditions with different amounts of dissolved calcium. Some of these conditions yielded insoluble calcium soap or microemulsion (perhaps L₃ in triolein system) as an additional phase formed \textit{in situ}. Foam stability results were compared with predictions of ESB analysis. It's found that

1. Unmodified (classic) ESB theory using equilibrium tensions does not work universally for predicting foam stability in the presence of oil, though it is generally applicable for nonionic surfactant in absence of calcium soap.

2. For anionic surfactant, the modified entry coefficient, $E_g$, instead of the classic entry coefficient, $E$, should be used to predict entry behavior of oil because it accounts for the electrical contribution to disjoining pressure in the pseudoemulsion films.

Both these conclusions are consistent with the literature, only that this study made a more systematic investigation using several techniques over a wider range of conditions than previous work.

3. Calcium soap particles facilitate entry of oil drop even in cases where $E_g < 0$ for the oil. The mechanism has been explained in Chapter 5. In this case, classic ESB
theory does apply once entry of hydrophobic particles occurs, i.e., disjoining isotherm for pseudoemulsion film between oil and air is no longer relevant.

(4) For conclusion in item 3, one sometimes has to invoke transient effect, especially for triolein or TO/HO1 systems. That is, E, S and B are initially positive but are negative at equilibrium. So foam breaks only during and first few minutes after foam generation. Transient is faster for nonionic surfactant since final stages of \( \gamma_{\text{AW}} \) approaching equilibrium are slowed for anionic surfactant by electrical repulsion between adsorbed ions and ions approaching surface.

These two points are novel with this work.

10.1.2 Adjusting Foam Stability

In this study several ways have been tried to adjust foam stability. For foams made from oil-free solutions of the anionic surfactant, addition of a suitable amount electrolyte (\( \text{CaCl}_2 \)) increased foam stability, as the counter-ion promotes surfactant adsorption at air-water surfaces. But too much electrolyte decreased the thickness of electrical double layer, reducing \( \Pi_{\text{max}} \) of the disjoining isotherm and made the foam less stable.

For foams with solutions of the anionic surfactant containing emulsified oils, effect of two potential boosters, n-dodecanol and an amine oxide surfactant (C\(_{14}\)DMAO), on foam stability was investigated for two situations where foam was highly unstable for both C16/HO1 and TO/HO1. Addition of n-dodecanol produced significant stabilization of foams both when calcium soap was present and when high levels of calcium had destabilized the foam at neutral pH. ESB theory proved useful in predicting this effect.
An amine oxide surfactant was less effective as a foam booster. It's found that, at comparable doses, C_{14}DMAO is less effective in decreasing $\gamma_{AW}$ and hence $E$ than n-dodecanol for the studied systems.

10.1.3 Effect of Calcium Soap on Foam Stability in the Absence of Oils

It was demonstrated that calcium soap, without dispersed oil, can destabilize foams of both surfactants. For anionic surfactant N25-3S, the foams were generally less stable than without calcium soap, even in some cases where soap particles were so small that the solutions appeared to be transparent or slightly bluish. One possible defoaming mechanism is that calcium soap molecules in the surfactant films decrease the first repulsion maximum of the disjoining isotherm curve and therefore produce less stable thin films. For higher concentrations of sodium oleate where solid soap particles precipitated in bulk solution causing them to appear turbid, the particles decreased foam stability presumably by bridging mechanism. For nonionic surfactant N25-7, no significant effect on foam stability was seen until many soap particles started to precipitate in bulk solution, presumably causing bridging which destabilized the foam.

Foam was less stable while precipitation was occurring (hours) than at equilibrium, perhaps because calcium oleate, which initially formed at the interfaces, was extracted as oleate concentration decreased to its equilibrium value.

A model for predicting the precipitation boundary of calcium oleate in micellar solution of anionic surfactant (N25-3S), including the enhancement of calcium content in the electrical double layers of surfactant micelles, was presented. This model assumes ideal mixing of N25-3S and oleate in micelles, and that micelles with small amounts of
sodium oleate behave similarly to N25-3S micelles. This model yielded results in agreement with experiment.

10.2 Possibilities for Future Research

10.2.1 Drainage of Foam Film and Pseudoemulsion Film

In this study there were some observations with thin films that are not fully understood. It worth putting more effort into studying and understanding thin film behavior in Scheludko cell and pseudoemulsion films. For example, an interesting observation with N25-3S in Chapters 5, 6 and 7 is that drainage was asymmetric for pseudoemulsion film with hexadecane or C16/HO1 but symmetric for triolein and TO/HO1, while foam film drainage in Sheludco cell of these systems (surfactant solutions with emulsified oils) was always asymmetric. The question is whether surface viscosity or oil viscosity or both determine the thinning behavior. One could measure surface viscosity and possibly do theoretical simulation to find conditions for asymmetric drainage in pseudoemulsion film.

It would be very useful for thin film study to improve the current equipment in this lab by adding function of measuring film thickness, e.g., get quantitative information on intensity of reflected light as function of position and time.

10.2.2 Stabilization of Foams with Nonionic Surfactants

In the absence of calcium soap one possibility for stabilizing foams made with nonionic surfactants is to add ionic surfactant to decrease $E_g$. In presence of oil and calcium soap, it may be harder to stabilize foam. Effect of LA and C$_{14}$DMAO were
studied with the anionic surfactant but not with the nonionic surfactant. That might be an interesting future study. LA should be able to decrease $\gamma_{aw}, \gamma_{ow}$ and lower $E, S, B$. Even better would be an anionic surfactant. Other experimental techniques would be useful for such study, e.g., measuring surface or interfacial viscosity and disjoining pressure curve to get quantitative information on $E_g$ and $\Pi_{max}$ (or $P_{Cmax}$).

10.2.3 Others

Other possible topics for future work are

(1) Increasing the percentage of oleic acid in oil mixtures. Additional phase(s) may form in some systems. The type and the amount of additional phase(s) may change with the content of the fatty acid. It would be interesting to see how these changes influence foam.

(2) Studying surfactant solutions with magnesium salts. Magnesium is another major component of natural hard water. Information about the effect of magnesium soap on foam would be useful for cleaning, surfactant oil recovery and other applications.
REFERENCES

Arnaudov, L.; Denkov, N. D.; S urgeva, I.; Durbut, P.; Broze, G.; Mehreteab, A. 2001 
  Langmuir 17, 6999.


  Langmuir 16, 1000.

  Langmuir 17, 969.

Baviere, M., Bazin, B., Aude, R. 1983 J. Colloid Interface Sci. 92, 580.

Bendure, R.L. 1975 Tappi, 58, 83.


Bergeron, V.; Cooper, P.; Fischer, C.; Giernmanske-Kahn, J.; Langevin, D.; Pouchelon, A. 


Chou, S. I.; Bae, J. H. 1983 J. Colloid and Interface Sci. 96, 192.


Garrett, P. R. 1979 *J. Colloid Interface Sci.* **69**, 107.

Garrett, P.R. 1980 *J. Colloid Interface Sci.* **76**(2), 587.


Garrett, P. R.; Moore, P. R. 1993 *J. Colloid and Interface Sci.* **159**, 214.


Manlowe, D. J.; Radke, C. J. 1990 *SPE Reservoir Eng.* 5(4), 495.


Peper, H. 1958 *J. Colloid Sci.* 13, 199.


Raney, K.H. 1985 Ph.D. thesis, Rice University,


Raney, K.H.; Miller, C.A. 1987 *J. Colloid Interface Sci.* 119, 539.


Scheludko, A; Exerowa, D. 1957 *Kolloid Z.* 155, 39.


Theander, K., and Pugh, R.J. 2001 *J. Colloid Interface Sci.* 239, 209.


Tsuge, H.; Ushida, J.; Hibino, S. 1984 *J. Colloid Interface Sci.* 100, 175.

Velev, O. D., Constantinides, G. N., Avraam, D. G., Payatakes, A. C., and Borwankar, R. P. 1995 *J. Colloid Interface Sci.* 175, 68.


Appendix I Experiment with Preformed Calcium Soap

It was mentioned in Chapter 5.3.4c that foam study with preformed calcium soap has been performed. Calcium oleate was prepared by mixing concentrated solutions of sodium oleate and calcium chloride. The precipitate was dried and ground into powder. This powder was then mixed with pure hexadecane or triolein at a weight ratio of 9 to 1. From Figure 5.17 we can see that these particles have a wide size distribution, e.g. from 2μ to 100μm.

Defoaming effect of such solid-oil mixture was tested with 0.01wt%N25-3S. As we can see from Figure AI.1 and Figure AI.2, defoaming effectiveness of the mixture is only slightly higher than that of the pure oils or solid particles alone, much less than that when calcium soap is formed in situ due to reaction between oleate acid in oil and calcium in the solution. This result doesn’t appear to be consistent with the result of pseudoemulsion film study, where the preformed particles diminish the stability of the pseudoemulsion film (Figure 5.18).

Figure AI.1 Effect of preformed calcium oleate, hexadecane and their mixture on foam stability

0.01%N25-3S

- hexadecane (0.02wt%)
- Ca(0I)2 (0.028wt%)
- hexadecane(0.018wt%)
+Ca(0I)2(0.002wt%)
Figure A1.2 Effect of preformed calcium oleate, triolein and their mixture on foam stability

0.01% N25-3S

![Graph showing foam height vs. time for different concentrations of triolein and Ca(OI)2.]

Configurations of this solid-oil mixture under different conditions must be considered. In pseudoemulsion film study, Figure A.3 is a reasonable representative of the oil-water interface since the oil drop is large (d ≈ 1mm). In this way, solid particles sitting at the interface will help destabilize pseudoemulsion film by creating local high curvature. When this mixture is dispersed in surfactant solutions, however, this configuration is less likely to be maintained. Since emulsified oil droplets are generally less than 10μm, smaller than (or comparable to) most of the solid particles, a large part of oil drops and soap particles are expected to be separate when dispersed in the solution. This is probably why significant synergism, i.e. higher defoaming efficiency with mixed hydrophobic solid-liquid formulations than with the individual components taken separately, was not observed here. On the contrary, forming calcium soap particles in situ by the reaction between fatty acid and calcium soap seems give a ‘good’ control of the position and the size of the solid particles, and thereafter leads to a large synergistic defoaming effect.
Appendix II Micelle Modeling

Nomenclature used in Stern and Donnan model

\[ A = \text{specific area of surfactant in the micelle, m}^2/\text{molecule} \]

\[ B = 0.328 \times 10^{10} \text{ (kmol/m}^3\text{)}^{1/2} \text{ at 25}^\circ\text{C in water} \]

\[ C_i = \text{concentration of species } i, \text{ kmol/m}^3 \]

\[ C_i^0 = \text{concentration at zero potential, kmol/m}^3 \]

\[ C_i^E = \text{excess concentration, kmol/m}^3 \]

\[ C_i^T = \text{total concentration, kmol/m}^3 \]

\[ C_S = \text{surfactant concentration, kmol/m}^3 \]

\[ e = \text{charge per electron, } 1.6 \times 10^{-19} \text{ coulomb} \]

\[ I = \text{ionic strength, kmol/m}^3 \]

\[ k = \text{Boltzmann constant, } 1.38 \times 10^{-23} \text{ J/(molecule}\times\text{K}) \]

\[ N_A = \text{Avogadro’s number, } 6.0238 \times 10^{23} \text{ molecules/kmol} \]

\[ T = \text{temperature, K} \]

\[ z_i = \text{valence of species, } i; z_S = \text{valence of surfactant} \]

\[ \Gamma_i = \text{surface excess concentration, kmol/m}^2 \]

\[ \delta_S = \text{thickness of Stern layer, m} \]

\[ \epsilon = \text{dielectric constant, equal to 80 for water} \]

\[ \kappa = \text{reciprocal of the Debye-Huckel characteristic thickness layer, m}^{-1} \]

\[ \psi = \text{potential, dimensionless} \]

\[ \psi_D = \text{Donnan-model potential, dimensionless} \]

\[ \psi_0 = \text{Stern-layer potential, dimensionless} \]
## Appendix III - Summary of experimental results in Chapter 5.

<table>
<thead>
<tr>
<th>Oil</th>
<th>pH</th>
<th>Hardness (ppm)</th>
<th>$H_{10}/H_{20}$</th>
<th>Drop contacting experiments</th>
<th>Scheludko cell</th>
<th>Pseudoemulsion film</th>
<th>Equilibrium E</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0.01wt%N25-3S + 0.01wt% oils</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>7</td>
<td>----</td>
<td>18.8/18.1</td>
<td>----</td>
<td>asymmetric drainage; final film breaks</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>C16/HOI</td>
<td>7</td>
<td>----</td>
<td>19.1/16.6</td>
<td>a</td>
<td>asymmetric drainage; final film breaks</td>
<td>asymmetric drainage; film stable at P&lt;120Pa</td>
<td>10.4</td>
<td>4.4</td>
</tr>
<tr>
<td>C16/HOI</td>
<td>9</td>
<td>300</td>
<td>4.0/2.1</td>
<td>solid particles at the interface</td>
<td>fast asymmetric drainage, broken by oil bridging or stable black film</td>
<td>fast asymmetric drainage; film ruptures facilitated by soap particles</td>
<td>3.7</td>
<td>204</td>
</tr>
<tr>
<td>TO/HOI</td>
<td>7</td>
<td>----</td>
<td>18.8/17.9</td>
<td>a</td>
<td>asymmetric drainage; final film breaks</td>
<td>symmetric drainage; film stable</td>
<td>8.1</td>
<td>145</td>
</tr>
<tr>
<td>TO/HOI</td>
<td>9</td>
<td>300</td>
<td>7.5/7.4</td>
<td>solid particles at the interface</td>
<td>fast asymmetric drainage, broken by oil bridging or stable black film</td>
<td>asymmetric drainage, stable white thin film</td>
<td>-1.4</td>
<td>-133</td>
</tr>
<tr>
<td><strong>0.1wt%N25-7 + 0.05wt% oils</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>7</td>
<td>----</td>
<td>19.0/14.9</td>
<td>----</td>
<td>asymmetric drainage; film stable</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>C16/HOI</td>
<td>7</td>
<td>----</td>
<td>11.4/7.3</td>
<td>a</td>
<td>asymmetric drainage; oils break film occasionally</td>
<td>slow symmetric drainage; film stable at P&lt;120Pa</td>
<td>3.2</td>
<td>174</td>
</tr>
<tr>
<td>C16/HOI</td>
<td>9</td>
<td>300</td>
<td>5.1/3.0</td>
<td>solid particles at the interface</td>
<td>asymmetric drainage; oils break film frequently</td>
<td>asymmetric drainage; film ruptures facilitated by soap particles</td>
<td>2.6</td>
<td>139</td>
</tr>
<tr>
<td>TO/HOI</td>
<td>7</td>
<td>----</td>
<td>18.9/14.8</td>
<td>a</td>
<td>asymmetric drainage; film stable</td>
<td>symmetric drainage; film stable</td>
<td>0.11</td>
<td>-112</td>
</tr>
<tr>
<td>TO/HOI</td>
<td>9</td>
<td>300</td>
<td>7.2/6.9</td>
<td>solid particles at the interface</td>
<td>asymmetric drainage; oils break film frequently</td>
<td>symmetric drainage; water later spread over the film</td>
<td>-0.5</td>
<td>-125</td>
</tr>
</tbody>
</table>

$H_{10}$ is foam height (cm) after 10 min; $H_{10}$ is foam height (cm) after 20 min. Initial foam height is 20cm.

*a*: No phenomenon of interest observed.

*b*: Presumably due to electrical contribution to disjoining pressure.
## Appendix IV: Summary of experimental results in Chapter 6.

<table>
<thead>
<tr>
<th>Oil</th>
<th>pH</th>
<th>( H_{10}/H_{20} )</th>
<th>Drop contacting experiments</th>
<th>Scheludko cell</th>
<th>Pseudoemulsion film</th>
<th>Equilibrium E</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%N25-3S without hardness</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>7</td>
<td>18.8/18.1</td>
<td>----</td>
<td>asymmetric drainage; final film breaks</td>
<td>----</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>C16/H0I</td>
<td>7</td>
<td>19.1/16.6</td>
<td>a</td>
<td>asymmetric drainage; final film breaks</td>
<td>asymmetric drainage; film stable at ( P&lt;120)Pa</td>
<td>10.4 (^b)</td>
<td>4.4</td>
</tr>
<tr>
<td>C16/H0I</td>
<td>9</td>
<td>19.1/18.0</td>
<td>convection, microemulsion(ME) droplets at the interface</td>
<td>initial asymmetric drainage, later surfaces less mobile</td>
<td>slow asymmetric drainage; film stable</td>
<td>4.0 (^b)</td>
<td>228</td>
</tr>
<tr>
<td>TO/H0I</td>
<td>7</td>
<td>18.8/17.9</td>
<td>a</td>
<td>asymmetric drainage; final film breaks</td>
<td>symmetric drainage; film stable</td>
<td>8.1 (^b)</td>
<td>145</td>
</tr>
<tr>
<td>TO/H0I</td>
<td>9</td>
<td>18.8/18.0</td>
<td>convection, ME or ( L_3 ) droplets at the interface</td>
<td>initial asymmetric drainage, later surfaces less mobile</td>
<td>symmetric drainage initially, dimple later expelled; film stable</td>
<td>-1.3</td>
<td>-92</td>
</tr>
<tr>
<td>0.1wt%N25-7 without hardness</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>7</td>
<td>19.0/14.9</td>
<td>----</td>
<td>asymmetric drainage; film stable</td>
<td>----</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>C16/H0I</td>
<td>7</td>
<td>11.4/7.3</td>
<td>a</td>
<td>asymmetric drainage; oils break film occasionally</td>
<td>slow symmetric drainage; film stable at ( P&lt;120)Pa</td>
<td>3.2</td>
<td>174</td>
</tr>
<tr>
<td>C16/H0I</td>
<td>9</td>
<td>15.8/8.5</td>
<td>convection, microemulsion(ME) droplets at the interface</td>
<td>symmetric drainage; film stable</td>
<td>----</td>
<td>2.3</td>
<td>127</td>
</tr>
<tr>
<td>TO/H0I</td>
<td>7</td>
<td>18.9/14.8</td>
<td>a</td>
<td>asymmetric drainage; film stable</td>
<td>symmetric drainage; film stable</td>
<td>0.11</td>
<td>-112</td>
</tr>
<tr>
<td>TO/H0I</td>
<td>9</td>
<td>19.0/15.1</td>
<td>convection, ME or ( L_3 ) droplets at the interface</td>
<td>symmetric drainage; film stable</td>
<td>----</td>
<td>-2.4</td>
<td>-196</td>
</tr>
</tbody>
</table>

\( H_{10} \) is foam height (cm) after 10 min; \( H_{10} \) is foam height (cm) after 20 min. Initial foam height is 20cm.

a: no phenomenon of interest observed.
b: presumably due to electrical contribution to disjoining pressure.
Appendix V: Summary of experimental results in Chapter 7.

<table>
<thead>
<tr>
<th>Oil</th>
<th>pH</th>
<th>Hardness (ppm)</th>
<th>$H_{10}/H_{20}$</th>
<th>Drop contacting experiments</th>
<th>Scheludko cell</th>
<th>Pseudoemulsion film</th>
<th>Equilibrium E</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01wt%N25-3S plus hardness and 0.02wt% oily additives at neutral pH</td>
<td>----</td>
<td>----</td>
<td>18.5/18.0</td>
<td>----</td>
<td>slow asymmetric drainage; broke before forming black film</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>C16/H01</td>
<td>7</td>
<td>0</td>
<td>18.5/13.9</td>
<td>a</td>
<td>as above</td>
<td>asymmetric drainage; stable at P120≤Pa.</td>
<td>10&lt;sup&gt;b&lt;/sup&gt;</td>
<td>414</td>
</tr>
<tr>
<td>C16/H01</td>
<td>7</td>
<td>300</td>
<td>12.0/10.5</td>
<td>a</td>
<td>quick asymmetrical drainage. stable black film.</td>
<td>asymmetric drainage. Film broke at or after dimple expulsion</td>
<td>3.3</td>
<td>180</td>
</tr>
<tr>
<td>C16/H01</td>
<td>7</td>
<td>2000</td>
<td>2.0/1.2</td>
<td>ME drops formed at oil-water interface</td>
<td>quick asymmetrical drainage; film broke at early stage of drainage</td>
<td>asymmetric drainage. Slow drop entry process.</td>
<td>1.5</td>
<td>82</td>
</tr>
<tr>
<td>hexadecane</td>
<td>7</td>
<td>2000</td>
<td>7.0/5.1</td>
<td>a</td>
<td>slow asymmetric drainage; broke before forming black film</td>
<td>asymmetric drainage. Fast drop entry process</td>
<td>2.4</td>
<td>82</td>
</tr>
<tr>
<td>TO/H01</td>
<td>7</td>
<td>0</td>
<td>19.0/18.7</td>
<td>a</td>
<td>slow asymmetric drainage; broke before forming black film</td>
<td>slow symmetric drainage, film stable</td>
<td>8.2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>152</td>
</tr>
<tr>
<td>TO/H01</td>
<td>7</td>
<td>300</td>
<td>19.5/18.7</td>
<td>a</td>
<td>quick asymmetrical drainage. stable black film</td>
<td>slow symmetric drainage, film stable</td>
<td>-1.6</td>
<td>-116</td>
</tr>
<tr>
<td>TO/H01</td>
<td>7</td>
<td>2000</td>
<td>10.1/1.6</td>
<td>a</td>
<td>quick asymmetrical drainage. stable black film</td>
<td>quick symmetric drainage, film stable</td>
<td>-3.3</td>
<td>-207</td>
</tr>
</tbody>
</table>

| 0.05wt%N25-3S plus hardness and 0.05wt% oily additives at neutral pH | | | | | | | 0.4 | 21 |
| C16/H01             | 7  | 2000           | 10.0/8.0        | Microemulsion (ME) forms    | ----            | ----                 | 0.6<sup>b</sup> | 0.3 |

$H_{10}$ is foam height (cm) after 10 min; $H_{10}$ is foam height (cm) after 20 min. Initial foam height is 20cm.

a: no phenomenon of interest observed.
b: presumably due to electrical contribution to disjoining pressure.
Appendix VI: Summary of experimental results in Chapter 8 - 0.01 wt%N25-3S with n-dodecanol (LA) as foam booster.

<table>
<thead>
<tr>
<th>Oil</th>
<th>pH</th>
<th>Hardness (ppm)</th>
<th>wt% of LA</th>
<th>H10/H20</th>
<th>Drop contacting experiments</th>
<th>Scheludko cell</th>
<th>Pseudoemulsion film</th>
<th>Equilibrium E</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16/HO1</td>
<td>9</td>
<td>300</td>
<td>0</td>
<td>4.0/2.1</td>
<td>insoluble soap at o/w interface</td>
<td>asymmetric drainage; stable black film or broke by oil bridging</td>
<td>asymmetric drainage; film breaks</td>
<td>3.7</td>
<td>204</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>9</td>
<td>300</td>
<td>0.001</td>
<td>12.5/9.1</td>
<td>as above</td>
<td>as above</td>
<td>as above</td>
<td>3.3</td>
<td>186</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>9</td>
<td>300</td>
<td>0.001</td>
<td>16.0/11.1</td>
<td>as above</td>
<td>as above</td>
<td>as above</td>
<td>1.1</td>
<td>59</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>9</td>
<td>300</td>
<td>0.005</td>
<td>19.6/14.1</td>
<td>as above</td>
<td>as above</td>
<td>----</td>
<td>-4.9</td>
<td>-236</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>7</td>
<td>2000</td>
<td>0</td>
<td>3.4/2.0</td>
<td>ME drop at o/w interface</td>
<td>asymmetric drainage; stable black film</td>
<td>asymmetric drainage, film breaks</td>
<td>1.5</td>
<td>82</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.0001</td>
<td>3.6/2.01</td>
<td>as above</td>
<td>as above</td>
<td>as above</td>
<td>1.5</td>
<td>82</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.001</td>
<td>17.9/16.0</td>
<td>as above</td>
<td>as above</td>
<td>as above</td>
<td>-0.2</td>
<td>-11</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.005</td>
<td>19.3/17.6</td>
<td>as above</td>
<td>as above</td>
<td>----</td>
<td>-4.4</td>
<td>-214</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>9</td>
<td>300</td>
<td>0</td>
<td>4.4/4.2</td>
<td>insoluble soap at o/w interface</td>
<td>asymmetric drainage; stable black film</td>
<td>asymmetric drainage, film stable</td>
<td>-1.4</td>
<td>-133</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>9</td>
<td>300</td>
<td>0.0001</td>
<td>----</td>
<td>as above</td>
<td>as above</td>
<td>as above</td>
<td>-1.9</td>
<td>-122</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>9</td>
<td>300</td>
<td>0.001</td>
<td>----</td>
<td>as above</td>
<td>as above</td>
<td>as above</td>
<td>-5.2</td>
<td>-310</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>9</td>
<td>300</td>
<td>0.005</td>
<td>18.5/16.6</td>
<td>as above</td>
<td>as above</td>
<td>symmetric drainage with several dimples, film stable</td>
<td>-8.6</td>
<td>-475</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>7</td>
<td>2000</td>
<td>0</td>
<td>4.2/4.0</td>
<td>a</td>
<td>asymmetric drainage; stable black film</td>
<td>symmetric drainage, film stable</td>
<td>-3.1</td>
<td>-207</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.0001</td>
<td>5.1/4.9</td>
<td>a</td>
<td>as above</td>
<td>----</td>
<td>-4.6</td>
<td>-278</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.001</td>
<td>17.4/16.0</td>
<td>a</td>
<td>as above</td>
<td>----</td>
<td>-6.6</td>
<td>-381</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.005</td>
<td>19.2/16.5</td>
<td>a</td>
<td>as above</td>
<td>----</td>
<td>-4.4</td>
<td>-4.1</td>
</tr>
</tbody>
</table>

H10 is foam height (cm) after 10 min; H10 is foam height (cm) after 20 min. Initial foam height is 20 cm. a: no phenomenon of interest observed.
Appendix VII: Summary of experimental results in Chapter 8 - 0.01\text{wt\%N25-3S with } C_{14}\text{DMAO as foam booster.}

<table>
<thead>
<tr>
<th>Oil</th>
<th>pH</th>
<th>Hardness (ppm)</th>
<th>wt% of $C_{14}\text{DMAO}$</th>
<th>$H_{10}/H_{20}$</th>
<th>Drop contacting experiments</th>
<th>Scheludko cell</th>
<th>Pseudoemulsion film</th>
<th>Equilibrium E</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16/HO1</td>
<td>9</td>
<td>300</td>
<td>0</td>
<td>4.0/2.1</td>
<td>insoluble soap at o/w interface</td>
<td>asymmetric drainage stable black film or broke by oil bridging</td>
<td>asymmetric drainage, film breaks</td>
<td>3.7</td>
<td>204</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>9</td>
<td>300</td>
<td>0.0001</td>
<td>1.8/1.7</td>
<td>as above</td>
<td>as above</td>
<td>---</td>
<td>4.0</td>
<td>228</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>9</td>
<td>300</td>
<td>0.001</td>
<td>2.2/2.1</td>
<td>as above</td>
<td>as above</td>
<td>---</td>
<td>3.8</td>
<td>216</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>9</td>
<td>300</td>
<td>0.005</td>
<td>2.9/2.8</td>
<td>as above</td>
<td>as above</td>
<td>---</td>
<td>0.6</td>
<td>21.4</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>7</td>
<td>2000</td>
<td>0</td>
<td>3.1/2.0</td>
<td>ME drops</td>
<td>asymmetric drainage stable black film</td>
<td>asymmetric drainage, film breaks</td>
<td>1.5</td>
<td>82</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.0001</td>
<td>2.8/2.0</td>
<td>as above</td>
<td>as above</td>
<td>---</td>
<td>1.5</td>
<td>82</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.001</td>
<td>2.8/2.0</td>
<td>as above</td>
<td>as above</td>
<td>---</td>
<td>-0.2</td>
<td>-11</td>
</tr>
<tr>
<td>C16/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.005</td>
<td>4.1/3.1</td>
<td>as above</td>
<td>as above</td>
<td>---</td>
<td>-4.4</td>
<td>-214</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>9</td>
<td>300</td>
<td>0</td>
<td>4.1/3.9</td>
<td>insoluble soap at o/w interface</td>
<td>asymmetric drainage stable black film</td>
<td>asymmetric drainage, film stable</td>
<td>-1.4</td>
<td>-133</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>9</td>
<td>300</td>
<td>0.0001</td>
<td>----</td>
<td>as above</td>
<td>as above</td>
<td>symmetric drainage with stratification, film stable</td>
<td>-1.5</td>
<td>-98</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>9</td>
<td>300</td>
<td>0.001</td>
<td>4.3/4.1</td>
<td>as above</td>
<td>as above</td>
<td>symmetric drainage with fingering pattern, film stable</td>
<td>-0.9</td>
<td>-62</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>9</td>
<td>300</td>
<td>0.005</td>
<td>14.0/9.6</td>
<td>as above</td>
<td>as above</td>
<td>strict symmetric drainage, film stable</td>
<td>-4.5</td>
<td>-284</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>7</td>
<td>2000</td>
<td>0</td>
<td>3.0/2.8</td>
<td>no phenomenon of interest observed</td>
<td>asymmetric drainage stable black film</td>
<td>symmetric drainage, film stable</td>
<td>-3.1</td>
<td>-207</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.0001</td>
<td>3.4/3.0</td>
<td>as above</td>
<td>as above</td>
<td>as above</td>
<td>-4.6</td>
<td>-278</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.001</td>
<td>6.9/5.3</td>
<td>as above</td>
<td>as above</td>
<td>as above</td>
<td>-6.6</td>
<td>-381</td>
</tr>
<tr>
<td>TO/HO1</td>
<td>7</td>
<td>2000</td>
<td>0.005</td>
<td>9.0/7.0</td>
<td>as above</td>
<td>as above</td>
<td>as above</td>
<td>-4.4</td>
<td>-4.1</td>
</tr>
</tbody>
</table>

$H_{10}$ is foam height (cm) after 10 min; $H_{10}$ is foam height (cm) after 20 min. Initial foam height is 20cm.