Interfacial and solution properties of binary mixtures containing partially fluorinated and hydrocarbon surfactants

By

Christopher Hill

A dissertation submitted to the University of Bristol in accordance with the requirements for award of the degree DOCTOR OF PHILOSOPHY in the

Faculty of Science

MAY 2019

Word count: Fifty nine thousand three hundred and fifty
Abstract

Use of fluorocarbon (FC) surfactants in industrial formulations is known to lead to environmental consequences, and as such these are often formulated as mixtures containing partially fluorinated and hydrocarbon (HC) surfactants. In this thesis, the solution, surface and bulk properties of three mixed surfactant systems each containing a partially fluorinated surfactant (anionic, non-ionic or zwitterionic) and a common anionic hydrocarbon (HC) surfactant (sodium dodecylsulfate) are investigated.

The surface and bulk properties of the individual FC surfactants were first of all characterised prior to studies of FC: HC surfactant mixtures. All FC surfactants were found to generate very low surface tensions ($\gamma_{\text{CMC}} < 20.0 \text{ mN m}^{-1}$) at low critical micelle concentrations ($< 2.00 \text{ mM}$).

Solution properties of the FC: HC surfactant mixtures were examined in terms of both critical aggregation concentrations (CACs) and dynamic surface tension decays ($\gamma(t)$). The $\gamma(t)$ decay data were dominated by the presence of FC surfactants in all mixtures, so much so that mixtures containing high bulk HC surfactant compositions produced equilibrium surface tensions ($\gamma_{\text{eq}}$) values of $\sim 18.7 \text{ mN m}^{-1}$. Contrast variation neutron reflectivity (NR) experiments allowed the composition of the air/water interface to be determined, showing domination of the more surface active FC surfactants even at low concentrations, which was further enhanced through dilution of the bulk solution.

Small-angle neutron scattering (SANS) experiments showed formation of mixed FC: HC surfactant micelles in all investigated systems, with sizes tending towards those of the individual FC surfactant micelles at high FC bulk compositions and vice versa. The mixed micelle compositions were similar to bulk compositions, unlike surface compositions.

These results have shown mixed systems containing partially fluorinated and HC surfactants achieve the desired solution properties of FC surfactants (low $\gamma_{\text{eq}}$ and CMC) even at both low FC compositions and concentrations, therefore providing important insight into the development of new low FC containing formulations.
Declaration

I declare that the work in this dissertation was carried out in accordance with the requirements of the University’s Regulations and Code of Practice for Research Degree Programmes and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate’s own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

Signed: ............................................................. Date: ..................................................
Acknowledgments

First and foremost I would like to thank my project supervisor Prof. Julian Eastoe for his invaluable advice, guidance, ability to provide great opportunities and music/gig recommendations throughout the course of this project. Our countless discussions over the past few years have helped shape the way I approach and solve problems in a systematic way and I have learned a lot from you. Thank you.

To my industrial supervisors Nigel Joslin and John Payne, thank you for the consistent support and for being so accommodating during my visit to Bentham. It was always great to discuss ideas with you both and the enthusiasm and interest you had for the project made it very enjoyable to be a part of. I hope our paths cross again in the future. Much gratitude goes to Angus Fire for provision of funding for the project.

Next I would like to extend my thanks to the instrument scientists at both ISIS and ILL who I had the pleasure of working alongside during many neutron scattering/reflection experiments: Sarah Rogers, Max Skoda, Mario Campana and Isabelle Grillo. You always went to great extremes to help run and analyse experiments and I am forever grateful.

The whole of this project would not have been as entertaining were it not for my man Addy. Cheers pal, one day you’ll be as good as the Illusionist.....I would also like to thank the past and present members of the Eastoe group: Gav, Joc, Jonny, Miguel, Masa and Gina for many great memories and for making the House of Eastoe such a fun group to be a part of.

Finally, special thanks go to all of my family and close friends for endless encouragement and support throughout the whole of my Ph.D., this would not have been possible without all of you.
List of publications

Below is a list of publications and publicity arising from work in this thesis:


C. Hill, A. Czajka, I. Grillo, S. E. Rogers, M. Campana, N. Joslin, J. Payne and J. Eastoe, *Surface and bulk properties of surfactant mixtures used in fire-fighting, Manuscript in preparation*

Article written about publication "*Surface and bulk properties of surfactants used in fire-fighting*" on ISIS website: https://www.isis.stfc.ac.uk/Pages/What-makes-a-good-fire-fighting-foam.aspx

# Contents

## 1 Introduction

1.1 Surfactants .................................................. 1

1.2 Types of surfactants .......................................... 2

1.3 Characteristic features of surfactants ................. 3

1.3.1 Surface tension ............................................. 4

1.3.2 Surface properties of surfactants .................. 4

1.3.3 Bulk properties of surfactants ...................... 10

1.4 Fluorocarbon and hydrocarbon surfactants ......... 11

1.5 Surfactant mixtures ....................................... 13

1.5.1 Mixing in binary surfactant systems ........... 14

1.5.2 Modeling binary surfactant systems ............. 15

1.6 Fire-Fighting Foams ....................................... 19

1.6.1 Environmental consequences of fluorocarbon surfactants in fire-fighting foams ................. 20

1.7 Project aims .................................................. 22

References ......................................................... 23

## 2 Experimental

2.1 Introduction ................................................... 29

2.2 Materials ....................................................... 29

2.3 Surfactant precipitation ................................... 31

2.4 Surfactant purification ..................................... 32

2.5 Surfactant Analysis .......................................... 33

2.5.1 NMR .............................................................. 33
2.5.2 Elemental Analysis ........................................... 41
2.5.3 Mass Spectrometry ........................................... 42
2.6 Techniques ..................................................... 46
  2.6.1 Equilibrium surface tension ................................ 46
  2.6.2 Dynamic surface tension ................................... 47
  2.6.3 Fluorescence ................................................. 48
  2.6.4 UV-Vis ......................................................... 49
  2.6.5 Small-angle neutron scattering (SANS) and neutron reflectivity (NR) ........................................... 49
References .......................................................... 50

3 Neutron scattering and reflectivity theory 51
  3.1 Neutron .......................................................... 51
  3.2 Neutron generation .............................................. 53
    3.2.1 Reactor based steady-state source ....................... 53
    3.2.2 Accelerator-based pulsed source ....................... 54
    3.2.3 Instruments ............................................... 56
  3.3 Scattering theory ............................................. 60
    3.3.1 Scattering of neutrons .................................. 61
    3.3.2 SANS Measurements ...................................... 64
    3.3.3 SANS approximations .................................... 67
  3.4 Reflectivity Theory .......................................... 71
    3.4.1 Reflection of light ...................................... 71
    3.4.2 Reflection of neutrons .................................. 72
    3.4.3 NR measurements ......................................... 73
    3.4.4 Modeling of NR data .................................... 75
References .......................................................... 76

4 Surface and bulk properties of fluorocarbon surfactants in fire-fighting foams 79
  4.1 Introduction .................................................. 80
  4.2 Materials and Methods ....................................... 82
## CONTENTS

4.2.1 Materials ................................................. 82
4.2.2 Methods ................................................ 82

4.3 Equilibrium surface tensions and critical micelle concentrations (CMCs) 84
4.3.1 Properties of NaPFO ................................... 84
4.3.2 Technical grade surfactants .......................... 86

4.4 Dynamic surface tension ................................. 87

4.5 Neutron reflectivity ..................................... 94
4.5.1 NaPFO ..................................................... 94
4.5.2 Technical Grade Surfactants ....................... 95

4.6 Small-angle neutron scattering ......................... 98

4.7 Conclusions ................................................. 103

References ...................................................... 105

5 Solution properties of fluorocarbon hydrocarbon surfactant mix-
tures 111

5.1 Introduction ............................................... 111

5.2 Materials and Methods .................................. 114
5.2.1 Materials ............................................... 114
5.2.2 Methods ............................................... 114

5.3 Critical aggregation concentrations for fluorocarbon hydrocarbon surfactant mixtures at different mole fractions ......................................................... 116
5.3.1 Validating the UV-Vis method ....................... 116
5.3.2 Fluorocarbon hydrocarbon surfactant mixtures ........ 117

5.4 Dynamic surface tension of fluorocarbon hydrocarbon surfactant mix-
tures ............................................................. 125
5.4.1 Dynamic surface tension of water: ethanol mixtures ........ 125
5.4.2 Fluorocarbon hydrocarbon surfactant mixtures ........ 126
5.4.3 Modeling of mixed system dynamic surface tension data ........ 138

5.5 Conclusions ............................................... 141

References ...................................................... 143

6 Investigations into the surface compositions of fluorocarbon hydro-

XI
carbon surfactant mixtures 149
6.1 Introduction ................................................. 149
6.2 Materials and Methods ................................. 152
  6.2.1 Materials .............................................. 152
  6.2.2 Methods ............................................... 153
6.3 Using neutron reflectivity to determine the composition and surface density parameters of mixed monolayers .............................. 154
6.4 Neutron reflectivity of sodium dodecylsulfate ..................... 156
6.5 Compositions and surface density parameters of fluorocarbon hydrocarbon surfactant mixtures ................................. 158
  6.5.1 Surface compositions above and below critical aggregation concentrations ........................................... 159
  6.5.2 Surface density parameters ............................... 164
6.6 Surface composition comparisons ................................ 169
6.7 Conclusions .................................................. 171
References ....................................................... 173

7 Composition and structure of mixed fluorocarbon hydrocarbon surfactant micelles 177
7.1 Introduction ................................................. 177
7.2 Materials and Methods ................................. 180
  7.2.1 Materials .............................................. 180
  7.2.2 Methods ............................................... 181
7.3 Aggregation behaviour of fluorocarbon hydrocarbon surfactant mixtures 182
  7.3.1 Aggregation behaviour of sodium dodecylsulfate at different concentrations ........................................... 182
  7.3.2 Composition of micelles containing fluorocarbon hydrocarbon surfactant mixtures ........................................... 185
  7.3.3 Structural changes in fluorocarbon hydrocarbon surfactant mixtures ........................................... 197
7.4 Alkane-induced swelling of mixed fluorocarbon hydrocarbon surfactant micelles ........................................... 205
  7.4.1 Swelling in individual surfactant micelles ..................... 205
# List of Tables

1 | **Introduction** | 1
--- | --- | ---
1.1 | Commonly encountered surfactant classes | 3
1.2 | Structures of hydrocarbon, perfluorinated and partially fluorinated surfactants | 12
1.3 | Comparisons between both the CMC and $\gamma_{CMC}$ data for a range of HC and FC surfactants. \(a\) data taken from Hines, \(b\) data taken from Eastoe, \(c\) data taken from Pradines, \(d\) data taken from Shinoda, \(e\) data taken from Eastoe, \(e\) data taken from Kissa | 12

2 | **Experimental** | 29
--- | --- | ---
2.1 | Surfactants used in this thesis | 30
2.2 | Data from $^1$H NMR spectra of the three industrial fluorocarbon surfactants (Figures 2.3, 2.5 and 2.7) | 40
2.3 | Data from $^{19}$F NMR spectra of the three industrial fluorocarbon surfactants (Figures 2.4, 2.6 and 2.8) | 41
2.4 | Theoretical and experimental results from elemental analysis | 42
2.5 | Mass Spectrometry Results | 42

3 | **Neutron scattering and reflectivity theory** | 51
--- | --- | ---
3.1 | Selected values for coherent scattering lengths and scattering length densities. Note: structure of AOT is $\text{(C}_8\text{H}_{17}\text{COO})\text{CH}_2\text{CHSO}_3^-\text{Na}^+$. Values taken from. | 62

4 | **Surface and bulk properties of fluorocarbon surfactants in firefighting foams** | 79
--- | --- | ---
4.1 Surfactants used in this Chapter ........................................ 82
4.2 Results from surface tension measurements of NaPFO from this study
compared to literature.21, 22 ............................................... 84
4.3 Results from surface tension measurements of the three technical grade
FC surfactants. .......................................................... 86
4.4 Effective diffusion coefficients calculated from the diffusion-only con-
trolled models at short and long time limits for Dynax DX1030, Dynax
DX2200 and Capstone 1157. The CMC data for the FC surfactants is
presented in Table 4.3. .................................................. 91
4.5 Parameters from analysis of Neutron Reflection Data of NaPFO. ρ is
the fitted scattering length density, τ the fitted monolayer thickness.
Γ_{CMC} is the surface excess concentration at the CMC and A_{CMC} is
the area per molecule at the CMC. ...................................... 95
4.6 Parameters from analyses of neutron reflectivity data of the three
technical grade FC surfactants. ρ is the fitted scattering length
density, τ the fitted monolayer thickness. Γ_{CMC} is the surface excess
concentration at the CMC and A_{CMC} is the area per molecule at the
CMC. ................................................................. 97
4.7 Parameters obtained by fitting SANS data to structural models. The
fitted background for all samples was 0.04. R_{eq} is the equatorial
radius of an ellipsoid, R_{pol} is the polar radius of the ellipsoid, aspect
ratio is defined as X = R_{eq}/R_{pol}, N_{agg} is the aggregation number,
Z is effective charge, Φ_{Fitted} is fitted volume fraction and Φ_{Calculated}
is calculated volume fraction based on sample composition. Critical
micelle concentrations have been taken as 1.37 mM and 0.02 mM for
Dynax 1030 and Dynax DX2200, respectively. Data taken on SANS2D.100
4.8 Parameters obtained by fitting SANS data to a structural model for
infinite lamellae. Critical micelle concentrations has been taken as
0.23 mM. T = 25 °C. Data taken on SANS2D. .......................... 102

5 Solution properties of fluorocarbon hydrocarbon surfactant mix-
tures .................................................................................. 111
5.1 Surfactants used in this Chapter ........................................ 114
5.2 Critical aggregation concentration results from mixed surface tension
measurements of Dynax DX1030, Dynax DX2200 and Capstone 1157
with SDS. Ideal CACs were calculated using Equation 1.22. .......... 119

XVI
5.3 Water: ethanol mixed system dynamic surface tension data, compared to literature results.\(^2\) (T = 25 °C). .................................................. 125

5.4 \(\gamma_{t=100s}\) values from DST measurements and \(\gamma_{eq}\) values from surface tension measurements for the Dynax DX1030: SDS mixed system at different mole fractions. Data for the individual surfactants are also reported. .................................................. 127

5.5 Time taken for the normalised \(\gamma(t)\) to decay to a surface tension of 0.50 and effective diffusion coefficients calculated from the diffusion-only controlled models at short and long time limits for the Dynax DX1030: SDS mixed systems.* Literature value for the SDS diffusion coefficient.\(^{55}\) 130

5.6 \(\gamma_{t=100s}\) values from DST measurements and \(\gamma_{eq}\) values from surface tension measurements for the Dynax DX2200: SDS mixed system at different mole fractions. Data for the individual surfactants are also reported. .................................................. 131

5.7 Time taken for the normalised \(\gamma(t)\) to decay to a surface tension of 0.50 and effective diffusion coefficients calculated from the diffusion-only controlled models at short and long time limits for the Dynax DX2200: SDS mixed systems.* Literature value for the SDS diffusion coefficient.\(^{55}\) 133

5.8 \(\gamma_{t=100s}\) values from DST measurements and \(\gamma_{eq}\) values from surface tension measurements for the Capstone 1157: SDS mixed system at different mole fractions. Data for the individual surfactants are also reported. .................................................. 134

5.9 Time taken for the normalised \(\gamma(t)\) to decay to a surface tension of 0.50 and effective diffusion coefficients calculated from the diffusion-only controlled models at short and long time limits for the Capstone 1157: SDS mixed systems.* Literature value for the SDS diffusion coefficient.\(^{55}\) 137

6 Investigations into the surface compositions of fluorocarbon hydrocarbon surfactant mixtures 149

6.1 Surfactants used in this Chapter .................................................. 152

6.2 Parameters associated with modeling the d-SDS neutron reflectivity data. \(\rho\) is the fitted scattering length density; \(\tau\) the fitted monolayer thickness. \(\Gamma_{CMC}\) is the surface excess concentration at the CMC and \(A_{CMC}\) is the area per molecule at the CMC. The data from literature have been taken from ref.\(^2\) .................................................. 156
6.3 Parameters from analysis of neutron reflectivity data for Dynax DX1030, Dynax DX2200, Capstone 1157 and d-SDS. $\rho$ is the fitted scattering length density, $\tau$ the fitted monolayer thickness. $\Gamma_{\text{CMC}}$ is the surface excess concentration at the CMC and $A_{\text{CMC}}$ is the area per molecule at the CMC. .................................................. 158

6.4 Surface compositions determined by modeling of the mixed FC: HC surfactant systems neutron reflectivity data. $\rho_{\text{fitted}}$ is the fitted scattering length density of the layer, $\chi_{\text{f-surf}}'$ is the calculated surface composition of the FC surfactants within the mixtures (calculated using Equation 6.4). The total concentration along with the relative (x CAC) concentrations have been included. ............................. 161

6.5 Structural parameters from model fitting of FC: h/ d-SDS mixed system neutron reflectivity data. $\tau_{\text{FC}}$ and $A_{\text{FC}}$ represent the thickness and area per molecule of the FC only, i.e. h-SDS contrast. $\tau_{\text{Total}}$ and $A_{\text{Total}}$ represent the total thickness and area per molecule, i.e. d-SDS contrast. Relative (x CAC) concentrations have been given, total concentrations are in Table 6.4. ................................. 166

6.6 $\Gamma$ values from analysis of contrast variation NR data for the FC: h/ d-SDS mixed systems. Where $\Gamma$ values represent the total surface excess and the surface excess of the individual components. $\chi_{\text{f-surf}}'$ is the calculated surface composition of the FC surfactant within the mixture. Relative (x CAC) concentrations have been given, total concentrations are shown in Table 6.4. ................................. 168

6.7 Surface compositions of the FC: HC surfactant mixtures at 2.00 x CAC from analysis of neutron reflectivity data and regular solution theory. ................................. 169

7 Composition and structure of mixed fluorocarbon hydrocarbon surfactant micelles .................................................. 177

7.1 Surfactants used in this Chapter ................................. 180

7.2 Scattering length densities and molecular volumes of the surfactants studied in this Chapter. ................................. 181
7.3 Parameters obtained by fitting SANS data to structural models. With increasing concentration, the fitted backgrounds are 0.005, 0.007 and 0.025 respectively. $R_{eq}$ is the equatorial radius of an ellipsoid, $R_{pol}$ is the polar radius of the ellipsoid, aspect ratio is defined as $X = \frac{R_{eq}}{R_{pol}}$, $N_{agg}$ is the aggregation number, $Z$ is effective charge, $\Phi_{Fitted}$ is fitted and $\Phi_{Calculated}$ is calculated volume fraction based on sample composition. Critical micelle concentration has been taken as 8.2 mM.

7.4 Calculated values of $\chi_f$ from using both SANS and iterative calculation for the 0.90: 0.10 and 0.50: 0.50 mole fraction mixtures (Dynax DX1030: SDS). Critical aggregation concentrations have been taken as 2.00 mM and 2.50 mM, respectively. The value of $\chi_f$ from SANS measurements was averaged from the SANS2D and LOQ data.

7.5 Parameters obtained by fitting the SANS data to structural models for the Dynax DX1030: SDS mixed system at a mole fraction of 0.10: 0.90 and concentration of 10 x CAC. CAC taken as 3.85 mM. $R_{eq}$ is the equatorial radius of an ellipsoid, $R_{pol}$ is the polar radius of the ellipsoid, aspect ratio is defined as $X = \frac{R_{eq}}{R_{pol}}$, $Z$ is effective charge, $\Phi_{Fitted}$ is fitted volume fraction and $\Phi_{Calculated}$ is calculated volume fraction based on sample composition.

7.6 Calculated values of $\chi_f$ from using both SANS and iterative calculation for the 0.50: 0.50 and 0.10: 0.90 mole fraction mixtures (Dynax DX2200: SDS). Critical aggregation concentrations have been taken as 0.05 mM and 0.05 mM, respectively. The value of $\chi_f$ from SANS measurements was averaged from the SANS2D and LOQ data. $\rho_{mixed}$ and $\rho_{calc}$ are the scattering length densities from fitting the data to structural models and calculated, assuming ideal mixing.

7.7 Calculated values of $\chi_f$ from using both SANS and iterative calculation for the 0.90: 0.10 and 0.50: 0.50 mole fraction mixtures (Capstone 1157: SDS). Critical aggregation concentrations have been taken as 0.15 mM and 0.53 mM, respectively. The value of $\chi_f$ from SANS measurements was averaged from the SANS2D and LOQ data. $\rho_{mixed}$ and $\rho_{calc}$ are the scattering length densities from fitting the data to structural models and calculated, assuming ideal mixing.
7.8 Parameters obtained by fitting SANS data to structural models. \( R_{eq} \) is the equatorial radius of an ellipsoid, \( R_{pol} \) is the polar radius of the ellipsoid, aspect ratio is defined as \( X = R_{eq}/R_{pol} \), \( N_{agg} \) is the aggregation number, \( Z \) is effective charge, \( \Phi_{Fitted} \) is fitted volume fraction and \( \Phi_{Calculated} \) is calculated volume fraction based on sample composition. The aggregation number was calculated using the value of \( \chi_{f-surf} \) determined from the mixed micelle composition analysis. The concentration was fixed at 50 mM.

7.9 Parameters obtained by fitting SANS data to structural models. \( R_{eq} \) is the equatorial radius of an ellipsoid, \( R_{pol} \) is the polar radius of the ellipsoid, aspect ratio is defined as \( X = R_{eq}/R_{pol} \), \( N_{agg} \) is the aggregation number, \( Z \) is effective charge, \( \Phi_{Fitted} \) is fitted volume fraction and \( \Phi_{Calculated} \) is calculated volume fraction based on sample composition. The concentration was fixed at 100 mM.

7.10 Parameters obtained by fitting SANS data to structural models. \( R_{minor} \) is the minor radius, aspect ratio is defined as \( X = R_{eq}/R_{pol} \), thickness relates to layer of the lamellae, \( R_{eq} \) is the equatorial radius of an ellipsoid, \( R_{pol} \) is the polar radius of the ellipsoid, \( Z \) is effective charge, \( \Phi_{Fitted} \) is fitted volume fraction and \( \Phi_{Calculated} \) is calculated volume fraction based on sample composition. CACs used for the mixtures were 0.15, 0.53 and 1.70 mM for the 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 mole fractions, respectively. CAC data shown in Chapter 5.

7.11 Parameters obtained by fitting SANS data to structural models. \( R_{eq} \) is the equatorial radius of an ellipsoid, \( R_{pol} \) is the polar radius of the ellipsoid, aspect ratio is defined as \( X = R_{eq}/R_{pol} \), \( R_{minor} \) is the minor radius, \( \Phi_{Fitted} \) is fitted volume fraction and \( \Phi_{Calculated} \) is calculated volume fraction based on sample composition. The concentration was fixed at 50 mM for each sample.

7.12 Parameters obtained by fitting SANS data to structural models. \( R_{eq} \) is the equatorial radius of an ellipsoid, \( R_{pol} \) is the polar radius of the ellipsoid, aspect ratio is defined as \( X = R_{eq}/R_{pol} \), \( R_{minor} \) is the minor radius, \( \Phi_{Fitted} \) is fitted volume fraction and \( \Phi_{Calculated} \) is calculated volume fraction based on sample composition. The concentration was fixed at 50 mM for each sample.

8 Conclusions and Further Work

A Supplementary data
A.1 CMC Data from Tensiometry and Fluorescence. As described in the main text, these measurements were repeated three times for both techniques to ensure stability of measurements. The uncertainties were therefore taken from the max and minimum values obtained. 238

A.2 Parameters obtained by fitting Neutron reflection to both double and single layer models. FC Tail calculated $\rho = 2.9 \times 10^{-6} \text{ Å}^{-2}$, Head Group calculated $\rho = 2.0 \times 10^{-6} \text{ Å}^{-2}$. T= 25 °C. ... 246

A.3 Parameters obtained by fitting Neutron reflection to both double and single layer models. FC Tail calculated $\rho = 3.6 \times 10^{-6} \text{ Å}^{-2}$, Head Group calculated $\rho = 5.5 \times 10^{-6} \text{ Å}^{-2}$. T= 25 °C. ... 246

A.4 Parameters obtained by fitting Neutron reflection to both double and single layer models. FC Tail calculated $\rho = 3.3 \times 10^{-6} \text{ Å}^{-2}$, Head Group calculated $\rho = 0.6 \times 10^{-6} \text{ Å}^{-2}$. T= 25 °C. ... 247

A.5 Parameters obtained by fitting SANS data to structural models. $R_{eq}$ is the equatorial radius of an ellipsoid, $R_{pol}$ is the polar radius of the ellipsoid, aspect ratio is defined as $X = R_{eq}/R_{pol}$, $N_{agg}$ is the aggregation number and $Z$ is effective charge. T= 25 °C. Data taken on D33. ... 249

A.6 Parameters obtained by fitting SANS data to a structural model for infinite lamellae. T= 25 °C. Data taken on D33. ... 249
## List of Figures

1 **Introduction**

1.1 Structure of a sodium dodecylsulfate surfactant molecule with hydrophobic tail and hydrophilic head group highlighted. ........................................... 2

1.2 Surfactant molecules spontaneously adsorbing at the air/water interface with increasing concentration until the CMC is reached. ........... 5

1.3 The surface tension ($\gamma$) is reduced as surfactant molecules adsorb to the air/water interface, simultaneously increasing the surface excess ($\Gamma$) until the CMC is reached. $A_{\text{CMC}}$ corresponds to the area per surfactant molecule at the air/water interface at the CMC. Figure taken from Ref.6 ......................................................... 6

1.4 Diffusion of surfactant molecules to the air/water interface. Once a surfactant molecule has diffused to the subsurface, it will either instantaneous adsorb at the air/water interface in accordance with the diffusion controlled model (1) or have to pass through an adsorption barrier (2). ......................................................... 7

1.5 Spherical micelles in solution. Non-polar hydrophobic tail groups shown to be oriented within the center of the micelle to minimise unfavourable interactions, and headgroups are solvated at the surface. 10

1.6 Showing how the surfactant micelle structure changes with increasing $P_C$. ................................................................. 11

1.7 Representation of the characteristic properties observed in a mixed surfactant system containing two different surfactants, illustrated by the different coloured head/ tail groups. Formation of both mixed micelles and monolayers are shown. ................................................................. 14

2 **Experimental**

2.1 Precipitation Process ................................................................. 31
LIST OF FIGURES

2.2 Foam fractionation set-up. .............................................. 32
2.3 $^1$H NMR of Dynax DX1030 ........................................ 34
2.4 $^{19}$F NMR of Dynax DX1030 ....................................... 35
2.5 $^1$H NMR of Dynax DX2200 ........................................ 36
2.6 $^{19}$F NMR of Dynax DX2200 ....................................... 37
2.7 $^1$H NMR of Capstone 1157 ......................................... 38
2.8 $^{19}$F NMR of Capstone 1157 ....................................... 39
2.9 Mass spectrometry data for Dynax DX1030 ....................... 43
2.10 Mass spectrometry data for Dynax DX2200 ....................... 44
2.11 Mass spectrometry data for Capstone 1157 ....................... 45
2.12 Krüss K100 force tensiometer .................................... 46
2.13 Krüss BP100 bubble pressure tensiometer ....................... 47

3 Neutron scattering and reflectivity theory 51

3.1 Neutron flux as a function of time at a steady-state source, such as ILL.
Left image is the intensity at the source, right image is intensity at the
detector (not to scale). Steady-state sources have high time-averaged
fluxes. .......................................................... 53

3.2 Neutron flux as a function of time at a pulsed source, such as ISIS.
Left image is the intensity at the source, right image is intensity at the
detector (not to scale). Pulsed sources are optimised for high brightness. 55

3.3 Schematic layout and photo of the LOQ instrument at ISIS. Schematic
Image taken from institute website, but altered by author. Photo
taken by author during an experiment with permission from the local
contact. .......................................................... 57

3.4 Schematic layout and photo of the FIGARO instrument at the ILL.
Schematic adapted from institute website. Photo taken by author
during an experiment with permission from the local contact. ....... 59

3.5 Vector relationship of the scattering vector $Q$. .................... 63

3.6 Schematic representation of $P(Q)$ and $S(Q)$ for both repulsive and
attractive homogeneous spheres and their contribution to $I(Q)$. Image
altered from. .................................................. 66

3.7 Typical $\ln[I(Q)]$ vs $Q^2$ Guinier plot for spherical micelles. The gradient
of the fitted red line will be $-R_g^2/3$. .............................. 68

XXIV
LIST OF FIGURES

3.8 Low Q/ Guinier region. Note that scattering particles are smaller than the probed range. ................................................. 68

3.9 High Q/ Porod region. Note that scattering particles are larger than the probed range. .................................................. 69

3.10 Typical $[I(Q)Q^4]$ vs Q Porod plot for spherical micelles. ................. 70

3.11 Showing how light is both reflected and refracted when passing through one medium to another with different optical properties. ................. 71

3.12 Geometry of the incident and scattered wave vectors ($K$ and $K'$) and the associated scattering vector ($Q$). .................................. 73

3.13 Specular reflection from a D$_2$O surface, showing both the critical edge ($Q_c$) and the sharp $Q^{-4}$ reflectivity fall off below $Q_c$. .............. 74

4 Surface and bulk properties of fluorocarbon surfactants in firefighting foams 79

4.1 (a) Surface Tension vs. ln(Concentration) for NaPFO. (b) Adsorption isotherm of NaPFO. Line fitted to pre-CMC data is a quartic function. T = 25 °C. ................................................................. 85

4.2 Surface Tension vs. ln(Concentration) for the three technical grade FC surfactants. Lines fitted to pre-CMC data are quartic functions. T = 25 °C. ................................................................. 86

4.3 Dynamic surface tension of Dynax DX1030, Dynax DX2200 and Capstone 1157 at concentrations above and below the respective CMCs. CMC data is shown in Table 4.3. Note in log scale: 3 = 10$^3$ ms. T = 25 °C. ................................................................. 89

4.4 Dynamic surface tension of the three FC surfactants plotted vs. $t^{1/2}$ and $t^{-1/2}$. The lines are least square fits to the data. The concentrations and temperatures are the same as in Figure 4.3. ................. 90

4.5 DST curves for Dynax DX1030, Dynax DX2200 and Capstone 1157 at concentrations of 1.25 x CMC, 1.25 x CMC and 0.63 x CMC, respectively. The red lines theoretical calculations using Equations 1.8 and 1.11, respectively. Note: the long time model has been used to predict the $\gamma(t)$ of Dynax DX2200 at longer times than measured. 93

4.6 Surface excess of NaPFO obtained by analysis of neutron reflectivity data. Critical micelle concentration was taken as 25 mM. T = 25 °C. 94
4.7 Surface excesses obtained by analyses of neutron reflectivity data. Lines are a guide to the eye. Critical micelle concentrations have been taken as 0.23 mM, 1.37 mM and 0.02 mM for Capstone 1157, Dynax 1030 and Dynax DX2200 respectively. $T = 25 \, ^\circ\mathrm{C}$. 96

4.8 Small-angle neutron scattering profiles for Dynax DX1030 and Dynax DX2200, with fitted functions shown as lines. Critical micelle concentrations have been taken as 1.37 mM and 0.02 mM for Dynax 1030 and Dynax DX2200, respectively. $T = 25 \, ^\circ\mathrm{C}$. 99

4.9 Small-angle neutron scattering profiles for Capstone 1157, with fitted functions shown as lines. Data have been offset by multiplied by 4, 16 and 36 respectively for clarity. Critical micelle concentration has been taken as 0.23 mM. $T = 25 \, ^\circ\mathrm{C}$ 101

5 Solution properties of fluorocarbon hydrocarbon surfactant mixtures 111

5.1 Showing the CMC determination of SDS from UV-Vis measurements. $T = 21 \, ^\circ\mathrm{C}$. 117

5.2 The two methods utilised for CAC determination. 118

5.3 Critical aggregation concentration vs. mole fraction of SDS for the Dynax DX2200: SDS mixed systems. Red circles are data from surface tension measurements ($T = 25 \, ^\circ\mathrm{C}$), blue circles are data from UV-Vis measurements ($T = 21 \, ^\circ\mathrm{C}$) and black circles are calculated ideal values using RST. 120

5.4 Critical aggregation concentration vs. mole fraction of SDS for the Capstone 1157: SDS mixed systems. Red circles show data from surface tension measurements ($T = 25 \, ^\circ\mathrm{C}$), blue circles show data from UV-Vis measurements ($T = 21 \, ^\circ\mathrm{C}$) and black circles show calculated ideal results from RST. 122

5.5 Critical aggregation concentration vs. mole fraction of SDS for the Dynax DX1030: SDS mixed systems. Red circles show data from surface tension measurements ($T = 25 \, ^\circ\mathrm{C}$), blue circles show data from UV-Vis measurements ($T = 21 \, ^\circ\mathrm{C}$) and black circles show calculated ideal results from RST. 123

5.6 Comparison of water: ethanol dynamic surface tension data from this work and literature. $T = 25 \, ^\circ\mathrm{C}$ 126
5.7 Raw and normalised dynamic surface tension plots of the Dynax DX1030: SDS mixed systems. The key shown in (a) represents the data in both graphs. All samples measured at respective CACs (see Table 5.2). Note: in log scale $3 = 10^3$ ms. $T = 25 \degree C$.

5.8 Dynamic surface tension of the Dynax DX1030: SDS mixed systems plotted vs. $t^{1/2}$ and $t^{-1/2}$ for analysis of short and long time $D_{eff}$ values. Data for the individual surfactants are also shown. The lines are least square fits to the data. The concentrations and mole fractions are the same as in Figure 5.7. $T = 25 \degree C$.

5.9 Raw and normalised dynamic surface tension plots of the Dynax DX2200: SDS mixed systems. The key shown in (a) represents the data in both graphs. All samples measured at respective CACs (see Table 5.2). $T = 25 \degree C$.

5.10 Dynamic surface tension of the Dynax DX2200: SDS mixed systems plotted vs. $t^{1/2}$ and $t^{-1/2}$ for analysis of short and long time $D_{eff}$ values. Data for the individual surfactants are also shown. The lines are least square fits to the data. The concentrations and mole fractions are the same as in Figure 5.9. $T = 25 \degree C$.

5.11 Raw and normalised dynamic surface tension plots for the Capstone 1157: SDS mixed systems. The key shown in (a) represents the data in both graphs. All samples measured at respective CACs (see Table 5.2). $T = 25 \degree C$.

5.12 Dynamic surface tension of the Capstone 1157: SDS mixed systems plotted vs. $t^{1/2}$ and $t^{-1/2}$ for analysis of short and long time $D_{eff}$ values. Data for the individual surfactants are also shown. The lines are least square fits to the data. The concentrations and mole fractions are the same as in Figure 5.11. $T = 25 \degree C$.

5.13 DST for the FC: HC mixed systems at a mole fraction of 0.50: 0.50. All concentrations are at respective CACs (Table 5.2). The red, dark blue and cyan lines are theoretical calculations using Equations 1.8 and 1.11, respectively. Note: the long time model has been used to predict the $\gamma(t)$ of the Dynax DX2200: SDS mixed system at longer times than measured.

6 Investigations into the surface compositions of fluorocarbon hydrocarbon surfactant mixtures
6.1 Showing the two contrasts used in this Chapter. In (a) h-SDS is of low contrast and so reflection from FC surfactant is highlighted, Equation 6.1 is then applied. (b) The reflection of the overall layer is seen, Equations 6.2 and 6.4 are then be applied. ........................................ 155

6.2 (a) Neutron reflectivity profiles of d-SDS at concentrations above and below the CMC (8.2 mM) in NRW. Fitted functions shown as lines. (b) Surface excess vs. concentration plot as determined by analysis of the neutron reflectivity data. Data from Lu et al. also shown. Dashed line is a guide to the eye. T = 25 °C. .......................... 157

6.3 Neutron reflectivity profiles of FC: d-SDS mixed systems at three mole fractions: 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 (FC: d-SDS) in NRW. All data are at 2.00 x CAC to ensure monolayer saturation. The neutron reflectivity profiles of each component at concentrations above the CMC are also shown. The overall concentrations in the mixture are shown in Table 6.4. Fitted functions shown as lines. T = 25 °C. .......................................................... 160

6.4 Neutron reflectivity profiles of FC: d/h-SDS mixed systems at three mole fractions: 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 (FC: d/h-SDS) in NRW. All data are at 2.00 x CAC to ensure monolayer saturation. The neutron reflectivity profiles of each component at concentrations above the CMC are also shown. The overall concentrations in the mixture are shown in Table 6.4. Fitted functions shown as lines. T = 25 °C. .......................................................... 165

7 Composition and structure of mixed fluorocarbon hydrocarbon surfactant micelles 177

7.1 (a) Small-angle neutron scattering profiles of sodium dodecylsulfate (SDS) in D$_2$O. The critical micelle concentration of SDS is 8.2 mM. The lines through the data are fitted functions. (b) Porod approximations from the above data. T = 25 °C. .............................. 183

7.2 (a) SANS profiles of Dynax DX1030: d/ h-SDS mixed systems in D$_2$O at a mole fraction of 0.90: 0.10 and concentration of 10 x CAC. The critical aggregation concentration for this mole fraction is 2.0 mM. (b) Ratio of the SANS scattering intensities from the two above isotopic combinations (Dynax DX1030: h-SDS)/ (Dynax DX1030: d-SDS). T = 25 °C. ......................................................... 187
7.3 SANS profiles of Dynax DX1030: d/ h-SDS mixed systems in D_2O at a mole fraction of 0.50: 0.50 and concentration of 10 x CAC. The CAC for this mole fraction is 2.5 mM. T = 25 °C .......................... 188

7.4 SANS profiles of Dynax DX1030: d/ h-SDS mixed system in different contrast solvents at a mole fraction of 0.10: 0.90 at 10 x CAC. The CAC for this mole fraction is 3.85 mM. T = 25 °C .......................... 190

7.5 SANS profiles of Dynax DX2200: SDS mixed systems in D_2O at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90. (a) shows the scattering profiles of the 0.90: 0.10 mole fraction samples at multiple concentrations, (b) and (c) are h/d-SDS contrast samples at 100 x CAC. The CAC used for these mole fractions were 0.01 mM, 0.05 mM and 0.05 mM, respectively. T = 25 °C. ................................. 192

7.6 SANS profiles of Capstone 1157: h/ d-SDS mixed systems in D_2O at mole fractions of 0.90: 0.10 and 0.50: 0.50 and concentration of 20 x CAC. The CAC used for these mole fractions were 0.15 mM and 0.53 mM respectively. T = 25 °C. ................................. 194

7.7 SANS profiles of Capstone 1157: d/ h-SDS mixed systems in different contrast solvents at a mole fraction of 0.10: 0.90 at 20 x CAC. The CAC for this mole fraction is 1.70 mM. T = 25 °C. ................................. 196

7.8 SANS profiles of Dynax DX1030: h-SDS mixed systems at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 and an overall concentration of 50 mM. Fitted functions shown as lines. Porod approximations of the high Q region of the same data set. T = 25 °C. 198

7.9 SANS profiles of Dynax DX2200: h-SDS mixed systems at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 and an overall concentration of 100 mM. Fitted functions shown as lines. T = 25 °C. 200

7.10 SANS profiles of Capstone 1157: h-SDS mixed systems at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 and an overall concentration of (a) 50 mM and (b) 10 x CAC. CACs used for the mole fractions were 0.15, 0.53 and 1.70 mM, respectively. CAC data shown in Chapter 5. Fitted functions shown as lines. T = 25 °C. 202

7.11 Elucidation of the different regions of interest for a D_2O-h/d-SDS-h/d-cyclohexane system. ................................. 205

7.12 SANS profiles of h-SDS with and without addition of h-cyclohexane in D_2O at a fixed concentration of 50 mM. Porod approximations of the data at high Q show the increase in the size of the micelles. Fitted functions shown as lines. T = 25 °C. 206
7.13 SANS profiles of Dynax DX1030 with and without addition of h-cyclohexane in D$_2$O at a fixed concentration of 50 mM. Porod approximations of the data at high Q show the increase in the size of the micelles. Fitted functions shown as lines. $T= 25^\circ C$ ........................................ 207

7.14 SANS profiles of Dynax DX1030: SDS mixed systems with and without addition of h-cyclohexane at mole fractions of 0.90: 0.10, 0.50: 0.50, 0.10: 0.90, at fixed concentration of 50 mM. Fitted functions shown as lines. $T= 25^\circ C$ ................................................................. 210

7.15 SANS profiles of Dynax DX2200: SDS mixed systems with and without addition of h-cyclohexane at mole fractions of 0.90: 0.10, 0.50: 0.50, 0.10: 0.90, at fixed concentration of 50 mM. Fitted functions shown as lines. $T= 25^\circ C$ ................................................................. 211

7.16 SANS profiles of Capstone 1157: SDS mixed systems with and without addition of h-cyclohexane at mole fractions of 0.90: 0.10, 0.50: 0.50, 0.10: 0.90, at fixed concentration of 50 mM. Fitted functions shown as lines. $T= 25^\circ C$ ................................................................. 212

8 Conclusions and Further Work 225

A Supplementary data 233

A.1 Method used to determine critical micelle concentration . . . . . . 237

A.2 Surface tension and fluorescence data for the three partially fluorinated surfactants. Surface tension data recorded at $T= 25^\circ C$, fluorescence recorded at $T= 21^\circ C$ ................................................................. 240

A.3 Representative dynamic surface tension runs for the three partially fluorinated surfactants. $T= 25^\circ C$ ................................................................. 242

A.4 Neutron Reflection Profiles for Three Technical FC surfactants in NRW. Critical micelle concentrations have been taken as 1.37 mM, 0.02 mM and 0.23 mM for Dynax DX1030, Dynax DX2200 and Capstone 1157, respectively. Fitted functions shown as lines. $T= 25^\circ C$. ........................................ 244

A.5 Neutron Reflection Profiles of the three partially fluorinated surfactants in D$_2$O. Critical micelle concentrations have been taken as 1.37 mM, 0.02 mM and 0.23 mM for Dynax DX1030, Dynax DX2200 and Capstone 1157, respectively. Fitted functions shown as lines. $T= 25^\circ C$.246

XXX
A.6 Small-angle neutron scattering data for the three partially fluorinated surfactants. Data recorded on D33 at the ILL. Critical micelle concentrations have been taken as 1.37 mM, 0.02 mM and 0.23 mM for Dynax DX1030, Dynax DX2200 and Capstone 1157, respectively. Fitted functions shown as lines. T= 25 °C. 

A.7 Surface Tension vs. ln(Concentration) for both the Dynax DX1030: SDS and Dynax DX2200: SDS mixed systems at varying mole fractions. T= 25 °C. 

A.8 Raw UV-Vis data for the Dynax DX1030: SDS mixed system at multiple concentrations/compositions. The CACs are determined through plots of max A (λ = 496 nm) vs. concentration. T= 21 °C. 

A.9 Raw UV-Vis data for the Dynax DX2200: SDS mixed system at multiple concentrations/compositions. The CACs are determined through plots of max A (λ = 496 nm) vs. concentration. T= 21 °C. 

A.10 Raw UV-Vis data for the Capstone 1157: SDS mixed system at multiple concentrations/compositions. The CACs are determined through plots of max A (λ = 496 nm) vs. concentration. T= 21 °C. 

A.11 Water ethanol mixed systems. T= 25 °C. 

A.12 Dynamic surface tension profiles of SDS at multiple concentrations above and below the respective CMC. CMC taken as 8.2 mM. T= 25 °C. 

A.13 DST for the Dynax DX1030: SDS mixed systems at mole fractions of 0.90:0.10, 0.75:0.25, 0.25:0.75 and 0.10:0.90. All concentrations are at respective CACs. CACs presented in Chapter 5. The red, dark blue and cyan lines are theoretical calculations using Equations 1.8 and 1.11, respectively. 

A.14 DST for the Dynax DX2200: SDS mixed systems at mole fractions of 0.90:0.10, 0.75:0.25, 0.25:0.75 and 0.10:0.90. All concentrations are at respective CACs. CACs presented in Chapter 5. The red, dark blue and cyan lines are theoretical calculations using Equations 1.8 and 1.11, respectively. Note: the long time model has been used to predict the γ(t) of the Dynax DX2200: SDS mixed system at longer times than measured.
A.15 DST for the Capstone 1157: SDS mixed systems at mole fractions of 0.90:0.10, 0.75: 0.25, 0.25: 0.75 and 0.10: 0.90. All concentrations are at respective CACs. CACs presented in Chapter 5. The red, dark blue and cyan lines are theoretical calculations using Equations 1.8 and 1.11, respectively. 264

A.16 Neutron reflectivity profiles of Dynax DX2200: d-SDS and Capstone 1157: d-SDS mixed systems at three mole fractions: 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 (FC: d-SDS) in NRW. All data are at 2.00 x CAC to ensure monolayer saturation. Data for the fitted functions can be found in Chapter 6. T= 25 °C 266

A.17 Neutron reflectivity profiles of Dynax DX1030: d/h-SDS, Dynax DX2200: d/h-SDS and Capstone 1157: d/h-SDS mixed systems at three mole fractions: 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 (FC: d/h-SDS) in NRW. All data are at 0.25 x CAC. T= 25 °C 268

A.18 SANS profiles of Dynax DX1030: d/h-SDS mixed systems in D₂O at a mole fraction of 0.90: 0.10 and concentrations of 5, 10 and 20 x CAC. Data on the right is the ratio of the scattering intensities from the two isotopic combinations (FC: h-SDS)/ (FC: d-SDS). T= 25 °C 271

A.19 SANS profiles of Dynax DX1030: d/h-SDS mixed systems in D₂O at a mole fraction of 0.50: 0.50 and concentrations of 5, 10 and 20 x CAC. Data on the right is the ratio of the scattering intensities from the two isotopic combinations (FC: h-SDS)/ (FC: d-SDS). T= 25 °C 272

A.20 SANS profiles of Dynax DX2200: d/h-SDS mixed systems in D₂O at a mole fraction of 0.50: 0.50 and concentrations of 25, 50 and 100 x CAC. Data on the right is the ratio of the scattering intensities from the two isotopic combinations (FC: h-SDS)/ (FC: d-SDS). T= 25 °C 273

A.21 SANS profiles of Dynax DX2200: d/h-SDS mixed systems in D₂O at a mole fraction of 0.10: 0.90 and concentrations of 100 x CAC. Data on the right is the ratio of the scattering intensities from the two isotopic combinations (FC: h-SDS)/ (FC: d-SDS). T= 25 °C 274

A.22 SANS profiles of Capstone 1157: d/h-SDS mixed systems in D₂O at a mole fraction of 0.90: 0.10 and concentrations of 10 and 20 x CAC. Data on the right is the ratio of the scattering intensities from the two isotopic combinations (FC: h-SDS)/ (FC: d-SDS). T= 25 °C 275
LIST OF FIGURES
A.23 SANS profiles of Capstone 1157: d/h-SDS mixed systems in D2 O at a
mole fraction of 0.50: 0.50 and concentrations of 5, 10 and 20 x CAC.
Data on the right is the ratio of the scattering intensities from the
two isotopic combinations (FC: h-SDS)/ (FC: d-SDS). T= 25 ◦ C . . . 276
A.24 SANS profiles of Dynax DX1030: h-SDS mixed systems as well as
Dynax DX1030 and h-SDS at the respective concentrations present
within the mixed system at mole fractions of 0.90: 0.10, 0.50: 0.50
and 0.10: 0.90. Fitted functions shown as lines. T = 25 ◦ C. . . . . . . 278
A.25 SANS profiles of Dynax DX2200: h-SDS mixed systems as well as
Dynax DX2200 and h-SDS at the respective concentrations present
within the mixed system at mole fractions of 0.90: 0.10, 0.50: 0.50
and 0.10: 0.90. Fitted functions shown as lines. T = 25 ◦ C. . . . . . . 279
A.26 SANS profiles of Capstone 1157: h-SDS mixed systems as well as
Capstone 1157 and h-SDS at the respective concentrations present
within the mixed system at mole fractions of 0.90: 0.10, 0.50: 0.50
and 0.10: 0.90. Fitted functions shown as lines. T = 25 ◦ C. . . . . . . 280
A.27 Guinier and Porod Approximations for the Capstone 1157: SDS mixed
systems at 50 mM . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 281
A.28 Guinier and Porod Approximations for the Capstone 1157: SDS mixed
systems at 10 x CAC . . . . . . . . . . . . . . . . . . . . . . . . . . . 282
A.29 SANS profiles of Dynax DX2200 and Capstone 1157 with and without
addition of h-cyclohexane in D2 O at a fixed concentration of 50 mM
and Porod approximations of the high Q data. Fitted functions shown
as lines. T= 25 ◦ C. . . . . . . . . . . . . . . . . . . . . . . . . . . . . 283
A.30 Porod approximations of Dynax DX1030: h-SDS: h-cyclohexane systems.284
A.32 Porod approximations of Capstone 1157: h-SDS: h-cyclohexane systems.286

XXXIII


Chapter 1

Introduction

This thesis is concerned with investigating mixed surfactant systems containing partially fluorinated and hydrocarbon (HC) surfactants in terms of solution, surface and bulk properties. It is therefore important to firstly introduce surfactants; the features that give them their complex and interesting properties, and how they are commonly applied in industry, with particular emphasis on fire-fighting foam formulations. The section on fire-fighting foam formulations has been adapted from a recently published literature review.\(^1\) In addition to this, the relevant background regarding the thermodynamic treatment of mixed surfactant systems will be discussed in terms of adsorption at the air/water interface and aggregation within the bulk.

1.1 Surfactants

Surfactants are an important class of compound being key components in many diverse industrial products and processes from the petroleum industry, to fire-fighting foams.\(^2\)–\(^4\) The term surfactant is a contraction of the phrase, SURFace ACTive AgeNT which embodies an important characteristic of these chemicals; the propensity to adsorb and therefore change the properties of interfaces. The reason why surfactant molecules have the capability to locate at an interface (for example air/water) is primarily due to their dual-natured amphiphilic chemical structure, bearing both hydrophilic and hydrophobic components. Such compounds can therefore satisfy these dual-solubility characteristics by residing at an interface, whereby the hydrophobic entities can free themselves of the polar solvent environment and hydrophilic portions can remain in close contact with water. The structure of a typical surfactant, sodium dodecylsulfate (SDS), is shown below in Figure 1.1.


SDS possesses a charged moiety forming the hydrophilic section, referred to as the head group, and a non-polar hydrocarbon chain referred to as the tail group. It is because of their dual nature, both strong polar and non-polar characteristics in a single molecule, that surfactants exhibit extraordinary properties and are used to stabilise an extensive range of colloidal systems. Examples include paints, inks, crop protection chemicals, drugs and food products. Their presence is often invaluable in modifying the rheological or wetting characteristics of formulations, by introducing hydrophobicity and oleophobicity to surfaces.

1.2 Types of surfactants

As previously mentioned, the propensity of surfactants to collect at the air/water interface can be used to influence the physicochemical properties of colloidal systems. The classification of different surfactant compounds is generally by the head group type, with the different surfactants possessing individual characteristics providing specific properties. Within aqueous systems there are four general categories of surfactant: anionic, cationic, nonionic and zwitterionic. In Table 1.1 examples of these different surfactant classes can be seen for common hydrocarbon (HC) surfactants.

In aqueous systems, both ionic surfactants dissociate to yield surface active moieties and counterions. Interestingly, certain ionics have been shown to exhibit antimicrobial properties. The hydrophilic nature of non-ionic on the other hand is gained through the interaction of strong polar groups such a polyethylene oxide. Zwitterionics contain both anionic and cationic moieties within the same molecule and are characterised by the ability to assume a net charge which is dependent
CHAPTER 1. INTRODUCTION

<table>
<thead>
<tr>
<th>Surfactant class</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic</td>
<td><img src="image" alt="Anionic Structure" /></td>
</tr>
<tr>
<td>Non-ionic</td>
<td><img src="image" alt="Non-ionic Structure" /></td>
</tr>
<tr>
<td>Zwitterionic</td>
<td><img src="image" alt="Zwitterionic Structure" /></td>
</tr>
<tr>
<td>Cationic</td>
<td><img src="image" alt="Cationic Structure" /></td>
</tr>
</tbody>
</table>

Table 1.1: Commonly encountered surfactant classes

on pH. Taking the example in Table 1.1, at high pH the carboxylic acid group is neutralised and thus the compound is anionic, and at low pH the tertiary amine group is protonated making the nitrogen assume a net positive cationic charge.

Further division of surfactant types is then determined by the nature of the hydrophobic tail, which can introduce additional favourable properties.\(^6\) Within this subdivision, there are a wide variety of different surfactant types encountered, but only the surfactant types investigated in this thesis will be discussed in detail. These are HC surfactants, perfluorinated (fully fluorinated) surfactants and partially fluorinated surfactants. Fluorocarbon (FC) surfactants often display greater surface activities compared to their HC counterparts and the properties that lead to this behaviour are discussed below in Section 1.4.\(^4, 6, 7\)

1.3 Characteristic features of surfactants

The dual-natured amphiphilic structure of surfactants has been discussed as leading to the propensity of the compounds to congregate and therefore modify the properties of interfaces. Therefore, when present in aqueous solution, there are characteristic features that all surfactant molecules display.
1.3.1 Surface tension

An interface is defined as the area where two bulk phases meet, and because the molecular environment of each phase is different, there is an associated interfacial free energy. At the air/water interface, the free energy is referred to as the surface free energy, or surface tension ($\gamma$). The $\gamma$ arises due to an imbalance of attractive intermolecular interactions at a liquid surface. For example, water molecules are subjected to unequal short range attraction forces at the air/water interface compared to the bulk and undergo a net inward pull to the bulk phase. To counteract this excess energy, the surface contracts and reduces the exposed surface area, explaining why drops and bubbles are spherical. Minimisation of the contact area with the gas phase is a spontaneous process and to create an additional surface a minimum amount of work ($W_{\text{min}}$) is required. The $\gamma$ (units: N m$^{-1}$ or J m$^{-2}$) is then defined as the minimum amount of work ($W_{\text{min}}$) required to create a new unit area ($\Delta A$) of that interface:

$$W_{\text{min}} = \gamma \Delta A \quad (1.1)$$

A surfactant is a substance that will adsorb to a surface and significantly alter $\gamma$, thereby changing the amount of work required to expand the liquid surface. The driving force for surfactant adsorption at the air/water interface is the unfavourable hydrophobic interaction experienced within the bulk phase. Water molecules within the bulk interact strongly through both hydrogen bonding and van der Waals interactions. The incorporation of a hydrophobic surfactant tail dissolved within the bulk causes significant distortions of this solvent bonding network, therefore increasing the free energy of the system, this is linked to the hydrophobic effect. Thus, less work is required to bring a surfactant molecule to the surface than a water molecule, so the migration of the hydrophobic surfactant molecule will be both spontaneous and favourable. The result is the spontaneous formation of an orientated surfactant monolayer, which reduces $\gamma$ of pure water ($\sim 72$ mN m$^{-1}$ at 298 K) due to the replacement of high energy polar water molecules by a layer of lower energy non-polar surfactant tails.

1.3.2 Surface properties of surfactants

Equilibrium surface tension

As already stated, adsorption is a defining characteristic of surfactant molecules. When dissolved in aqueous solution, surfactants adsorb at the air/water interface generating an orientated monolayer whereby the hydrophilic head groups are solvated...
in the water phase and the hydrophobic tails are orientated into the gas phase. Increasing the concentration of surfactant molecules in the solution leads to a reduction in $\gamma$, continuing until the air/water interface is fully accommodated and is near maximum coverage. Above certain concentrations, further minimisation of the free energy of the system is achieved through self-aggregation (micellisation) of surfactant molecules, forming structures in the bulk phase which keep both the surfactant head and tail groups solvated in preferred environments. This well-defined concentration is known as the critical micelle concentration (CMC). Both the CMC and range at which adsorption takes place depends on the surfactants molecular structure. The process of surfactant adsorption at the air/water interface with increasing concentration is presented pictorially in Figure 1.2.

Figure 1.2: Surfactant molecules spontaneously adsorbing at the air/water interface with increasing concentration until the CMC is reached.

A time-averaged value for the concentration of surfactant molecules at the surface can be determined through thermodynamic treatment of $\gamma$ variations with composition. Referred to as the surface excess ($\Gamma$), this term is defined as the concentration of surfactant molecules in a surface plane, relative to that at a similar plane in the bulk and provides a quantitative description of surfactant adsorption. The thermodynamic equation, first derived by Gibbs, is provided below:

$$\Gamma = -\frac{1}{mRT} \frac{d\gamma}{d\ln C} \quad (1.2)$$

where $\Gamma$ (mol m\(^{-2}\)) is the surface excess, $R$ (J K\(^{-1}\) mol\(^{-1}\)) is the gas constant, $T$ (K) is temperature, $\gamma$ (N m\(^{-1}\)) is surface tension and $C$ (mol m\(^{-3}\)) is concentration. The prefactor $m$ is dependent on the surfactant type and structure, as well as the presence of extra electrolyte in the aqueous phase. For non-ionic and zwitterionic surfactants, a value of 1 for the pre-factor has been confirmed, and in the absence of extra electrolyte, $m = 2$ has been confirmed for ionic surfactants. From the determination of surface excess at the CMC ($\Gamma_{\text{CMC}}$), the area per molecule at the CMC ($A_{\text{CMC}}$) can be estimated as follows:
CHAPTER 1. INTRODUCTION

\[ A_{\text{cmc}} = \frac{1}{\Gamma_{\text{cmc}} N_a} \]  

(1.3)

where \( \Gamma_{\text{cmc}} \) (mol m\(^{-2}\)) is the surface excess at the CMC (mol m\(^{-3}\)), \( A_{\text{cmc}} \) (Å\(^2\)) is the area per molecule at the CMC and \( N_{\text{extrna}} \) (mol\(^{-1}\)) is the Avogadro number. The \( A_{\text{CMC}} \) is defined as the average area one surfactant molecule occupies at the air/water interface. For example, sodium perfluorooctanoate has \( \Gamma_{\text{CMC}} \) and \( A_{\text{CMC}} \) values of \( 4.0 \times 10^{-6} \) mol m\(^{-2}\) and 42.0 Å\(^2\), respectively. From Figure 1.3 it is possible to see how these equations are used in practice when applied to a typical \( \gamma \) vs. ln(concentration) plot.

Figure 1.3: The surface tension (\( \gamma \)) is reduced as surfactant molecules adsorb to the air/water interface, simultaneously increasing the surface excess (\( \Gamma \)) until the CMC is reached. \( A_{\text{CMC}} \) corresponds to the area per surfactant molecule at the air/water interface at the CMC. Figure taken from Ref. 6

The Figure shows the behaviour of surfactant molecules in water, i.e. decreasing \( \gamma \) with increasing surfactant concentration until the CMC is reached. The reason \( \gamma \) is constant after the CMC is due to "saturation" of the air/water interface with surfactant molecules (see Figure 1.2). This quantity of surface tension at the CMC (\( \gamma_{\text{CMC}} \)) is a useful comparison for the performance of different surfactant types. All of these defined parameters are influenced by both the surfactant structure and identity of the hydrophobic tail. For example, fluorocarbon (FC) surfactants often display greater surface activities compared to the HC counterparts. The reason for this behaviour is discussed in Section 1.4.
Dynamic surface tension

When a fresh interface is formed, surfactant molecules must first diffuse from the bulk of the solution to the interface, before adsorbing at the air/water interface. This dynamic process means that the equilibrium surface tension ($\gamma_{eq}$) of a surfactant solution is not achieved instantaneously. In an expanding surface, $\Gamma$ will be generally less than $\Gamma_{eq}$, tending to this limiting value at only high effective surface ages. Hence, there will be a net flow of surfactant molecules from the bulk to the air/water interface and $j_{ads} > j_{des}$. In the converse case of a contracting surface, $\Gamma$ is greater than $\Gamma_{eq}$ and there is a net flow of surfactants from the air/water interface to the bulk. The time dependence of adsorption can be described simply as:

$$\frac{d\Gamma}{dt} = j_{ads} - j_{des} \quad (1.4)$$

The flow of surfactant molecules to the air/water interface causes a decay in the $\gamma$ from the solvent tension ($\gamma_0$) to $\gamma_{eq}$, where $\Gamma_{eq}$ has been reached. There are two main models for describing the transport of surfactant molecules to the air/water interface, these being diffusion controlled and mixed kinetic-diffusion. Figure 1.4 shows these two models pictorially.

Figure 1.4: Diffusion of surfactant molecules to the air/water interface. Once a surfactant molecule has diffused to the subsurface, it will either instantaneous adsorb at the air/water interface in accordance with the diffusion controlled model (1) or have to pass through an adsorption barrier (2).

Both models begin by defining a subsurface as an imaginary plane a few molecular diameters below the interface. In the diffusion controlled mechanism, surfactant molecules are assumed to diffuse from the bulk into the subsurface, before adsorbing directly at the air/water interface. The diffusion process from the bulk to subsurface is the rate determining step, and the time scale of adsorption from the subsurface to the air/water interface is very fast ($\sim$ ns). In the mixed kinetic-diffusion model,
the rate determining step is assumed to be the transport of surfactant molecules from the subsurface to the air/water interface, and an adsorption barrier hinders this mechanism. Rather than adsorbing, a surfactant molecule will therefore back diffuse into the bulk, thus lengthening the dynamic surface tension (DST) decay. Increased surface pressure, lower availability of ‘vacant’ adsorption sites, steric and orientational constraints can all lead to this adsorption barrier.\textsuperscript{13}

**Diffusion controlled**

Ward and Tordai were the first to describe both the diffusion of surfactant molecules from the bulk to the air/water interface and back diffusion.\textsuperscript{14} Surfactant molecules adsorb directly at the subsurface at the start of the adsorption process, and it is assumed that every molecule arriving at the interface is likely to arrive at an empty site. As the $\Gamma$ increases, there is an increased probability that a surfactant molecule will arrive at an already occupied site and back diffusion must then be considered.\textsuperscript{13} The Ward and Tordai Equation is given below in the usual quoted form:\textsuperscript{14}

$$\Gamma(t) = 2c_0\sqrt{\frac{Di}{\pi}} - 2\sqrt{\frac{D}{\pi}} \int_0^{\sqrt{t}} c_s d(\sqrt{t-\tau})$$  \hspace{1cm} (1.5)

where $c_0$ (mol m$^{-3}$) is the bulk surfactant concentration, $D$ (m$^2$ s$^{-1}$) the monomer diffusion coefficient, $c_s$ (mol m$^{-3}$) the concentration in the subsurface, and $\tau$ is a dummy variable of integration. Owing to the convolution integral to account for back diffusion, an analytical solution for the surface tension decay ($\gamma(t)$) cannot be obtained.\textsuperscript{15} Instead, limiting law approximations determined by Miller et al. can be used in the limits of $\gamma$ close to either $\gamma_0$ or $\gamma_{eq}$.\textsuperscript{16}

**Diffusion controlled short time approximation, $t \to 0$**

As previously mentioned, there will be no back diffusion at the start of the adsorption process. Therefore neglecting this term from Equation 1.5 leads to:

$$\Gamma(t) = 2c_0\sqrt{\frac{Di}{\pi}}$$  \hspace{1cm} (1.6)

The surfactant solution can be treated as dilute at the start of the adsorption process, i.e. when $\gamma \to \gamma_0$, and the linear Henry isotherm can be used to relate $\Gamma$ and $\gamma$:\textsuperscript{13}

$$\gamma - \gamma_0 = -mRT\Gamma$$  \hspace{1cm} (1.7)

Substituting Equation 1.7 into 1.6 gives the short time approximation as:
\[ \gamma(t)_{t \to 0} = \gamma_0 - 2mRTc \left( \frac{Dt}{\pi} \right)^{1/2} \]  

(1.8)

Where \( m \) has the same definition as in Equation 1.2. Plots of \( \gamma_t \) vs. \( t^{1/2} \) will therefore linearise at the beginning of the adsorption process with \( \gamma(t) \) approaching the solvent surface tension (\( \gamma_0 \)) as \( t \to 0 \). The gradient of the straight line is then used to determine the effective diffusion coefficient (\( D_{\text{eff}} \)) at short times:

\[ D_{\text{eff}} = \frac{\pi}{4} \left[ \frac{\text{gradient}}{mRTc} \right]^2 \]  

(1.9)

**Diffusion controlled long time approximation, \( t \to \infty \)**

As \( t \to \infty \), the subsurface concentration (\( c_s \)) approaches the bulk concentration (\( c_0 \)). This allows \( c_s \) to be factored outside the back diffusion integral in Equation 1.5, which now tends to unity as \( t \to \infty \). Hence:

\[ \Delta c_{t \to \infty} = c_0 - c_s = \Gamma \sqrt{\frac{\pi}{4Dt}} \]  

(1.10)

With both the Gibbs Equation (\( d\gamma = -mRTd\ln C \)) and taking the limit in Equation 1.10 as \( \Delta c \to 0 \), the long time approximation can be stated as:

\[ \gamma(t)_{t \to \infty} = \gamma_{\text{eq}} + \frac{mRT\Gamma^2}{2c} \left( \frac{\pi}{Dt} \right)^{1/2} \]  

(1.11)

Plots of \( \gamma_t \) vs. \( t^{-1/2} \) will therefore linearise at the end of the adsorption process with \( \gamma_t \) approaching \( \gamma_{\text{eq}} \) as \( t \to \infty \). The gradient of the straight line is then used to determine \( D_{\text{eff}} \) at long times:

\[ D_{\text{eff}} = \left( \frac{mRT^2\pi^{1/2}}{2c \cdot \text{gradient}} \right)^2 \]  

(1.12)

Both Equations 1.8 and 1.11 consider the adsorption process as a diffusion only mechanism, as derived from the Ward and Tordai Equation.\(^{14}\) In this work, the diffusion only mechanism has been considered and these Equations will be used to determine the DST adsorption mechanisms in Chapters 4 and 5.
1.3.3 Bulk properties of surfactants

Above a defined concentration (CMC) at which the air/water interface is near full saturation, surfactant molecules begin to aggregate to form micelles in the bulk phase. At concentrations above the CMC, the system consists of free surfactant molecules, an orientated monolayer, and micellised surfactant molecules in the bulk, with all the states being in equilibrium. By undergoing micellisation, surfactant molecules form structures whereby both the hydrophobic and hydrophilic moieties are solvated in the preferred environment, minimising the unfavourable, high energy interactions between the hydrophobic tails and water molecules. Therefore, in aqueous solutions, favourable interactions between the non-polar hydrophobic tails groups are maximised and the polar head groups remain surrounded by water. Figure 1.5 shows the structure of typical spherical micelles in water.

![Figure 1.5: Spherical micelles in solution. Non-polar hydrophobic tail groups shown to be oriented within the center of the micelle to minimise unfavourable interactions, and headgroups are solvated at the surface.](image)

A variety of different micelle shapes and sizes can be adopted, with a typical micelle consisting of $\sim 50 - 200$ surfactant molecules. Israelachvili et al. determined that the size and shape of surfactant micelles is strongly driven by the molecular structure, in particular: the volume of the surfactant tail group ($v$), the area of the surfactant headgroup at the interface ($a_o$) and the maximum extended surfactant tail group length length ($l_c$). Taking the ratio of volume to surface area, the term critical packing parameter ($P_C$) is defined:

$$P_C = \frac{v}{a_0 l_c} \quad (1.13)$$

The volume of the surfactant tail group varies with the length of the hydrophobic tail as well as degree of chain branching, whilst $a_o$ is mainly determined by electrostatic and head group hydration. $P_C$ is a useful quantity since it allows for
predictions of the surfactant aggregate shape and size to be made. The main types of surfactant micelle morphologies based on $P_C$ are shown in Figure 1.6.

![Figure 1.6: Showing how the surfactant micelle structure changes with increasing $P_C$.](image)

The different $P_C$ values can be determined in the following way. Considering a spherical micelle with a core radius (R) made up of N molecules, the volume of the core $V = N \frac{4\pi R^3}{3}$, the surface area of the core $A = N a_o = 4\pi R^2$, and hence $R = \frac{3V}{a_o}$ are determined from simple geometrical relations. If the micelle core is packed with surfactant tails without any empty space, then $R$ cannot exceed $l_c$. Introducing this constraint into the expression for $R$ leads to the following relationship: $0 \leq \frac{V}{a_o l_c} \leq \frac{1}{3}$, thus explaining the $P_C$ for spherical micelles. This same logic can be expressed for the other presented micellar structures and are reported in the following reference.

### 1.4 Fluorocarbon and hydrocarbon surfactants

For FC surfactants, at least one hydrogen atom has been replaced with fluorine in the hydrophobic tail group. Both the extent of fluorination and position of the fluorine atoms affects the characteristic properties of these surfactants. As mentioned above, FC surfactants can be classified as either perfluorinated or partially fluorinated. In perfluorinated surfactants, the hydrogen atoms have all been replaced by fluorine atoms, whereas partially fluorinated surfactants contain both hydrogen and fluorine atoms. Examples of these different surfactant types are shown below in Table 1.2.
Fluorine is the most electronegative of the elements and the C-F bond is therefore both very strong and chemically stable. This leads to FC surfactants having properties such as high thermal and chemical stabilities. For this reason, FC surfactants can be used in harsh environments in which HC surfactants would quickly be degraded, such as elevated temperatures, strong acidity/alkalinity, and reductive/oxidative environments. Additional properties stem from the weak intramolecular interactions between FC surfactants, which results in low dielectric constants, high vapour pressures, high compressibilities as well as high surface activities. FC surfactants display greater surface activities than their HC counterparts, producing reductions of water from 72 to \( \sim 15-25 \text{ mN m}^{-1} \) at very low concentrations. Comparisons between CMC and \( \gamma_{\text{CMC}} \) values for a range of HC and FC surfactants can be seen below in Table 1.3.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Type</th>
<th>CMC (mM)</th>
<th>( \gamma_{\text{CMC}} ) (mN m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)(CH(<em>2))(</em>{11})SO(_4)Na(^{[a]})</td>
<td>Anionic (HC)</td>
<td>7.9</td>
<td>37.0</td>
</tr>
<tr>
<td>CH(_3)(CH(<em>2))(</em>{11})(OCH(_2)CH(_2))(_5)OH(^{[b]})</td>
<td>Non-ionic (HC)</td>
<td>0.1</td>
<td>30.0</td>
</tr>
<tr>
<td>CH(_3)(CH(<em>2))(</em>{11})N(CH(_3))(_3)Br(^{[c]})</td>
<td>Cationic (HC)</td>
<td>10.0</td>
<td>37.0</td>
</tr>
<tr>
<td>CF(_3)(CF(_2))(_6)CO(_2)Na(^{[d]})</td>
<td>Anionic (FC)</td>
<td>36.0</td>
<td>24.6</td>
</tr>
<tr>
<td>CF(_3)(CF(_2))(_3)CH(_2)O(CH(_2)CH(_2)O)(_3)CH(_3)(^{[e]})</td>
<td>Non-ionic (FC)</td>
<td>2.0</td>
<td>24.0</td>
</tr>
<tr>
<td>CF(_3)(CF(_2))(_3)–8(CH(_2))(_2)S(CH(_2))(_2)N(^+)((\text{CH}_3\text{CH}_3\text{SO}_4)(^{[f]})</td>
<td>Zwitterionic (FC)</td>
<td>0.2</td>
<td>19.0</td>
</tr>
</tbody>
</table>

Table 1.3: Comparisons between both the CMC and \( \gamma_{\text{CMC}} \) data for a range of HC and FC surfactants. \(^{(a)}\) data taken from Hines, \(^{(b)}\) data taken from Eastoe, \(^{(c)}\) data taken from Pradines, \(^{(d)}\) data taken from Shinoda, \(^{(e)}\) data taken from Eastoe, \(^{(f)}\) data taken from Kissa.
The main reasons for the enhanced surface activities of FC surfactants compared to HC surfactants can be considered as follows. The cohesion of a liquid is due to the attractive forces between molecules, and although the presence of highly electronegative fluorine causes polarity in a C-F bond, a perfluorocarbon chain is overall non-polar and has a zero dipole moment. If, however, the FC chain is only partially fluorinated, polarity will be introduced into the surfactant molecule. In non-polar liquids, only the induced-dipole/induced-dipole dispersion interactions are of relevance and the strength of this interaction is determined by the polarisability of the interacting atoms. Therefore, because fluorine has a lower polarisability compared to hydrogen, weaker attractive interactions between the molecules are expected. The other reason for increased surface activities is concerned with the larger occupied volumes of perfluoroalkyl moieties. According to Krafft et al., the mean volumes of CF$_2$ and CF$_3$ groups can be estimated as 38 and 92 Å$^3$, whereas those of CH$_2$ and CH$_3$ are around 27 and 54 Å$^3$, respectively. In addition to these steric reasons, the average limiting cross-sectional area for a FC chain is 27 - 30 Å$^2$, which is larger than the range of 18 - 21 Å$^2$ achieved for a HC chain.

Comparison of the free energy associated with transferring one mole of CF$_2$ and CH$_2$ groups to the air/water interface lead to $\Delta G$ values of 5.10 and 2.60 kJ mol$^{-1}$, respectively. The more favourable free energy of transfer for CF$_2$ groups compared to CH$_2$, in conjunction with the relative larger size, shows the FC chains to be more hydrophobic than HC chains. This means that the FC surfactants will show an enhanced tendency to both self-assemble and collect at the air/water interface to alter the surface free energy. Hence, because of the unique chemistry of fluorine over hydrogen, it has been shown why FC surfactants possess both greater chemical and thermal stability as well as greater surface activities over HC analogues, making them useful in many different industrial applications.

1.5 Surfactant mixtures

Mixed surfactant systems constitute an area of research with great industrial importance, and as such are encountered in nearly all practical applications of surfactant molecules. These mixtures can arise from several different sources, for example in the natural polydispersity of commercial surfactants resulting from impurities in starting materials, or in deliberate formulations containing mixtures of different surfactant types to exploit synergistic, or sometimes antagonistic behaviour. Mixtures of this type are formulated because each surfactant provides a different behaviour and enhanced properties compared to the individual surfactants are often achieved. This field of research has seen a lot of activity in recent years and to address all of this is beyond the scope of this thesis. Therefore, only the relevant information
regarding mixed surfactant systems as well as the models used to characterise them will be discussed here, and the reader is referred to additional texts for further information.\textsuperscript{30, 32–35}

### 1.5.1 Mixing in binary surfactant systems

A wide range of surfactant types, including HC: HC mixtures and FC: HC mixtures, have been studied including all combinations of anionic, cationic, non-ionic and zwitterionic surfactants.\textsuperscript{30, 33, 36–40} Mixed surfactant systems exhibit the same general characteristic properties as previously discussed for individual surfactant systems, including adsorption at interfaces and micellisation above certain critical concentrations. However, in the case of mixed surfactant systems, either ideal or non-ideal mixing behaviour is observed, which provides an insight into how surfactants interact in solution.\textsuperscript{30} These different interaction types will be discussed further below. Therefore the behaviour of mixed systems can be altered through careful choice of the utilised surfactants, leading to either enhancement or reduction of a desirable or undesirable property. A mixed surfactant system showing the characteristic formation of mixed micelles and monolayers is shown below in Figure 1.7.

Figure 1.7: Representation of the characteristic properties observed in a mixed surfactant system containing two different surfactants, illustrated by the different coloured head/ tail groups. Formation of both mixed micelles and monolayers are shown.

In a simple aqueous solution containing one surfactant type, the distribution between the monomeric state, micelles and monolayers at the air/water interface depends on both the solution conditions and surfactant concentration.\textsuperscript{3} When considering binary surfactant mixtures, the distribution of these different states will
now also depend on the nature of the two surfactants and how they interact. For two surfactants with similarities in overall structure, the free energies associated with micellisation will be comparable and the environment experienced within the mixed micelles are likely to be similar to that of the individual components. This is because the hydrophobic effect, which drives both adsorption and micellisation, is not surfactant headgroup specific and the formation of randomly mixed surfactant micelles will therefore tend to be favoured. In this case, referred to as ideal mixing, the micelle and monomer compositions as well as the CMC of the mixture would be expected to be a simple function of the bulk concentration, compositions, and individual surfactant CMCs. For example, mixed systems containing two anionic HC surfactants of similar tail lengths have been shown to obey the thermodynamics of ideal mixing and many other reports have demonstrated this behaviour.

If, however, the structures of the two surfactants present in the mixed system have notable differences in hydrophilic headgroups, the interactions between them can be influenced. For example, electrostatic interactions between two surfactants can lead to significant non-ideal effects on mixed system properties, such as both substantially lower CMCs and $\gamma_{\text{CMC}}$ compared to the individual surfactants. When mixed surfactant systems produce lower CMCs than either of the constituent components, this is referred to as synergistic behaviour, with the opposite being referred to as antagonistic behaviour. In either case, the composition of both the mixed micelles and monolayer are likely to be more influenced by the surfactant with the higher surface activity. Therefore, instead of the distribution of components between the monomeric and micellar forms being a function of the free energies of micellisation of the single surfactants, the interaction between the two surfactants within the mixed system must also be considered. As an examples of this, when non-ionic/ cationic HC surfactants are mixed with anionic HC surfactants, there is a reduction in the repulsive interactions between the negatively charged anionic head groups within the mixed micelles and negative deviations from ideal behaviour (synergistic) are displayed. On the other hand, binary mixtures of FC and HC surfactants are often reported as having higher CMCs than either of the constituent components, therefore exhibiting positive deviations from ideality (antagonism). The reason for this is explained due to the lack of affinity between the FC and HC chains, however this will be discussed in more detail in Chapters 5, 6 and 7.

1.5.2 Modeling binary surfactant systems

Due to great practical/ industrial importance of mixed surfactant systems, much work has gone into developing theories to effectively described and model the behaviour of them. One of the first successful models to describe mixing in ideal surfactant systems was developed by Clint, through investigation into the micellisation of mixed
non-ionic surfactants. Most notably, a model for calculating the mixed $CMC_m$ from the individual surfactant CMCs was derived. For complex non-ideal mixtures, a thermodynamic model proposed by Rubingh is generally employed. The model, referred to as Regular Solution Theory (RST), contains a central assumption that the entropy of mixing is ideal and that mixed micelles can be treated as separate phases. The theory has been very successful in describing both $CMC_m$ and mixed micelle compositions in non-ideal systems. Extensions in the previous treatment for describing mixed micelles in aqueous solution through the use of RST were developed by Rosen to detail the composition of mixed monolayers at the air/water interface. The relevant equations from Rubingh and Rosen for describing the mixing behaviour in non-ideal binary surfactant systems are described below.

**Regular solution theory**

In a mixed surfactant system containing surfactants 1 and 2, the concentrations of each component can be written as:

$$C_1 = \alpha C \quad \text{and} \quad C_2 = (1 - \alpha)C$$  \hspace{1cm} (1.14)

where $C_1$, $C_2$, $\alpha$ and $(1-\alpha)$ are the concentrations and bulk compositions of surfactants 1 and 2, respectively, and $C$ is the total concentration. Regarding formation of micelles in the surfactant mixture, the Equations applied in the derivation of Rubingh’s model are:

$$\mu_1 = \mu_1^0 + RT\ln C_1$$  \hspace{1cm} (1.15)

where $\mu_1$ is the chemical potential of surfactant 1, $\mu_1^0$ is the standard chemical potential assuming the activity coefficient of this surfactant is equal to unity, $R$ is the gas constant and $T$ is temperature. At or above the CMC of surfactant 1, a similar expression is observed:

$$\mu_{1m} = \mu_{1m}^0 + RT\ln CMC_1$$  \hspace{1cm} (1.16)

where $\mu_{1m}$ is chemical potential of surfactant 1 in the pure micelles and $CMC_1$ is the CMC of surfactant 1. In the mixed micelle, the chemical potential of surfactant 1 in the mixed micelles ($\mu_{1m}^m$) is then expressed as:

$$\mu_{1m}^m = \mu_{1m}^0 + RT\ln f_1 \chi_1$$  \hspace{1cm} (1.17)

where $f_1$ and $\chi_1$ are the activity coefficient and mixed micelle composition of sur-
factant 1, respectively. At equilibrium, the chemical potential of the individual surfactants in the bulk solution must be equal to the chemical potential of the surfactant molecules in the mixed micelle, i.e. $\mu_1 = \mu_1^m$. From Equations 1.15, 1.16 and 1.17 an expression for the concentration of surfactant 1 in the bulk solution can be obtained in terms of its CMC, mixed micelle composition and activity coefficient in the micelle:

$$C_1 = \chi_1 f_1 CMC_1$$  \hfill (1.18)

The above procedure can then be repeated for surfactant 2, relating its bulk concentration ($C_2$) to its critical micelle concentration ($CMC_2$), activity coefficient ($f_2$) and composition in the mixed micelle ($1 - \chi$):

$$C_2 = (1 - \chi_1) f_2 CMC_2$$  \hfill (1.19)

Before mixed micelle formation, the concentrations of surfactants 1 and 2 in bulk solution are dependent on both the bulk compositions ($\alpha$ and $(1 - \alpha)$) and the total concentration ($C$). Considering formation of mixed micelles ($CMC_m$), it is assumed that the individual surfactant concentrations within the bulk solution are equal to their respective concentrations in the mixed micelles:

$$\alpha CMC_m = \chi f_1 CMC_1 \quad \text{and} \quad (1 - \alpha) CMC_m = (1 - \chi) f_2 CMC_2$$  \hfill (1.20)

Combining the above Equations, an expression relating the mixed micelle concentration to the compositions of each surfactant in the bulk solution, the individual CMCs and the activity coefficients are obtained:

$$\frac{1}{CMC_m} = \frac{\alpha}{f_1 CMC_1} + \frac{(1 - \alpha)}{f_2 CMC_2}$$  \hfill (1.21)

If ideal mixing is assumed between surfactants 1 and 2 so that $f_1 = f_2 = 1$, then:

$$\frac{1}{CMC_m} = \frac{\alpha}{CMC_1} + \frac{(1 - \alpha)}{CMC_2}$$  \hfill (1.22)

In ideal mixing, the model can therefore easily be solved for any number of surfactant components in the mixed system. For non-ideal systems, activity coefficients must first be determined. A general form for the activity coefficients in the micellar pseudophase can be determined by considering the thermodynamics of mixing. In mixtures of liquids, the excess free energy of mixing, $G^m$, can be expressed as:
\[ G^m = RT(\chi_1 \ln f_1 + (1 - \chi_1) \ln f_2) \]  \hspace{1cm} (1.23)

where all terms have the same definition. The excess free energy of mixing is defined in terms of an excess enthalpy of mixing, \( H^m \), and an excess entropy of mixing, \( S^m \):

\[ G^m = H^m - TS^m \]  \hspace{1cm} (1.24)

In RST, \( S^m \) is assumed to be ideal.\textsuperscript{32} This then allows the substitution of \( H^m \) in place of \( G^m \) and for binary mixed systems, the excess enthalpy of mixing is represented by:

\[ H^m = \beta \chi_1 (1 - \chi_1) RT \]  \hspace{1cm} (1.25)

where \( \beta \) is a dimensionless parameter that multiplied by RT represents a net difference in the interaction energy between the mixed and unmixed systems.\textsuperscript{30} For synergistic and antagonistic mixed systems, negative and positive \( \beta \) values are displayed, respectively. Substituting Equation 1.25 in place of \( G^m \) in Equation 1.23 allows for determination of the activity coefficients for both surfactants:

\[ f_1 = \exp(\beta(1 - \chi_1)^2) \quad \text{and} \quad f_2 = \exp(\beta(\chi_1)^2) \]  \hspace{1cm} (1.26)

\( f_1 \) and \( f_2 \) are both functions of the unknowns \( \beta \) and \( \chi_1 \), and Equation 1.21 therefore cannot be solved to provide predictions of the CMC\textsubscript{m}. With knowledge of both experimentally determined CMC\textsubscript{m} values and the individual surfactants CMCs, \( \beta \) and \( \chi_1 \) can be obtained by iterative solutions of:

\[ \frac{(\chi_1)^2 \ln \left( \frac{\alpha \text{CMC}_m}{\chi_1 \text{CMC}_1} \right)}{(1 - \chi_1)^2 \ln \left( \frac{(1 - \alpha) \text{CMC}_m}{(1 - \chi_1) \text{CMC}_2} \right)} = 1 \]  \hspace{1cm} (1.27)

\[ \beta = \frac{\ln \left( \frac{\alpha \text{CMC}_m}{(\chi_1 \text{CMC}_1)} \right)}{(1 - \chi_1)^2} \]  \hspace{1cm} (1.28)
This treatment for describing mixed micelles was extended by Rosen to describe the composition of mixed monolayers at the air/water interface, which again is determined through iterative solutions to the following Equations:\(^{30, 47}\)

\[
(\chi'_1)^2 \ln \left( \frac{\alpha C_m}{\chi'_1 C^0_1} \right) = 1
\]

\[
(1 - \chi'_1)^2 \ln \left( \frac{(1 - \alpha)C_m}{(1 - \chi'_1)C^0_2} \right) = 1
\]

\[
\beta' = \frac{\ln \left[ \frac{\alpha C_m}{(\chi'_1 C^0_1)} \right]}{(1 - \chi'_1)^2}
\]

where \(\beta'\) is the interaction parameter at the air/water interface, \(\chi'_1\) is the mole fraction of surfactant 1 in the total mixed monolayer, \(C^0_1, C^0_2\) and \(C_m\) are the molar concentrations in the solution phase of surfactant 1, surfactant 2 and the mixture, respectively.

In this work, iterative calculations were carried out using MATLAB and details of the code used for the calculations are provided in the Appendix. RST has been used extensively within the literature as a way of describing the composition of both mixed micelles and monolayers, often providing comparable results with experimentally determined values. Further discussion regarding the utilisation of RST along with experimental techniques such as small-angle neutron scattering and neutron reflection will be discussed in the relevant results Chapters.

### 1.6 Fire-Fighting Foams

Fire-fighting foams were developed primarily to deal with the hazards posed by liquid fuel and oil fires. The first mention of using foams to fight fires was by British scientist J. Johnson, who patented the idea in 1877, stating that the fire will be starved of any oxygen due to both the frothy conditions and low density of the foam.\(^{48}\) His recommended chemical foams were formulated by mixing two liquid solutions, one containing sodium bicarbonate and saponine, and the other containing aluminium sulphate. The first fire test using this formulation, carried out in 1904, was successful during a naphtha storage tank fire in Russia.\(^{49}\) Fires need three conditions in order to spread and persist, these being oxygen, fuel and heat. The low density of the fire-fighting foams are therefore able to affect all three of these conditions at the same time by excluding oxygen from the fuel surface, cooling the
fuel to below the ignition point and trapping the fuel vapour within the HC layer.\textsuperscript{50}

The 1960’s saw the development of synthetic Aqueous Film Forming Foams (AFFF), through the introduction of perfluorinated surfactants into the formulations. This was found to improve both the flow and fuel tolerance properties compared to the existing foams,\textsuperscript{1} due to the very low $\gamma$ values achieved by FC surfactants, improved spreading over the fuel fires and the oleophobic properties of the FC surfactants.\textsuperscript{31, 48, 49} The most common FC surfactants initially incorporated into AFFFs were PFOS (perfluoroctanesulphonate) and PFOA (perfluorooctanoic acid). However, due to the strength of the C-F bond, the FC surfactants are very stable and unlikely to degrade within the environment, therefore leading to impacts on both environmental and human health.\textsuperscript{49} As a result, from the 2000’s up until now, the main aims in the fire-fighting foam industry have been to move away from the use of FC surfactants in AFFF formulations.

1.6.1 Environmental consequences of fluorocarbon surfactants in fire-fighting foams

FC surfactants used in fire-fighting foams have historically been produced by two different methods: electrochemical fluorination (ECF) and telomerisation.\textsuperscript{51} ECF-based FC surfactants break down to form PFOS (perfluoroctanesulphonate) and PFOA (perfluorooctanoic acid), which are recognised as having negative impacts on both environment and human health due to pronounced persistence, variable degrees of bioaccumulation potential and toxicity.\textsuperscript{6, 7, 22, 51–55} For example, it has been identified that FC with C\textsubscript{8} - C\textsubscript{15} chain lengths are hazardous pollutants.\textsuperscript{55} For these reasons, and as a result of legislative pressures, in 2002 many countries started to phase out the use of ECF-based FC surfactants in fire-fighting foams and now all modern fire-fighting foams contain partially fluorinated surfactants produced by telomerisation, also known as fluorotelomers.\textsuperscript{49} Fluorotelomers have proved to be a good alternative to ECF-based FC surfactants, by delivering fast control and extinction under a diverse range of flammable liquid applications. Although the breakdown of fluorotelomers leads to the formation of a 6:2 fluorotelomer sulphonate (not PFOS or PFOA), which are neither bioaccumulative nor toxic, the strength of the C-F bond still hinders biodegradability.\textsuperscript{49}

As a way to utilise less FC surfactants within fire-fighting foam formulations, fluorine-free (FF) fire-fighting foams have been developed.\textsuperscript{1} Advances in FF fire-fighting foams have seen them meeting international approvals for fire-fighting requirements, whilst at the same time being more environmentally benign.\textsuperscript{49, 51, 53, 56} However, in situations such as extinguishing liquid fuel fires, the performance of FF fire-fighting foams is not as effective as the FC surfactant containing AFFF products
and as such a high demand still exists. AFFFs are formulated to contain complex mixtures of both FC and HC surfactants, and these mixtures display superior properties for fuel fire extinguishment.\textsuperscript{31} By gaining an in-depth understanding into both the solution and interfacial properties of mixtures containing FC and HC surfactants, it will be possible to investigate the possibility of using less FC surfactants in fire-fighting foam formulations.
1.7 Project aims

There are clear incentives to move away from the use of FC surfactants within industrial processes.\textsuperscript{49, 51–55, 57} As previously mentioned, there has been a lot of interest in the development of FF foams in the recent years, and although these formulations provide a great alternative to FC containing formulations, they do not perform as well as FC containing formulations for liquid fuel fire extinguishment. AFFF formulations contain complex mixtures of both FC and HC surfactants and a clear alternative would be to reduce the amount of FC surfactants in the formulation, whilst ensuring they remain as effective as they currently are. To practically achieve this, there must be a clear understanding of the important properties associated with common industrial FC surfactants as both single and multi component systems. The main focus of this thesis is to therefore carry out in-depth investigations into the solution, surface and bulk properties of mixed surfactant systems containing partially fluorinated and HC surfactants.

In this work, the solution, surface and bulk properties of three partially fluorinated surfactants used in fire-fighting foams, each bearing a different headgroup (anionic, non-ionic and zwitterionic) have been investigated when mixed with a common anionic HC surfactant (sodium dodecylsulfate). As briefly discussed above, mixing FC and HC surfactants can often lead to antagonistic behaviour and in extreme cases even demixing. A primary aim is to therefore determine the interactions between the three FC surfactants and HC surfactant in the mixed systems in terms of mixed CMCs and $\gamma$ reduction. In addition to this, it is necessary to investigate, both experimentally and theoretically, the composition of mixed FC: HC monolayers and micelles. By developing an in-depth understanding into these important properties, it will be possible to determine whether the benefits of having FC surfactants within a formulation can still be achieved at low compositions and concentrations. This would therefore aid in the future design of new low FC containing fire-fighting foam formulations.
References


REFERENCES


REFERENCES


Hemming Information Services, 2013.


Chapter 2

Experimental

2.1 Introduction

This Chapter describes the preparation of the industrial fluorocarbon surfactants examined in this thesis. All industrial fluorocarbon surfactants were provided by commercial suppliers as liquid formulations. This Chapter details the processes that are needed to precipitate the surfactants from supplied commercial solutions so that experiments can be carried out on the pure surfactants. Table 2.1 shows the molecular structures of the surfactants used in the project and nomenclature used. Furthermore, the various common techniques used throughout this work and the associated experimental procedures are also outlined.

2.2 Materials

Below is a list of materials used in this thesis that were not provided by the industrial sponsor. All solvents were used as purchased unless otherwise stated. Water was obtained from a 5 L Milli-Q water purifier (18.2 MΩ cm).

- Acetone (Aldrich, 97 %)
- Cyclohexane (Aldrich, 99 %)
- D$_2$O (Aldrich, 99.9 %)
- d$_6$-DMSO (Aldrich, 99.9 %)
- Sodium dodecylsulfate (Aldrich, 99 %)
- Sodium perfluoroctanoate (Fluorochem, ≥ 99 %)
- Pyrene (Acros, puriss ≥ 99%)
- Orange-OT (Sigma-Aldrich, ≥ 75%)

<table>
<thead>
<tr>
<th>Surfactant Name</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td><img src="image" alt="Dynax DX1030" /></td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td><img src="image" alt="Dynax DX2200" /></td>
</tr>
<tr>
<td>Capstone 1157</td>
<td><img src="image" alt="Capstone 1157" /></td>
</tr>
<tr>
<td>Sodium Dodecylsulfate</td>
<td><img src="image" alt="Sodium Dodecylsulfate" /></td>
</tr>
<tr>
<td>Sodium Perfluoroctanoate</td>
<td><img src="image" alt="Sodium Perfluoroctanoate" /></td>
</tr>
</tbody>
</table>

Table 2.1: Surfactants used in this thesis

Dynax DX1030 is a C6 anionic fluorocarbon (FC) surfactant (IUPAC Name: 2-methyl-2-(3-((1H,1H,2H,2H-perfluoro-1-octyl)thio)propanamido)propane-1-sulfonate), Dynax DX2200 is a C8 non-ionic FC surfactant and Capstone 1157 is a C6 zwitterionic FC (IUPAC Name: N-(carboxymethyl)-N,N-dimethyl-3-(1H 1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-ammonium) Dynax™ is a trademark of Dynax Corporation and Capstone™ is a trademark or The Chemours Company.


2.3 Surfactant precipitation

As previously mentioned, all of the investigated FC surfactants were supplied as liquid formulations. Therefore, in order to purify the surfactants so they can be studied, it was necessary to use a non-solvent such as acetone to force precipitation of the crude product. The process is detailed below:

![Precipitation Process](image)

(a) Liquid Formulation
(b) Addition of Acetone
(c) Removal of solvent and drying
(d) Dried Surfactants. From left to right: Dynax DX1030, Dynax DX2200, Capstone 1157

Figure 2.1: Precipitation Process

The liquid formulations were added to a conical flask (~50 mL) and acetone was added with stirring, causing precipitation. The precipitated surfactants in solution were then passed through a Büchner funnel to remove excess solvent. The surfactants were then dried in a vacuum oven overnight at 60 °C. Once dried, attempts were made to purify the surfactants using techniques described below. In addition to this, conventional analytical techniques were carried out to determine structures.
2.4 Surfactant purification

Attempts were made to purify the industrial fluorocarbon surfactants using Soxhlet extraction and foam fractionation.

1. *Soxhlet extraction*
   Soxhlet extraction is used to remove residual inorganic material. Soxhlet extractions were carried out with acetone for 24 hours. After 24 hours, the solvent was removed by rotary evaporation.

2. *Foam fractionation*
   Foam fractionation is a technique utilised for removing trace quantities of surface-active impurities. A solution of surfactant in ultra-pure water was made up to 0.75 x CMC. Nitrogen gas was passed through a calcium sulfate drying set-up and a carbon filter, and then bubbled through aqueous solutions of HCl and NaOH, followed by several flasks of pure water before reaching the surfactant solution (Figure 2.2). The pure surfactant was recovered by rotary evaporation and dried in a vacuum oven overnight.

![Foam fractionation set-up.](image)

Figure 2.2: Foam fractionation set-up.
2.5 Surfactant Analysis

Nuclear magnetic resonance (NMR), elemental analysis and mass spectrometry were used to characterise the industrial FC surfactants shown in Table 2.1.

2.5.1 NMR

Proton and fluorine NMR for the three industrial FC surfactants were recorded on a JOEL 400 MHz machine (NMR service, School of Chemistry, University of Bristol). Processed spectra were further analysed using MestReNova software to obtain information on both the integration values and splitting of each proton/fluorine environment. Samples of ~10 mg (20 mg if weak intensities were given) were dissolved in approximately 2 mL of d$_6$-DMSO. The samples were thoroughly mixed by vortex and run through a pipette with a cotton wool bung to remove any undissolved surfactant. Due to incomplete deuteration of the solvents, residual proton signals are present, giving a quintet at 2.46 ppm for d$_6$-DMSO and a singlet at 3.29 ppm for D$_2$O. All $^1$H and $^{19}$F NMR spectra are shown below.
Figure 2.3: $^1$H NMR of Dynax DX1030
Figure 2.4: $^{19}$F NMR of Dynax DX1030
Figure 2.5: $^1$H NMR of Dynax DX2200
Figure 2.6: $^{19}$F NMR of Dynax DX2200
Figure 2.7: $^1$H NMR of Capstone 1157
Figure 2.8: $^{19}$F NMR of Capstone 1157
<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Molecular fragment</th>
<th>Integration</th>
<th>Identified proton</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dynax DX1030</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.32 - 1.39</td>
<td>-CH₂-C(CH₃)₂-NH-</td>
<td>8.00</td>
<td>f, g, h</td>
</tr>
<tr>
<td>2.20 - 2.28</td>
<td>-CH₂-CH₂-S-</td>
<td>2.05</td>
<td>b</td>
</tr>
<tr>
<td>2.61 - 2.75</td>
<td>-CH₂-CH₂-S-CH₂-CH₂-</td>
<td>6.06</td>
<td>a, c, d</td>
</tr>
<tr>
<td>8.09 - 8.14</td>
<td>-CO-NH-C(CH₃)₂-</td>
<td>1.13</td>
<td>e</td>
</tr>
<tr>
<td><strong>Dynax DX2200</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.06 - 1.08</td>
<td>-CF₂-CH₂-CH₂-</td>
<td>2.21</td>
<td>a</td>
</tr>
<tr>
<td>1.15 - 1.72</td>
<td>-S-CH₂-CH-</td>
<td>28.31</td>
<td>c</td>
</tr>
<tr>
<td>1.90 - 2.21</td>
<td>-CH₂-CH-</td>
<td>15.03</td>
<td>d</td>
</tr>
<tr>
<td>2.64 - 2.77</td>
<td>-CH₂-CH₂-S-</td>
<td>2.10</td>
<td>b</td>
</tr>
<tr>
<td>6.57 - 7.51</td>
<td>-CO-NH₂</td>
<td>30.00</td>
<td>e</td>
</tr>
<tr>
<td><strong>Capstone 1157</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.65 - 1.77</td>
<td>-CH₂-CH₂-CH₂-</td>
<td>2.00</td>
<td>e</td>
</tr>
<tr>
<td>2.43 - 2.64</td>
<td>-CF₂-CH₂-CH₂-</td>
<td>2.03</td>
<td>a</td>
</tr>
<tr>
<td>2.85 - 2.94</td>
<td>-NH-CH₂-CH₂-</td>
<td>2.05</td>
<td>d</td>
</tr>
<tr>
<td>2.95 - 3.03</td>
<td>-CH₂-N⁺(CH₃)₂-CH₂-</td>
<td>5.99</td>
<td>g, h</td>
</tr>
<tr>
<td>3.37 - 3.47</td>
<td>-CH₂-N⁺(CH₃)₂-CH₂-</td>
<td>3.66</td>
<td>i, f</td>
</tr>
<tr>
<td>7.42 - 7.49</td>
<td>-SO₂-NH-CH₂-</td>
<td>1.00</td>
<td>c</td>
</tr>
</tbody>
</table>

Table 2.2: Data from ¹H NMR spectra of the three industrial fluorocarbon surfactants (Figures 2.3, 2.5 and 2.7).
### Table 2.3: Data from $^{19}$F NMR spectra of the three industrial fluorocarbon surfactants (Figures 2.4, 2.6 and 2.8).

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Molecular fragment</th>
<th>Integration</th>
<th>Identified fluorine</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dynax DX1030</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-125.77 - -125.52</td>
<td>-CF$_2$-CF$_2$-CH$_2$-</td>
<td>2.00</td>
<td>f</td>
</tr>
<tr>
<td>-122.90 - -122.29</td>
<td>-CF$_2$-CF$_2$-CF$_2$-CH$_2$-</td>
<td>4.01</td>
<td>d, e</td>
</tr>
<tr>
<td>-121.80 - -121.38</td>
<td>CF$_3$-CF$_2$-CF$_2$-</td>
<td>1.93</td>
<td>c</td>
</tr>
<tr>
<td>-113.24 - -112.96</td>
<td>CF$_3$-CF$_2$-CF$_2$-</td>
<td>1.97</td>
<td>b</td>
</tr>
<tr>
<td>-80.22 - -80.04</td>
<td>CF$_3$-CF$_2$-</td>
<td>3.12</td>
<td>a</td>
</tr>
<tr>
<td><strong>Dynax DX2200</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-125.68 - -125.45</td>
<td>-CF$_2$-CF$_2$-CH$_2$-</td>
<td>2.00</td>
<td>h</td>
</tr>
<tr>
<td>-122.83 - -121.03</td>
<td>-CF$_2$-(CF$_2$)$_5$-CF$_2$-</td>
<td>9.99</td>
<td>c, d, e, f, g</td>
</tr>
<tr>
<td>-113.29 - -112.73</td>
<td>CF$_3$-CF$_2$-CF$_2$-</td>
<td>1.93</td>
<td>b</td>
</tr>
<tr>
<td>-80.16 - -79.93</td>
<td>CF$_3$-CF$_2$-</td>
<td>3.38</td>
<td>a</td>
</tr>
<tr>
<td><strong>Capstone 1157</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-127.30 - -127.10</td>
<td>-CF$_2$-CF$_2$-CH$_2$-</td>
<td>2.00</td>
<td>f</td>
</tr>
<tr>
<td>-124.28 - -123.59</td>
<td>-CF$_2$-CF$_2$-CF$_2$-CH$_2$-</td>
<td>3.93</td>
<td>d, e</td>
</tr>
<tr>
<td>-122.93 - -122.60</td>
<td>CF$_3$-CF$_2$-CF$_2$-</td>
<td>1.94</td>
<td>c</td>
</tr>
<tr>
<td>-114.77 - -114.42</td>
<td>CF$_3$-CF$_2$-CF$_2$-</td>
<td>1.94</td>
<td>b</td>
</tr>
<tr>
<td>-82.38 - -82.23</td>
<td>CF$_3$-CF$_2$-</td>
<td>3.16</td>
<td>a</td>
</tr>
</tbody>
</table>

The proton NMR spectra generally show good agreement with the provided structures for the industrial FC surfactants. The only proton environment that could not be assigned was the $b$ proton in Capstone 1157. For the other surfactants, the $b$ proton is equivalent and provides a triplet at $\sim 2.20 - 2.77$ ppm. It is possible that the $b$ proton environment in Capstone 1157 is disguised by another peak.

The fluorine NMR spectra are all well characterised, showing good agreement with integration values. These data are also comparable to previous studies which were based on characterising similar FC surfactants.\(^2\)

#### 2.5.2 Elemental Analysis

Samples were submitted for elemental analysis of C, H, F, N and S where applicable (micro-analytical laboratory, School of Chemistry, University of Bristol). Samples of $\sim 5$ mg were needed for C, H, N and S analysis and samples of $\sim 10$ mg were needed for F analysis. Each sample was submitted three times to check for reproducibility. From the repeat measurements, the typical error for the percentage mass was found to be approximately between 0.3 - 0.7 %. The averaged results presented in Table 2.4 show generally good agreement between theoretical and experimentally determined
values. The values for fluorine are generally lower than expected due to the strength of the C-F bond.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Theoretical %</th>
<th>Experimental %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Dynax DX1030</td>
<td>29.57</td>
<td>2.81</td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td>42.75</td>
<td>5.15</td>
</tr>
<tr>
<td>Capstone 1157</td>
<td>31.59</td>
<td>3.36</td>
</tr>
</tbody>
</table>

Table 2.4: Theoretical and experimental results from elemental analysis

### 2.5.3 Mass Spectrometry

Mass spectrometry was carried out on the micrOTOF spectrometer (Mass spectrometry Facility, University of Bristol). Each sample was prepared as a 1 mg/mL solution and submitted to the mass spectrometry service. The full spectra for each sample are shown below in Figures 2.9 - 2.11, and the table summarising the obtained molecular ion peaks compared to each surfactants molecular weight are shown below in Table 2.5.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Molecular Weight</th>
<th>Molecular Ion Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td>609</td>
<td>586</td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td>1545</td>
<td>See spectra Figure 2.10</td>
</tr>
<tr>
<td>Capstone 1157</td>
<td>570</td>
<td>571</td>
</tr>
</tbody>
</table>

Table 2.5: Mass Spectrometry Results

There is good agreement between both the molecular weight and molecular ion peak for Dynax DX1030 and Capstone 1157. The difference of 23 m/z for Dynax DX1030 is due to the presence of Na$^+$ ions which do not show up in mass spectrometry. The spectra for Dynax DX2200 contains many peaks due to the complicated nature of the surfactants structure. There is an uncertainty associated with the number of acrylamide repeating units and thus many peaks are observed.
Figure 2.9: Mass spectrometry data for Dynax DX1030
Figure 2.10: Mass spectrometry data for Dynax DX2200
Figure 2.11: Mass spectrometry data for Capstone 1157
2.6 Techniques

Equilibrium and dynamic surface tension, fluorescence, UV-Vis, small-angle neutron scattering (SANS) and neutron reflectivity (NR) are the main techniques employed in this project to determine the solution, surface and bulk properties of both single and multi component surfactant systems. This sections aims to provide details of the experimental procedures involved in each technique and how they can be used to determine the relevant properties of surfactant systems.

2.6.1 Equilibrium surface tension

Surface tension measurements were carried out on a Krüss K100 force tensiometer using the Wilhemy plate method at 25 °C. The temperature was kept constant by use of a Grant LTD6G circulating water bath. The force exerted on a platinum plate when it is brought into contact with a liquid surface is measured and used to calculated the surface tension via Equation 2.1 below:

\[
\gamma = \frac{F}{L \cos \theta}
\]

where \(\gamma\) is surface tension, \(F\) is force, \(L\) is wetted length and \(\theta\) is the angle between the liquid and the plate. The plate is platinum because it is chemically inert, easy to clean and forms a contact angle, \(\theta\), of 0° (cos \(\theta = 1\)) with liquids. Hence, \(\gamma\) is calculated directly from \(F\).

Figure 2.12: Krüss K100 force tensiometer
Before the measurements, glassware was washed thoroughly with a dilute Decon solution and then with wash cycles of methanol and ultra pure water (Millipore, 18.2 MΩ cm). The cleaning cycles were repeated until the surface tension of water was returned as $72 \pm 0.2 \text{ mN m}^{-1}$ at $25^\circ\text{C}$. Stock surfactant solutions were prepared and aliquots were added to deionised water to give desired concentrations. Each concentration measurement was repeated over a period of up to 30 minutes to ensure equilibration. The plate was cleaned between repeats to ensure cleanliness by initially rinsing with methanol before placing in the blue flame of a Bunsen burner. Repeat measurements were made at each concentration until the surface tension was reproducible within a range of $\pm 0.2 \text{ mN m}^{-1}$. Attempts were made to model the data using the Gibbs adsorption isotherm, which relates the surface excess (inversely proportional to the area per molecule) to changes in the surface tension with concentration.

2.6.2 Dynamic surface tension

Dynamic surface tension measurements were carried out on a Krüss BP100 bubble pressure tensiometer using the maximum bubble pressure method at $25^\circ\text{C}$. The temperature was kept constant by use of a Grant LTD6G circulating water bath. The surface tension is measured as a function of surface age over a period of 0.01 - 100 s.

![Figure 2.13: Krüss BP100 bubble pressure tensiometer](image)
During the experiment, gas bubbles are generated in a liquid sample using a capillary connected to a pressure sensor. The pressure must work against the surface tension of the sample to increase the bubble size. When a gas bubble is produced in a liquid at the tip of capillary, its curvature initially increases and then decreases. The greatest curvature/pressure occurs when the radius of curvature is equal to the radius of the capillary ($r$). The capillary radius is determined using a calibration measurement carried out with a liquid with known surface tension, in this work it was water. Once $r$ is known, the surface tension can be calculated from the measured maximum pressure $p_{\text{max}}$ and the hydrostatic pressure $p_0$ resulting from the immersion depth and density of the liquid by:

$$\gamma_t = \frac{p_{\text{max}} - p_0 \cdot r}{2}$$

(2.2)

where $\gamma_t$ is the surface tension at a specific surface age, $p_{\text{max}}$ is the maximum pressure, $p_0$ is the hydrostatic pressure and $r$ is the measured radius of the capillary.

Before the measurements, glassware was washed thoroughly using the same procedure as for the equilibrium surface tension measurements. The cleaning cycles were repeated until the dynamic surface tension of water was returned as $72 \pm 1 \text{ mN m}^{-1}$ at $25 \degree C$. The capillary diameter was determined using H$_2$O and was used in the program to determine the surface tension values. The same capillary was used for all of the experiments and had a radius of $0.30 \pm 0.01 \text{ mm}$. Stock solutions at specific surfactant concentrations were prepared and left to equilibrate to temperature for $\sim 10$ minutes before measurements were made. Each measurement was repeated three times to ensure reproducibility. Data were analysed using the diffusion-controlled adsorption model determined by Ward and Tordai$^3$ and extended by Miller et al.$^4$ The diffusion controlled models are discussed in more detail in Chapter 1.

### 2.6.3 Fluorescence

Fluorescence measurements were carried out as described in ref$^5$ in quartz cuvettes at $21 \degree C$ on a Cary Eclipse (Varian) Fluorescence spectrometer. Pyrene was used as the hydrophobic fluorescent probe for determining the CMCs of the studied surfactants. A fixed concentration of Pyrene ($1.0 \times 10^{-3} \text{ mM}$) was added to sample vials from a known stock prepared in acetone. The acetone was allowed to evaporate off in air, leaving behind a known mass of the involatile pyrene, before the aqueous surfactant solutions were added over the concentration range of interest. Fluorescence emission spectra were collected after excitation at $\lambda = 337 \text{ nm}$, with a slit width of $5 \text{ nm}$ for excitation and emission. Each measurement was repeated three times.
2.6.4 UV-Vis

UV-Vis measurements were carried out in quartz cuvettes at $\sim 21^\circ$C using an Evolution 300 UV-Vis spectrophotometer. Orange OT was used as the hydrophobic probe for determining the CACs of mixed surfactant systems, and the same method was carried out as for the Fluorescence measurements. UV-Vis absorbance spectra were taken between $\lambda = 400 - 600$ nm. Each measurement was repeated three times.

2.6.5 Small-angle neutron scattering (SANS) and neutron reflectivity (NR)

Small-angle neutron scattering (SANS) experiments were performed on D33 at the Institute Laue-Langevin (ILL, Grenoble, France) and SANS 2D or LOQ at the ISIS facility (Rutherford Appleton Laboratory, Didcot, UK). Neutron reflectivity (NR) experiments were performed on FIGARO at the Institute Laue-Langevin (ILL, Grenoble, France) and INTER or SURF at the ISIS facility (Rutherford Appleton Laboratory, Didcot, UK). Details on the specific instrument configuration will be provided in the relevant Chapters. The relevant theory behind both SANS and NR experiments will be discussed in the following Chapter.
References


Chapter 3

Neutron scattering and reflectivity theory

To be able to realise the relationship between molecular structure and physical properties within a colloidal system, the molecular organisation both at the surface (air/water) and within the bulk of a system must be determined. The most obvious and versatile method for determination of bulk and surface properties (size, shape, structure, molecular orientation and surface composition) are scattering techniques, as they provides direct measurements of the interaction between particles and incident radiation (e.g. X-ray, light, neutron). The colloidal size range is approximately between 10 - 10^4 Å, so valuable information can be obtained by scattering methods provided that the incident wavelength, \( \lambda \), falls within this range. Micelles and microemulsions have a size generally on the order of 10^2 Å and are therefore well characterised by X-rays (\( \lambda = 0.5 \text{ - } 2.3 \text{ Å} \)) and neutrons (\( \lambda = 0.1 \text{ - } 30 \text{ Å} \)). For larger aggregates, however, light scattering (\( \lambda = 4000 \text{ - } 8000 \text{ Å} \)) is most suitable.

The following sections will summarise the theory behind both small-angle neutron scattering (SANS) and neutron reflectivity (NR) and how one would use such techniques to further characterise colloidal systems. It should be noted that many books exist providing in depth accounts of the fundamental science of neutron scattering and reflectivity techniques: for example, but not limited to.1–5 It is firstly important to describe why neutrons, as opposed to other incident types of radiation, are the ideal tool for studying the colloidal systems of interest.

3.1 Neutron

A neutron is an uncharged subatomic particle, with mass = 1.67 x 10^{-27} kg, spin = \( \frac{1}{2} \), and a magnetic moment = - 1.91 nuclear magnetons. Neutrons and protons
constitute nearly the entire mass of atomic nuclei, and are both collectively referred to as nucleons. Neutrons have a mean lifetime of approximately 1000 seconds as a free particle, but are stable when bound in an atomic nucleus.\textsuperscript{2} They can be classified according to their wavelength and energy: “epithermal” for short wavelengths (\(\lambda \sim 0.1 \text{ Å}\)) and “thermal”/ “cold” for long wavelengths (\(\lambda \sim 10 \text{ Å}\)). The desired range of \(\lambda\) can be altered by moderation of the neutrons during their production.

The interaction of neutrons with matter occurs through strong, weak, gravitational and electromagnetic interactions. It is the strong nuclear force and magnetic moments that make neutrons a unique probe for both scattering and reflection experiments. Since neutron interaction probability is low, they usually penetrate well through matter allowing for investigating into bulk condensed matter. Neutrons can also be reflected off of a surface at glancing angles thereby acting as a surface probe. This, along with other important advantages that neutrons have over alternative forms of radiation can be summarised as follows:\textsuperscript{2}

- Neutrons are non-destructive and therefore do not significantly perturb the system under investigation.

- The wavelength of a particle can be related to its momentum via the de Broglie equation

\[
\lambda = \frac{h}{mv}
\]  

where \(h\) is Planck’s constant (\(6.63 \times 10^{-34} \text{ J s}\)) and \(v\) the particle velocity. The associated kinetic energy is then given by

\[
E = \frac{1}{2}mv^2 \quad \text{or} \quad E = \frac{h^2}{2m} \cdot \frac{1}{\lambda^2}
\]  

Because the energy and wavelength of a particle depends on its velocity, it is possible to select a specific neutron wavelength by the time-of-flight technique (discussed later). Therefore, the energy and wavelength of neutrons can be set to the appropriate energy and length scales required for condensed matter investigations.

- Unlike X-rays, neutrons are scattered from materials by interacting with the nucleus of an atom rather than the electron cloud, and the scattering power (cross-section) of an atom is therefore not strongly related to its atomic number. There is a strong nuclear dependence on the scattering which allows isotopes of the same element to have substantially different neutron scattering lengths. Therefore, isotopic substitution (contrast variation) can be used to label different parts of a molecule for comprehensive investigations.
CHAPTER 3. NEUTRON SCATTERING AND REFLECTIVITY THEORY

3.2 Neutron generation

There are two main ways in which a neutron beam can be produced. One method is by nuclear fission in a reactor-based neutron source (Institut Laue-Langevin, ILL, Grenoble), and the other is in an accelerator-based neutron source (ISIS Facility at the Rutherford Appleton Laboratory, Didcot, UK). A brief description of these two methods is given below.

3.2.1 Reactor based steady-state source

In a reactor based steady-state source, neutrons are traditionally produced by nuclear fission of $^{235}$U nuclei, generating a constant neutron flux. Figure 3.1 shows the neutron flux as a function of time for a continuous reactor source. The cross-section for neutron-induced fission of $^{235}$U is only high for slow neutrons with energies in the meV range, whereas the fast neutrons produced by fission have high energies in the MeV range. The initial high energy of these neutrons (MeV) are reduced by repeated collisions with low mass nuclei (usually D or H) in a moderator, producing thermal neutrons. The moderation process produces neutrons which, as well as being slowed down for maintaining the fission reaction, have wavelengths suitable for performing neutron scattering experiments. The neutron energy distribution can be shifted to higher energy (shorter $\lambda$) by allowing the neutrons to go into thermal equilibrium with a “hot source” (At the ILL this is a graphite block at 2400 K), or lower energies with a “cold source” such as liquid deuterium at 25 K.²

![Figure 3.1: Neutron flux as a function of time at a steady-state source, such as ILL. Left image is the intensity at the source, right image is intensity at the detector (not to scale). Steady-state sources have high time-averaged fluxes.](image-url)
The $\lambda$ selection can be achieved through either Bragg scattering from a crystal monochromator, or by velocity selection through mechanical choppers. Using these techniques provides a high quality and high flux neutron beam with narrow wavelength distributions for neutrons scattering experiments. Continuous reactor based sources measure some of the neutrons all of the time.

### 3.2.2 Accelerator-based pulsed source

In an accelerator-based neutron source, H$^-$ ions are initially accelerated in a Linear ACcelerator (Linac) to 70 MeV. The beam is then injected in bunches into a synchrotron, operating at 50 Hz, and accelerated further to 800 MeV. When in the synchrotron, the H$^-$ ions pass through very thin alumina foil which strips both electrons, producing a proton beam. The high-energy proton beam is then accelerated further and directed into heavy metal target (e.g. Ta, W) under constant cooling to dissipate the heat from the proton beam. The collision leads to the release of neutrons primarily in a process known as spallation, meaning the break-up of a bombarded nucleus into several parts. High energy neutrons are produced after the interaction between the particle beam and the nuclei in the target, which are slowed down by a moderator cf. the fission process. However, for an accelerator-based pulsed source, the moderator is relatively small so that the pulsed time structure of the neutron flux does not broaden too much. A consequence of this is that the neutrons produced by accelerator-based sources are under-moderated and many more high-energy neutrons are produced compared to a reactor source. There are four moderators at ISIS: two use water at room temperature, one uses liquid methane at 100 K and the fourth consists of liquid hydrogen at 20 K. Fast neutrons are slowed down to speeds required for neutron scattering experiments. The spallation process produces less heat per useful neutron compared to fission, meaning pulsed sources are able to deliver higher neutron intensity than those achieved at steady-state sources, as shown below in Figure 3.2.
Figure 3.2: Neutron flux as a function of time at a pulsed source, such as ISIS. Left image is the intensity at the source, right image is intensity at the detector (not to scale). Pulsed sources are optimised for high brightness.

The high intensity of the neutron pulse is ideally suited to the time-of-flight (TOF) technique. This technique is able to exploit the high intensity of the pulse and can compensate for the low time-averaged flux. In general, the TOF technique measures the time taken for a neutron to travel from a pulsed point to a point detector, via the sample. Assuming elastic scattering (i.e. initial and final neutron energies are the same, $E_i = E_f$) then:

$$t = \frac{m_n L \lambda}{h}$$

where $m_n$ is the mass of a neutron, $h$ is Planck’s constant, $L$ is the flight path and $\lambda$ is the neutron wavelength. The neutron wavelength can therefore be determined. The use of TOF removes the need to monochromate the neutron beam and thus, even though the raw flux initially produced by an accelerator-based source is lower than that of a reactor source, the final flux available for scattering experiments is comparable. Spallation based sources measure all of the neutrons some of the time.
3.2.3 Instruments

Throughout this work, SANS experiments were carried out on the LOQ and SANS2D beam lines at ISIS, and the D33 diffractometer at ILL. NR experiments were carried out on the SURF and INTER beam lines at ISIS, and the FIGARO instrument at ILL. Due to the different characteristics of reactor and pulsed sources, SANS and NR experiments performed differ on these instruments, brief summaries are given below.

SANS instruments

Typically, a SANS beam line has a two dimensional area detector in a vacuum tank between 2 and 20 m after the sample. On D33, at the ILL, a continuous stream of neutrons with no time structure is produced hence the neutrons are monochromated before they can be used (i.e. fixed neutron $\lambda$). To be able to access a wide Q range, at constant $\lambda$, the scattering intensity must be measured at various different angles. This is achieved by varying the sample-to-detector distance using a movable detector. Neutrons with a wavelength of $\lambda = 6$ Å and two sample-detector positions (2.0 and 7.5 m) are used on D33 providing an accessible Q range of 0.005 – 0.2 Å$^{-1}$. The reader is referred to the following reference for more information.

At ISIS (spallation source), a polychromatic "white" beam of neutrons is produced and a range of neutron $\lambda$ are used. The energy analysis of the scattered beam is obtained by use of the TOF method. Unlike D33, multiple angles are not necessary due to the broad range of neutron $\lambda$, hence the detector for example on LOQ is fixed. After interaction with the sample, the neutron beam passes into a vacuum tube containing a $^3$He gas filled detector which is placed 4.5 m from the sample. The $\lambda$ obtained on LOQ are defined by the disc chopper and are 2.2 - 10.0 Å, giving a Q-range of 0.006 - 0.24 Å$^{-1}$ on the main detector, more information can be found elsewhere. A schematic of LOQ is shown below in Figure 3.3.

SANS2D differs from LOQ in that it combines a large range of neutron wavelengths (2 - 14 Å) and two movable 1 m$^2$ detectors ($L_2 = L_1 = 2$ to 12 m), which leads to an extremely wide Q-range of 0.002 - 3.0 Å$^{-1}$. More detail can be found elsewhere. Information regarding instrument configuration will be given in each results Chapter.
(a) Schematic layout of the LOQ instrument at ISIS.

(b) Photo of the sample environment/ pit for the LOQ instrument at ISIS.

Figure 3.3: Schematic layout and photo of the LOQ instrument at ISIS. Schematic Image taken from institute website, but altered by author. Photo taken by author during an experiment with permission from the local contact.
NR instruments

Reflectivity experiments measure the specular reflectivity $R(Q)$ as a function of the wave-vector transfer, $Q$. Measurements can be carried out with either a horizontal or vertical sample geometry, with the horizontal geometry being used in all of the experiments in this work as it is ideal for studying liquid surfaces. PTFE adsorption troughs are used for studying the structure and composition of surface layer in solution. In general, a narrow neutron beam, collimated by a pair of slits, is incident on the sample at a grazing incidence angle and reflected into a single detector or a small area detector. Measurements can be made using a fixed $\lambda$ and changing the angle of incidence, or by using a fixed angle of incidence and TOF to produce a wide range of neutron $\lambda$. All of the instruments used in this work use the TOF method.

FIGARO (Fluid interfaces grazing angles reflectometer) is a high flux, versatile, TOF horizontal neutron reflectometer. On FIGARO, a chopper pair gives a neutron $\lambda$ range between 2 and 30 Å. The incident beam is at 0.62° and the angle can be altered to 3.8° to produce a possible $Q$ range of 0.0045 to 0.42 Å$^{-1}$. More information regarding FIGARO can be found in Ref.11 A schematic of FIGARO along with a photo of the instrument is shown below in Figure 3.4.

At ISIS, both INTER13 and SURF14 were used. On INTER, measurements are taken using a single point detector and fixed grazing incidence angles (0.8° and 2.3°). INTER has an incident neutron wavelength band of 0.5 Å$\leq \lambda \leq$ 16 Å leading to a $Q$ range of 0.03 Å$^{-1} \leq \lambda \leq$ 1.0 Å$^{-1}$. On SURF, the incident beam is inclined at 1.51° from the horizontal and this angle can be varied to either 0.35° and 0.65° using either a computer-controlled goniometer, or a 3 x demagnifying curved supermirror for liquid surfaces. SURF has incident wavelengths of 0.55 - 6.8 Å at 50 Hz and an associated $Q$ range of 0.048 - 1.1Å$^{-1}$. Information regarding instrument configuration will be given in each results Chapter.
Figure 3.4: Schematic layout and photo of the FIGARO instrument at the ILL. Schematic adapted from institute website.\cite{12} Photo taken by author during an experiment with permission from the local contact.
3.3 Scattering theory

When radiation interacts with and is scattered by matter (regardless of the type of radiation), interference patterns are produced which provides information about spatial and or temporal correlations within a sample. Different scattering events can occur, and are summarised below:

- Elastic - Characterised by no change in the energy of the incident radiation, but a change in the scattering vector.

- Inelastic - Scattering in which exchange of energy and momentum between the incident radiation and the sample causes both the direction and the energy of the radiation to change, hence incident radiation looses or gains energy.

- Coherent - Scattering in which the incident radiation wave interacts with all the nuclei in a sample in a coordinated fashion. Hence, the scattered waves from all nuclei have definite relative phases and can thus interfere with each other.

- Incoherent - Scattering in which the incident radiation wave interacts indepen
dently with each nucleus in a sample. Hence, the scattered waves from different nuclei have random relative phases and do not interfere with each other.
The coherent scattering from ordered nuclei produces constructive or destructive interference patterns, which can be used to obtain structural information. The incoherent scattering, however, is from unordered nuclei and information regarding the dynamics of the system are provide. To put this information in the context of the scattering of neutrons by matter, it is important to understand how a neutron is scattered by an individual fixed nucleus.

### 3.3.1 Scattering of neutrons

The scattering of neutrons by a single nucleus can be described in terms of a cross section, $\delta$, measured in barns (1 barn $= 10^{-28}$ m$^2$). The nucleus $\delta$ is equivalent to the effective area presented to the passing neutron, which when hit by neutrons, leads to isotropic scattering, meaning with equal probability in any direction. The reason for this is because, as previously mentioned, neutrons interact with atoms via nuclear rather than electrical forces, which are very short range and on the order of a few femtometres ($\sim 10^{-15}$ m). Neutron wavelengths used for scattering experiments ($\sim 10^{-10}$ m) are so much larger (x 100,000) than the nuclear dimension and the nucleus therefore acts as a point scatterer, scattering waves isotropically. In contrast to this, X-rays are scattered by electrons and atomic electron clouds are on the same length scale as the radiation ($\sim 10^{-10}$ m). In the scattering process they appear as extended objects and cannot be considered as points.

The scattering process of neutrons by matter can alter the momentum and energy of both the neutrons and matter. Scattering is not necessarily elastic as for a single, fixed nucleus due to a certain amount of free movement by the atoms within the matter. A result of this being that the atoms can recoil during a collision with a neutron, or if they are moving when the neutron arrives, can impart or absorb energy. As is usual in collisions, the total energy and momentum are conserved, i.e. the energy lost by the neutron in the scattering event is gained by the sample.

The strength of an interaction between a bound nucleus and a free neutron is quantified by the isotope dependent scattering length, $b$, of an atom. Thus, from known $b$ values, it is possible to define the mean coherent scattering length density (SLD) of a compound, a measurement of its scattering power. This is determined by summing the $b$ contributions from all atoms within the compound and dividing by the molecular volume:

$$SLD = \frac{1}{V_m} \sum_i b_{i,coh}$$  \hspace{1cm} (3.4)

where $b_{i,coh}$ is the coherent scattering length of the $i^{th}$ atom in the molecule and $V_m$ is the molecular volume. In general, the appropriate $V_m$ is not known, but can be
computed from the known bulk density of the material \( (D_{\text{bulk}}) \) and the molecular weight \( (M_w) \):

\[
V_m = \frac{M_w}{D_{\text{bulk}} N_a}
\]

where \( N_a \) is Avogadro’s number. Therefore combining Equations 3.4 and 3.5 gives:

\[
SLD = \frac{D_{\text{bulk}} N_a}{M_w} \sum_i b_{i,\text{coh}}
\]

Both the \( b_{i,\text{coh}} \) and \( SLD (\rho) \) values for selected atoms and molecules are given below in Tables 3.1a and 3.1b, respectively. Note the significant difference in \( b_{i,\text{coh}} \) between hydrogen and deuterium, which is commonly exploited in contrast variation experiments, allowing selective regions of a molecular structure to be highlighted by varying the solvent contrast (\( H_2O / D_2O \)).

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>( b_{i,\text{coh}} ) / ( 10^{-12} \text{ cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{H})</td>
<td>-0.374</td>
</tr>
<tr>
<td>(^2\text{H(D)})</td>
<td>0.667</td>
</tr>
<tr>
<td>(^{12}\text{C})</td>
<td>0.665</td>
</tr>
<tr>
<td>(^{16}\text{O})</td>
<td>0.580</td>
</tr>
<tr>
<td>(^{19}\text{F})</td>
<td>0.565</td>
</tr>
<tr>
<td>(^{32}\text{S})</td>
<td>0.285</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \rho ) / ( 10^{10} \text{ cm}^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2O )</td>
<td>-0.560</td>
</tr>
<tr>
<td>( D_2O )</td>
<td>6.356</td>
</tr>
<tr>
<td>h-AOT</td>
<td>0.542</td>
</tr>
<tr>
<td>d-AOT</td>
<td>5.180</td>
</tr>
</tbody>
</table>

(a) Selected values of coherent scattering lengths, \( b_{i,\text{coh}} \).

(b) Scattering length density values for selected molecules.

Table 3.1: Selected values for coherent scattering lengths and scattering length densities. Note: structure of AOT is \((C_8H_{17}COO)CH_2CHSO_3^- \text{Na}^+\). Values taken from.

The scattering vector

In a SANS measurement, structural information about a system on different length scales are probed in reciprocal space by detecting the number of scattering neutrons (scattering intensity \( I(Q) \)) as a function of the scattering vector, \( Q \), shown schematically below in Figure 3.5.

In this case, the incident and scattered beam of neutrons have wave vectors \( K \) and \( K' \) respectively and by definition, the angle between these wave vectors is the scattering angle, \( 2\theta \). As previously mentioned, in a SANS experiment only the coherent elastic interactions between the neutron beam and sample are considered.
The only change is in the direction of the wave vector, thus $K = K'$ and $Q$ can therefore be related to the wave vectors by the relationship:

$$Q = K - K'$$  \hspace{1cm} (3.7)

Hence, simple trigonometry allows the magnitude of $Q$ to be related to both the scattering angle and the incident wavelength ($\lambda$) in the following way:

$$\sin \theta = \frac{Q/2}{K}$$ \hspace{1cm} (3.8)

The magnitude of the wave vector, or angular wavenumber, is defined as $\frac{2\pi}{\lambda}$. Substituting this in for $K$ leads to:

$$Q = \frac{4\pi \sin \theta}{\lambda}$$ \hspace{1cm} (3.9)

The magnitude of $Q$ quantifies the length in reciprocal space of the scatterer and is commonly expressed in units of Å$^{-1}$, hence large structures will scattering at low $Q$ (low $\theta$/ long $\lambda$) and small structures scattering at higher $Q$ (high $\theta$/ short $\lambda$). The magnitude of $Q$ could also be considered a window of observation, whereby at low-$Q$ the window is very large and multiple aggregates within the system can be studied and vice versa.
3.3.2 SANS Measurements

SANS is an experimental technique that uses elastic neutron scattering at small scattering angles (<10°) to investigate structure over length scales of 1-100 nm, hence length scales commensurate with the size of self-assembled micelles. For a monodispersed homogenous scattering system of radius R in a solvent, the normalised SANS intensity I(Q) (cm⁻¹) is as follows:

\[ I(Q) = \left( \frac{N}{V} \right) V_p^2 \Delta \rho^2 P(Q, R) S(Q) \] (3.10)

where \( \left( \frac{N}{V} \right) \) is the number density of particles, \( V_p \) is the particle volume, \( \Delta \rho^2 \) is the difference in SLD between the scatterer \( \rho_{\text{SLD}} \) and the solvent \( \rho_s \). The first three terms in Equation 3.10 are independent of Q and account for the absolute intensity of scattering. This is referred to as the scale factor, \( S_F \), which can be defined as:

\[ S_F = \left( \frac{N}{V} \right) \Delta \rho^2 V_p^2 = \phi_p \Delta \rho^2 V_p \] (3.11)

where \( \phi_p \) is the volume fraction of the particles. The scale factor provides a measure of the validity of a model when analysing SANS data, i.e. the \( S_F \) determined from the fit can be compared to the calculated value. The last two terms in the equation are Q-dependent functions. \( P(Q, R) \) is the particle form factor, which describes intra-particle informations such as size and shape. \( S(Q) \) is the structure factor, which describes the scattering due to inter-particle correlations.

Form factor, \( P(Q) \)

There are various expressions of \( P(Q) \) for a wide range of shapes such as spheres, ellipsoids, cylinders and discs, all of which are commonly encountered in soft matter. The form factors for these shapes can be found in the literature.\(^{15, 16} \) The \( P(Q) \) of a monodispersed spherical particle with radius, R, is shown below:

\[ P(Q, R) = \left[ \frac{3(\sin QR - QR \cos QR)}{(QR)^3} \right]^2 \] (3.12)
For ellipsoids, the $P(Q)$ is shown below. When $R_a < R_b$ the ellipsoid is said to be oblate (disc-like), when $R_a = R_b$ the equations effectively tend to that of the sphere form factor above and when $R_a > R_b$ the ellipsoid is said to be prolate (rod-like).

$$P(Q, \alpha) = \frac{Scale}{V} f^2(Q) + bkg$$  \hspace{1cm} (3.13)

where: $F(Q, \alpha) = \frac{3(\Delta \rho) V (\sin[Qr(R_a, R_b, \alpha)] - [Qr\cos[Qr(R_a, R_b, \alpha)]]}{Qr(R_a, R_b, \alpha)}$  \hspace{1cm} (3.14)

and: $r(R_a, R_b, \alpha) = \left[ R_b^2 \sin^2 \alpha + R_a^2 \cos^2 \alpha \right]^{1/2}$  \hspace{1cm} (3.15)

where $\alpha$ is the angle between the axis of the ellipsoid and the Q-vector, $V$ is the volume of the ellipsoid, $R_a$ is the polar radius of the ellipsoid, $R_b$ is the equatorial radius of the ellipsoid and $\Delta \rho$, the contrast, is the scattering length density difference between the scattering ellipsoid and the solvent. For more information, refer to the following reference\textsuperscript{17}

The scattering intensity $I(Q)$ for dilute, randomly oriented, "infinitely large" sheets or lamellae is:

$$I(Q) = scale \frac{2\pi P(Q)}{Q^2 T} + bkg$$  \hspace{1cm} (3.16)

The form factor is:

$$P(Q) = \frac{2\Delta \rho^2}{Q^2} (1 - \cos(Q\sigma)) = \frac{4\Delta \rho^2}{Q^2} \sin^2 \left( \frac{QT}{2} \right)$$  \hspace{1cm} (3.17)

where $T$ is the total layer thickness and $\Delta \rho$ is the difference in the scattering length density between the solvent and the scatterer. For more information, refer to the following reference\textsuperscript{18}

In the case of sufficiently dilute systems, particles are non-interacting and the $P(Q)$ describes the scattering profile. However, often there are interactions between the particles (i.e. repulsion between charged surfactant headgroups) and the scattering data cannot be modeled using the $P(Q)$ alone and a structure factor ($S(Q)$) is applied.
Structure factor, $S(Q)$

The structure factor $S(Q)$ accounts for the types of interactions present within the system, for example: attractive, repulsive or excluded volume, hence relates to interparticle interactions. The structure factor for spherical particles with low attractive interactions can be approximated by a hard-sphere potential, $S_{hs}(Q)$, which is given by:

$$S_{hs}(Q) = \frac{1}{(1 - n_p f(R_{hs} \phi_{hs}))}$$

(3.18)

where $f$ is the atomic form factor, $R_{hs}$ is the hard-sphere radius and $\phi_{hs}$ is the hard-sphere volume fraction. As previously mentioned, $S(Q)$ is equal to one for sufficiently dilute, non-interacting systems. For interacting systems, however, an effective method for reducing $S(Q)$ is by either diluting the system or by addition of a salt.\textsuperscript{2, 19, 20} Figure 3.6 shows schematically the effect of $S(Q)$ on the $I(Q)$ vs. $Q$ SANS plots. Repulsive interactions lead to a push down of $I(Q)$ at low $Q$ values, as commonly observed in charged surfactant micelles. On the other hand, attractive interactions tend to increase the $I(Q)$ at low $Q$ values, as transient large particles are formed.

Figure 3.6: Schematic representation of $P(Q)$ and $S(Q)$ for both repulsive and attractive homogeneous spheres and their contribution to $I(Q)$. Image altered from.\textsuperscript{2}
3.3.3 SANS approximations

The first step in analysing SANS data involves using traditional graphical plots related to limiting forms of the SANS profiles in both low-Q (Guinier region) and high-Q (Porod region) regions, providing information of the particle size and shape. Information regarding these approximations are give below.

**Guinier approximation**

The Guinier approximation relates the low-Q region of the scattering to the radius of gyration \((R_g)\), which represents the effective size of the scattering particle, whether it is a micelle, polymer chain etc.\(^{21, 22}\) The usefulness of this plot stems from the fact that the obtained \(R_g\) is independent of the absolute intensity of any model. In the low-Q region for a dilute system, the single particle form factor \(P(Q,R)\) (Equation 3.12) simplifies to:\(^{23}\)

\[
P(Q,R) = 1 - \frac{Q^2 R_g^2}{3}
\]  
(3.19)

where \(R_g\) is related to the shape of the particles by:

- **Spheres and cylinders** \(R_g = \left(\frac{3}{5}\right)^{1/2} R\) \(R\) = sphere or cylinder radius
- **Thin Discs** \(R_g = \frac{R}{4^{1/2}}\) \(R\) = disc radius
- **Rods** \(R_g = \frac{L}{12^{1/2}}\) \(L\) = rod length

As previously mentioned, \(S(Q)\) is equal to one for sufficiently dilute, non-interacting systems. Hence, assuming that the particles are not interacting and the system is dilute, Equation 3.10 becomes:

\[
I(Q) = \phi_p \Delta \rho^2 V_p \exp \left( - \frac{Q^2 R_g^2}{3} \right) \quad \text{hence} \quad \ln[I(Q)] = \ln[I_o] - \frac{Q^2 R_g^2}{3}
\]  
(3.20)

**Note relationship**: \(1 - X^2 \approx \exp(-X^2)\)

As shown below in Figure 3.7, a plot of \(\ln[I(Q)]\) vs \(Q^2\) yields a linear region with an associated gradient of \(-R_g^2/3\) which is solved to determine \(R_g\) for spherical particles.
Figure 3.7: Typical $\ln[I(Q)]$ vs $Q^2$ Guinier plot for spherical micelles. The gradient of the fitted red line will be $-R_g^2/3$.

The limit for this approximation is such that $QR_g < \sqrt{3}$, which is obtained when the probed range $(2\pi/Q)$ is larger than the particle size (i.e. low-Q domain), see Figure 3.8. It is therefore important that $R_g$ is determined from the correct Q-range.

Figure 3.8: Low Q/ Guinier region. Note that scattering particles are smaller than the probed range.

When analysing the scattering from elongated objects, the Guinier approximation is modified and uses scattering from the intermediate Q-domain. For example, for a cylinder of length $L$ and radius $R$, the intermediate-Q Guinier approximation is:

$$I(Q) = \frac{I_o}{Q} \exp \left( -\frac{Q^2R_g^2}{2} \right)$$  \hspace{1cm} (3.21)
The intermediate-Q Guinier plot of $\ln[Q \cdot I(Q)]$ vs $Q^2$ produces an associated slope $-R_g^2/2$. Hence, the Guinier approximation can be used to determine different geometries by plotting specific functions against $Q^2$. The various geometries, and associated obtained dimension are summarised below:

- $\ln[I(Q)]$ vs $Q^2$ Associated gradient $= -\frac{R_g^2}{3}$ (Sphere)
- $\ln[I(Q) \cdot Q]$ vs $Q^2$ Associated gradient $= -\frac{R_g^2}{2}$ (Cylinder)
- $\ln[I(Q) \cdot Q^2]$ vs $Q^2$ Associated gradient $= -\frac{R_g^2}{1}$ (Disk)

The most probable particle shapes can therefore be predicted through comparison of the three different $I(Q) \cdot Q^x$ vs $Q^2$ plots, and identifying the plot that gives a linear decay.

**Porod approximation**

The intensity in the high-Q domain is from a smaller region than the scattering object and SANS intensity is sensitive to scattering from local interfaces as opposed to the overall inter-particle correlations, as can be seen below in Figure 3.9.

![High Q/ Porod Region](image)

**Figure 3.9:** High Q/ Porod region. Note that scattering particles are larger than the probed range.

The Porod approximation is applied to the high-Q domain for a system of non-interacting particles to determine the fractal dimensions of the scattering object. The Porod law is as follows:
\[ I(Q) = 2\pi \Delta \rho^2 \left( \frac{S}{V} \right) Q^{-4} \]  

(3.22)

where \( S/V \) is the surface to volume ratio (cm\(^{-1}\)). The Porod approximation is valid for smooth interfaces, above a Q value of \( 1/R \). From the Equation below, the average area per surfactant head group, \( A \), can be estimated, with the assumption that all of the surfactants are located at the interface.

\[ A = \left( \frac{S/V}{N_s} \right) \]  

(3.23)

where \( N_s \) is the number density of surfactant molecules (surfactant concentration multiplied by Avogadro’s number). The Porod approximation also allows for estimations of the particle radius (\( R \)) to be made. For example, a plot of \([I(Q).Q^4] \) vs Q (shown in Figure 3.10) produces a first maximum at \( Q \sim 2.7/R \) and a minimum at \( Q \sim 4.5/R \). Simple mathematical manipulation allows determination of the spherical radius.

![Figure 3.10: Typical [I(Q).Q^4] vs Q Porod plot for spherical micelles.](image)

The Guinier and Porod approximations provide simple mathematical relations that allow for first estimations of both the size and shape of colloidal particles.\(^2\) The approximations can only be applied to dilute, non-interacting systems.\(^2\) However, these criteria can be met for non-ideal systems by adding salt to screen interactions between charged micelles, or additional dilution, which would both validate the assumption that \( S(Q) = 1 \) in the low Q domain. These initial approximations are then used to aid in the final fitting procedures.
CHAPTER 3. NEUTRON SCATTERING AND REFLECTIVITY THEORY

3.4 Reflectivity Theory

So far it has been shown that in a SANS experiment, neutrons are able to provide information on the structure of bulk matter. In addition to this, neutrons are also sensitive to surface structure when they are incident on smooth, flat surfaces at sufficiently low angles. Surface reflection of this type is specular, meaning that the angle of incidence, $\theta_i$, is equal to the angle of reflection, $\theta_r$. The reflection of neutrons is of great interest in surface science, since it allows the structure of the uppermost layers of a material to be probed. In this Section, the reader will be given an application-based summary of the fundamental principles underpinning the NR technique, with a particular focus on how this translates into a practical understanding of what can be successfully measured and studied. Before the theory of NR is presented, a brief summary on the reflection of light will be provided.

3.4.1 Reflection of light

It is well known that when light travels from one medium to another with different optical properties (i.e. from air to water), it changes direction and is thus refracted. The degree to which the light is refracted depends upon both the refractive index ($n$) of the media and angle of incidence ($\theta_i$), described as the angle between the ray incident on a surface and the line perpendicular to the surface at the point of incidence, called the normal (see Figure 3.11).

![Figure 3.11: Showing how light is both reflected and refracted when passing through one medium to another with different optical properties.](image-url)
The refractive index of a material is a dimensionless number and describes how fast light can pass through the material:

\[ n = \frac{c}{v} \quad (3.24) \]

where \( c \) is the speed of light in a vacuum and \( v \) is the phase velocity of light in the material. The refractive indices are 1.00 and 1.33 respectively for air and water, meaning that light will travel 1.33 times slower in water compared to air. For example, if light moves from a medium of refractive index \( n_1 \) to a medium of \( n_2 \), with an incidence angle to the surface normal of \( \theta_1 \), the refraction angle \( \theta_2 \) can be calculated from Snell’s law:

\[ n_1 \sin \theta_1 = n_2 \sin \theta_2 \quad (3.25) \]

hence, when light passes from air to water (higher refractive index), the angle of refraction is smaller than the angle of incidence and light will be refracted towards the normal. The higher the refractive index, the closer to the direction of the normal the light will refract.

### 3.4.2 Reflection of neutrons

The total reflection of thermal neutrons was first demonstrated by Fermi et al.\textsuperscript{26} and since then has become an important technique within surface science.\textsuperscript{25} The phenomenon follows the same fundamental equations as described above, but with different refractive indices. The neutron refractive index of a material is a function of both the scattering length density (SLD) of its constituent nuclei and the neutron wavelength. It can be calculated using conservation of energy, i.e. the kinetic energy (total) of the neutron in a vacuum is the same as total energy of the neutron inside the medium. The kinetic energy of a neutron is given by:

\[ E = \frac{\hbar^2 K^2}{2m} \quad (3.26) \]

where \( \hbar \) is the reduced Planck’s constant (\( \hbar = \frac{h}{2\pi} \)), \( K \) is the incident wave vector and \( m \) is the mass of the neutron. The total energy inside the medium is given by the kinetic energy of a neutron plus the average potential inside of the medium:

\[ E = \frac{\hbar^2 K^2}{2m} + \nabla \quad (3.27) \]
where \( V = \frac{2\pi \hbar^2}{m} \rho \) and \( \rho \) is SLD. Conservation of energy gives:

\[
\frac{\hbar^2 K^2}{2m} = \frac{\hbar^2 K'^2}{2m} + V \quad \text{hence} \quad K'^2 - K^2 = 4\pi \rho
\]  

(3.28)

since the refractive index is given by \( \frac{K'}{K} \), and \( K \) is given by \( \frac{2\pi}{\lambda} \), the refractive index simplifies to:

\[
n \approx 1 - \frac{\lambda^2 \rho}{2\pi}
\]  

(3.29)

As with light, total reflection may occur when neutrons pass from a medium of higher refractive index to one of lower refractive index. Since the refractive index for most media is less than unity, by typically of the order of \( 10^{-6} \), total external reflection is observed at very small critical glancing angles instead of the total internal reflection experienced with light.\(^{25}\)

### 3.4.3 NR measurements

The reflection of neutrons is shown in Figure 3.12. As with SANS, only elastic scattering is considered in NR. This is when the moduli of the incident and reflected wave vectors, \( K \) and \( K' \) are equivalent (\(|K| = |K'|\)).\(^2\) The neutrons undergo specular reflection, which has already been defined as when \( \theta_i = \theta_r \).

![Figure 3.12: Geometry of the incident and scattered wave vectors (K and K') and the associated scattering vector (Q).](image-url)
Hence, the scattering vector, \( Q \), is perpendicular to the material surface (Z direction), and is given as:

\[
Q = \frac{4\pi\sin\theta}{\lambda}
\]  

(3.30)

where the terms have the same definitions as already defined.

The essence of a neutron reflection experiment is to measure the reflected intensity \( R(Q) \) as a function of \( Q \). This can be controlled by varying either the \( \lambda \) of the incident neutron beam or changing the angle of incidence, \( \theta \). If the neutron beam contains a range of \( \lambda \) (ISIS, spallation source) then for a given angle \( \theta \), a range of \( Q \) will be provided. In the case of a monochromatic beam (ILL, continuous source), the range of \( Q \) is controlled by adjusting the incident angle.

For a plane wave incident upon a surface, if the first medium is air \( n_1 \approx 1 \), total external reflection occurs below a critical edge \( Q_c \), defined as:

\[
Q_c = \sqrt{\frac{16\pi\Delta\rho}{}}
\]  

(3.31)

where \( \Delta\rho \) is the difference in SLD between the two media of interest. For a clean D\(_2\)O surface, \( Q_c \) appears at \( \sim 0.018 \) Å\(^{-1} \), below which \( R(Q) = 1 \). The region in which \( R(Q) = 1 \) is utilised to determine instrument calibration scale factors.\(^2\) Above \( Q_c \), the reflectivity falls off sharply as \( Q^{-4} \), as shown in Figure 3.13.

![Figure 3.13: Specular reflection from a D\(_2\)O surface, showing both the critical edge (\( Q_c \)) and the sharp \( Q^{-4} \) reflectivity fall off below \( Q_c \).](image)

74
3.4.4 Modeling of NR data

NR is used to investigate variations in the composition and thickness of thin layers as a function of depth averaged over the horizontal plane of the sample. The experimental reflectivity is related to the square of the Fourier transform of the scattering length density (SLD), $\rho(z)$, normal to the surface. For neutrons, $\rho(z) = \Sigma_i n_i(z) \cdot b_i$, where $n_i$ and $b_i$ are the number density and scattering length of the $i$th component and $z$ is the direction perpendicular to the surface. For surfactant films of this kind, the measured reflectivity curve can be modeled in terms of a single, uniform layer to fit for thickness, $\tau$, and a scattering length density, $\rho$. These values are related to the surface coverage, $\Gamma$, and area per molecule, $A$, in the following way:

$$A = \frac{\Sigma b_i}{\rho \tau} = \frac{1}{\Gamma N_a} \quad (3.32)$$

where $\Sigma b_i$ is the sum of neutron scattering lengths of nuclei over the surfactant molecule, $\Gamma$ is the surface coverage and $N_a$ is the Avogadro number. Therefore analysis of the NR data provides a direct probe of the surface density parameters of surfactant molecules at the air/water interface, which can be directly compared with surface tension measurements with analysis using the Gibbs adsorption isotherm.
References


Chapter 4

Surface and bulk properties of fluorocarbon surfactants in fire-fighting foams

Hypothesis: Reports on the colloidal and interfacial properties of fluorocarbon (FC) surfactants used in fire-fighting foam formulations are rare. This is primarily because these formulations are complex mixtures of different hydrocarbon (HC) and fluorocarbon (FC) surfactants. By developing a greater understanding of the individual properties of these commercial FC surfactants, links can be made between structure and respective surface/bulk behaviour. Improved understanding of structure-property relationships of FC surfactants will therefore facilitate the design of more environmentally responsible surfactant replacements.

Experiments: Surface properties of three partially fluorinated technical grade surfactants were determined using tensiometry and neutron reflection (NR), and compared with a research-grade reference surfactant (sodium perfluorooctanoate (NaPFO)). To investigate the bulk behaviour and self-assembly in solution, small-angle neutron (SANS) scattering was used.

Findings: All FC surfactants in this study generate very low surface tensions (<20 mN m\(^{-1}\)) which are comparable, and in some cases, lower than fully-fluorinated surfactant analogues. The complementary techniques (tensiometry and NR) allowed direct comparison to be made with NaPFO in terms of adsorption parameters such as surface excess and area per molecule. Surface tension data for these technical grade FC surfactants were not amenable to reliable interpretation using the Gibbs adsorption equation, however NR provided reliable results. SANS has highlighted how changes in surfactant head group structure can affect bulk properties. This work therefore provides fresh insight into the structure property relationships of some industrially relevant FC surfactants, highlighting properties which are essential for development of more environmentally friendly replacements.

4.1 Introduction

Hydrocarbon fuel fires pose a serious threat and as such require a rapid response. Hence, effective and efficient fire-extinguishing agents are needed to prevent reignition of these fires. Historically, water has long been used for suppressing fires, however it is ineffective for oily liquid fuel fires.\(^1\) Early advances (1920s - 1950s) in fire-fighting found that incorporation of proteinacious materials, such as hydrolysed hoof and horn meal, as well as other natural products, namely saponine or liquorice were beneficial.\(^1\)\(^,\)\(^2\) The 1960s saw progress mainly in the use of synthetic surfactant formulations, which lead to the development of what are now known as aqueous film forming foams (AFFFs). AFFFs were and still are the most effective formulations for extinguishing fires involving flammable liquid fuels.\(^3\) As with most commercial formulations, AFFFs comprise complex mixtures, incorporating major components such as a solvent (typically a glycol ether), fluorocarbon (FC) (perfluorinated anionic
Fluorocarbon (FC) surfactants are distinctly different from hydrocarbon (HC) surfactants in various respects. Although the polar headgroups of HC and FC surfactants may be similar, non-polar FC tails have both hydrophobic and oleophobic (oil-repelling) properties, compared to HC surfactants which are considered to be only hydrophobic. Hence, FC surfactants exhibit both hydrophobic and oleophobic characteristics, which in fire-fighting applications, account for their effectiveness. In addition to this, FC surfactants generally display greater surface activity compared to HC analogues. Fluorine has a lower polarisability than hydrogen; therefore, the total dispersion interaction is lower for the interaction between fluorinated chains. Hence, FC surfactants are expected to have weaker attractive intermolecular forces than similar HC surfactants. In comparison to those of analogous HC, FC surfactants have larger volume of perfluoroalkyl moieties and larger limiting cross-sectional area. As a result, FC surfactants show an enhanced tendency to self-assemble, and collect at the air-water interface to reduce the surface energy. For this reason, incorporation of FC surfactants into AFFFs leads to an increase in spreading coefficient over a hydrocarbon fuel surface, therefore more efficient extinguishment. More information can be found in the following references.

Although FC surfactants have many useful interfacial properties, and appear in a diverse range of applications, it has been known for many years that they are not environmentally friendly. For example, it has been identified that FC with C₈ - C₁₅ chain lengths are hazardous pollutants. These molecules eventually break down to form PFOS (perfluorooctanesulphonate) and PFOA (perfluorooctanoic acid), which are recognised as having negative impacts on the environment and human health due to pronounced persistence, variable degrees of bioaccumulation potential and toxicity. Although new FC surfactants have been designed which are not bioaccumulative or toxic, the strength of the C-F bond hinders biodegradability.

The current understanding underpinning the use of AFFFs for fire-fighting applications is primitive and largely empirically based. As a result of this, few attempts have been made to model or investigate the behaviour of fire-fighting foam formulations from chemical perspectives. Therefore, it is important to develop a more fundamental understanding of how the surfactants adsorb and self-assemble, both individually and as mixed systems in mimics of the real formulations (FC: HC surfactant mixtures).

This study is based on understanding the important structure-property relationships for individual FC surfactants used in typical fire-fighting foam applications. Studies with techniques such as force tensiometry, neutron reflection (NR) and small-angle neutron scattering (SANS) have allowed the determination of the important properties of typical AFFF FC surfactants from a chemical perspective. As well, this
work demonstrates how changing the head group on a FC surfactant (anionic, non-ionic and zwitterionic) feeds through to marked changes to the interfacial properties of the surfactants.

4.2 Materials and Methods

4.2.1 Materials

The preparation of the partially fluorinated surfactants has been described in Chapter 2. NaPFO (CAS 335-95-5) was prepared and purified by the following method. Perfluorooctanoic acid (CAS 335-67-1) of stated purity $\geq 99\%$ was obtained from Fluorochem, converted into the appropriate metal salt by reaction with the stoichiometric amount of sodium hydroxide, and purified by recrystallisation from a mixture of ethanol and propanol (1:1, vol:vol). Pyrene (Acros, puriss $\geq 99\%$), deuterium oxide (Aldrich, 99.9 %) were used as received.

<table>
<thead>
<tr>
<th>Surfactant Name</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td><img src="image" alt="Dynax DX1030" /></td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td><img src="image" alt="Dynax DX2200" /></td>
</tr>
<tr>
<td>Capstone 1157</td>
<td><img src="image" alt="Capstone 1157" /></td>
</tr>
<tr>
<td>Sodium Perfluorooctanoate</td>
<td><img src="image" alt="Sodium Perfluorooctanoate" /></td>
</tr>
</tbody>
</table>

Table 4.1: Surfactants used in this Chapter

4.2.2 Methods

Surface Tension Measurements

Surface tension measurements were carried out on a Krüss K100 force tensiometer using the Wilhemy plate method at $25^\circ C$. The method used for the measurements,
along with cleaning steps were discussed in Chapter 2.

**Fluorescence**

Fluorescence measurements were carried out as described in ref\(^{17}\) in quartz cuvettes at 25 °C on a Cary Eclipse (Varian) Fluorescence spectrometer. The method used for the measurements were discussed in Chapter 2.

**Dynamic Surface Tension measurements**

Surface tension measurements were carried out on a Krüss BP100 bubble pressure tensiometer at 25 °C. The method used for the measurements, along with cleaning steps were discussed in Chapter 2.

**Neutron Reflection**

Neutron reflection (NR) measurements were conducted using the INTER beam-line on Target Station 2 at the ISIS facility (Rutherford Appleton Laboratory, Didcot, UK).\(^{18}\) Measurements were taken using a single point detector and fixed grazing incidence angles (0.8° and 2.3°). The absolute reflectivity was calibrated with respect to the direct beam and the reflectivity from a clean D\(_2\)O surface. The NR experiments were carried out in two contrasts, pure D\(_2\)O and null reflecting water (NRW; 8 mol% D\(_2\)O in H\(_2\)O with an SLD of 0). A pippette was used on each sample to suck off any air bubbles and also to remove the initial surface layer in case any hydrophobic impurities were present. The data were fit using MOTOFIT, written for IGOR Pro.\(^{19}\)

**Small-Angle Neutron Scattering**

SANS measurements were performed on SANS 2D at the ISIS facility (Rutherford Appleton Laboratory, Didcot, UK) and D33 at the Institut Laue-Langevin (ILL, Grenoble, France). On SANS 2D, a simultaneous \(Q\)-range of 0.004 – 0.6 Å\(^{-1}\) was achieved with a neutron wavelength range of 1.75 < \(\lambda\) < 15.5 Å and a source-sample-detector distance \(L1 = L2 = 4\) m. The D33 instrument used neutrons with a wavelength of \(\lambda\) = 6 Å and two sample-detector positions (2 and 7.5 m) providing an accessible \(Q\) range of 0.005 – 0.2 Å\(^{-1}\). All samples were made in D\(_2\)O, using 2 mm path length rectangular quartz cells at a 25 °C. Raw SANS data were reduced by subtracting the scattering of the empty cell and the D\(_2\)O background and normalised to an appropriate standard using the instrument-specific software. SANS data were fit using the analysis package SasView.
4.3 Equilibrium surface tensions and critical micelle concentrations (CMCs)

Important parameters to determine for surfactants are how effective they are at reducing aqueous surface tension ($\gamma$) and respective critical micelle concentrations (CMCs). In fire-fighting applications, properties such as foamability, foam stability and spreading are linked to $\gamma$ reductions. For example, it is often believed that employing surfactants at their CMCs gives the best foam performance.\(^{20}\)

Results from characterisation of the pure research-grade surfactant, sodium perfluorooctanoate (NaPFO) were compared to literature data.\(^{21, 22}\)

4.3.1 Properties of NaPFO

An equilibrium $\gamma$ vs. ln (concentration) plot of NaPFO is shown in Figure 4.1 having a clear break point at the CMC, with no minimum or shoulder, which would be indicative of hydrophobic impurities. The CMC was determined by taking the second derivative of the $\gamma$ vs. ln(concentration) plots, and then applying a Gaussian distribution function, where the minimum was taken to be the value of the CMC. This method is described in the Appendix.\(^{23}\) Quartic functions were then fit through the pre-CMC surface tension data, to generate local tangents, then the Gibbs adsorption isotherm was used to estimate the surface excess ($\Gamma_{\text{CMC}}$) and the area per molecule ($A_{\text{CMC}}$) at the CMC (see Chapter 1 for more information), data shown in Table 4.2.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$\gamma_{\text{CMC}}$/ (mN m$^{-1}$)</th>
<th>CMC/ (mM)</th>
<th>$\Gamma_{\text{CMC}}$/ (10$^{-6}$ mol m$^{-2}$)</th>
<th>$A_{\text{CMC}}$/ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaPFO (This Study)</td>
<td>22.6 ± 0.1</td>
<td>25.00 ± 0.05</td>
<td>4.07 ± 0.20</td>
<td>40 ± 2</td>
</tr>
<tr>
<td>NaPFO (Literature)</td>
<td>24.6</td>
<td>30.0</td>
<td>4.0</td>
<td>42</td>
</tr>
</tbody>
</table>

Table 4.2: Results from surface tension measurements of NaPFO from this study compared to literature.\(^{21, 22}\)
Figure 4.1: (a) Surface Tension vs. ln(Concentration) for NaPFO. (b) Adsorption isotherm of NaPFO. Line fitted to pre-CMC data is a quartic function. T = 25 °C.

Similar results for NaPFO have been reported for both $\Gamma_{\text{CMC}}$ and $A_{\text{CMC}}$ and are comparable to the results achieved here.$^{21,22}$ This shows that the standard tensiometric method used here is amenable for analysis of pure research-grade FC surfactants of this kind.
4.3.2 Technical grade surfactants

Equilibrium $\gamma$ vs. $\ln$(concentration) plots for the three FC surfactants are shown in Figure 4.2. Dynax DX2200 (non-ionic) and Capstone 1157 (zwitterionic) show clear break points at their respective CMCs, therefore relatively accurate CMC values can be determined. On the other hand, Dynax DX1030 (anionic) shows a minimum in the curve, followed by an increase in surface tension, which is indicative of hydrophobic impurities, as first recognised by Mysels et al.\textsuperscript{24, 25} CMCs were determined using the same method as previously mentioned, this is also true for calculation of both the surface excess ($\Gamma_{\text{CMC}}$) and the area per molecule ($A_{\text{CMC}}$), data shown in Table 4.3. Although it has been possible to attain CMC values, fluorescence probe measurements have been used to provide additional CMC values, showing good agreement. Data presented in the Appendix.

![Figure 4.2: Surface Tension vs. ln(Concentration) for the three technical grade FC surfactants. Lines fitted to pre-CMC data are quartic functions. T = 25 °C.](image)

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$\gamma_{\text{CMC}}$/ (mN m$^{-1}$) ± 0.1</th>
<th>CMC/ (mM) ± 0.05</th>
<th>$\Gamma_{\text{CMC}}$/ (10$^{-6}$ mol m$^{-2}$) ± 0.2</th>
<th>$A_{\text{CMC}}$/ (Å$^2$) ± 0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td>19.2 ± 0.1</td>
<td>1.37 ± 0.05</td>
<td>1.8 ± 0.2</td>
<td>93 ± 3</td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td>19.6 ± 0.1</td>
<td>0.02 ± 0.02</td>
<td>4.1 ± 0.1</td>
<td>41 ± 2</td>
</tr>
<tr>
<td>Capstone 1157</td>
<td>15.6 ± 0.1</td>
<td>0.23 ± 0.02</td>
<td>5.8 ± 0.1</td>
<td>28 ± 1</td>
</tr>
</tbody>
</table>

Table 4.3: Results from surface tension measurements of the three technical grade FC surfactants.

Due to the nature of the surfactants, and the irregular forms of these surface tension isotherms (Figure 4.2), it is clear that problems will arise when attempting
to use the Gibbs adsorption isotherm as described above. This is reflected in the erratic and sometimes unphysical data shown in Table 4.3, and obtained results should therefore be considered with caution. Taking the surface tension curve of Dynax DX1030 as an example, it can be seen that the line fitted through the data is straight, suggesting from the Gibbs adsorption isotherm that $\Gamma$ is essentially constant. However, this clearly cannot be the case, as the surface tension is reducing. It might be expected that NaPFO and anionic Dynax DX1030 should achieve similar values for both surface excess and $A_{\text{CMC}}$ due to their similar tail structures and head groups, however, this is also not seen in the results. Dynax DX1030 was found to have an $A_{\text{CMC}}$ two times larger and a surface excess lower than NaPFO, suggesting that use of the Gibbs adsorption isotherm for these technical grade surfactants should be treated with caution. In addition, anionic Dynax DX1030 and zwitterionic Capstone 1157 are similar in both molecular size and level of fluorination (see structures in Table 4.1), therefore similar values for $A_{\text{CMC}}$ and $\Gamma_{\text{CMC}}$ would be expected. The anionic charge on Dynax DX1030 would be expected to cause an increase in $A_{\text{CMC}}$; and thus a decrease in $\Gamma_{\text{CMC}}$ due to head group repulsion, however the difference observed between Capstone 1157 and Dynax DX1030 does not fit in with this. Dynax DX2200 is non-ionic with repeating acrylamide units: a similar molecule was studied by Dupont $et\ al.$\textsuperscript{26} Their work was carried out with a tris(hydroxymethyl)acrylamidomethane (THAM)-derived telomer bearing a perfluorohexyl hydrophobic chain. In that case, $\Gamma_{\text{CMC}} = 2.68 \times 10^{-6}$ mol m$^{-2}$ and a $A_{\text{CMC}}$ of $62 \pm 2$ Å$^2$, was observed.

Therefore, it seems that using tensiometric techniques and analysis with the Gibbs adsorption isotherm is not appropriate for accurate detail on the interfacial properties of these technical grade FC surfactants, resulting in unphysical values for both $A_{\text{CMC}}$ and $\Gamma_{\text{CMC}}$. As a way to circumvent this issue and to determine these important parameters of interest, Neutron Reflectivity has been employed and these data will be discussed in Section 4.5.

### 4.4 Dynamic surface tension

Another important property to determine for the partially fluorinated surfactants is the dynamic surface tension (DST or $\gamma(t)$). When a fresh interface is formed, surfactant molecules must first diffuse from the bulk of the solution to the interface, before adsorbing at the air/water interface. This dynamic process means that the equilibrium surface tension ($\gamma_{\text{eq}}$) of a surfactant solution is not achieved instantaneously.\textsuperscript{27} Taking the example of fire-fighting foams, previous results have shown that fast DST behaviour leads to both quicker foam formation and formation of wetter foams, both of which are required for effective fire extinguishment.\textsuperscript{8, 27, 28} In addition to this, fast DST behaviour is required so that the very low $\gamma_{\text{CMC}}$ values
achieved by FC surfactants can be reached quickly. Here, the DST behaviour of the three partially fluorinated surfactants have been investigated using a Krüss BP100 at multiple concentrations above and below the respective CMCs and compared to the theoretical behaviour predicted by the diffusion-only model determined by Miller et al.29 (Equations 1.8 and 1.11 in Chapter 1).

For each surfactant, the $\gamma(t)$ was measured as a function of surface age over a period of 0.10 - 100 s, and each measurement was repeated three times to ensure reproducibility. The average data over the three repeats has been presented here, but the data for each run is included in the Appendix to display the reproducibility in the data collection. The DST curves for the three partially fluorinated surfactants at multiple concentrations are displayed below in Figure 4.3.
Figure 4.3: Dynamic surface tension of Dynax DX1030, Dynax DX2200 and Capstone 1157 at concentrations above and below the respective CMCs. CMC data is shown in Table 4.3. Note in log scale: $3 = 10^3$ ms. $T = 25 \degree C$.

Different $\gamma(t)$ decay behaviours are observed for the three FC surfactants. The two small molecule surfactants, Dynax DX1030 and Capstone 1157 (see structures in Table 4.1) both show relatively fast $\gamma(t)$ decays, reaching $\gamma_{eq}$ during the timescale of the experiment at concentrations above the respective CMCs. Non-ionic Dynax DX2200 has relatively slow DST behaviour, and does not reach $\gamma_{eq}$ within the timescale of the experiment. This is commensurate with previous studies on large molecular weight surfactants.\textsuperscript{30, 31} Dynax DX2200 has a larger $A_{CMC}$ compared to the other two FC surfactants, see below in Section 4.5, and the larger size of the surfactant is therefore likely to cause increased back diffusion due to less ‘vacant’ adsorption sites being available.\textsuperscript{27}

As stipulated by Miller et al., employment of the diffusion-only controlled models at short and long time limits can be used when $\gamma(t)$ is close to either the tension of the solvent ($\gamma_0$) or $\gamma_{eq}$ as $t \rightarrow 0$ or $\infty$, respectively.\textsuperscript{29} At concentrations below 5 x CMC, the data for Capstone 1157 has both an initial $\gamma_1 = \gamma_0$ and reaches $\gamma_{eq}$ during the timescale of the experiment, therefore representing data amenable for analysis using the diffusion controlled models at both short and long time limits. For Dynax DX1030 as $t \rightarrow 0$ $\gamma(t) \neq \gamma_0$ and as such can only be analysed appropriately at long times. For Dynax DX2200 as $t \rightarrow \infty$ $\gamma(t) \neq \gamma_{eq}$ and can therefore only be analysed appropriately at short times. Plots of $\gamma(t)$ vs. $t^{1/2}$ and $t^{-1/2}$ provide the DST decay at both short and long times in line with Equations 1.8 and 1.11 (Chapter 1). The plots for all three FC surfactants are shown below in Figure 4.4.
Figure 4.4: Dynamic surface tension of the three FC surfactants plotted vs. $t^{1/2}$ and $t^{-1/2}$. The lines are least square fits to the data. The concentrations and temperatures are the same as in Figure 4.3.
CHAPTER 4. SURFACE AND BULK PROPERTIES OF FLUOROCARBON SURFACTANTS IN FIRE-FIGHTING FOAMS

From the short time limit plots (Figures 4.4a, 4.4c and 4.4e), data become linear as $\gamma(t)$ approaches $\gamma_0$ and $t \to 0$. The issue with employing the short time approximation for Dynax DX1030 becomes clear from this plot, whereby it can be seen as $t \to 0 \gamma(t) \neq \gamma_0$. For this reason, the solvent tension variable has been allowed to float in the fit, thus become linear as $\gamma(t)$ approaches "$\gamma_0$". Using this method has been previously reported to describe the DST behaviour of highly surface active partially fluoinated surfactants.\textsuperscript{32}

For the long time plots (Figures 4.4b, 4.4d and 4.4f), data become linear as $\gamma(t)$ approaches $\gamma_{eq}$ and $t \to \infty$. Even though the data for Dynax DX2200 do not pass through $\gamma_{eq}$ as $t \to \infty$, the fitted function can be fixed to the $\gamma_{CMC}$ of Dynax DX2200 (see Table 4.3), therefore allowing appropriate analysis to be carried out in line with Miller \textit{et al.}\textsuperscript{29} As mentioned in Chapter 1, the effective surfactant diffusion coefficients ($D_{eff}$) can be calculated from the straight line region gradients using Equations 1.9 and 1.12. These data are shown below in Table 4.4.

<table>
<thead>
<tr>
<th>Concentration/ (x CMC)</th>
<th>Short time diffusion</th>
<th>Long time diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gradient/ $\gamma(t)$</td>
<td>$D_{eff}$/ 10$^{-10}$ m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Dynax DX1030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>-35.0</td>
<td>0.13</td>
</tr>
<tr>
<td>1.25</td>
<td>-37.5</td>
<td>0.15</td>
</tr>
<tr>
<td>0.63</td>
<td>-49.0</td>
<td>1.04</td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>-0.84</td>
<td>0.36</td>
</tr>
<tr>
<td>1.25</td>
<td>-0.30</td>
<td>0.18</td>
</tr>
<tr>
<td>0.63</td>
<td>-0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>Capstone 1157</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>-40.5</td>
<td>5.83</td>
</tr>
<tr>
<td>1.25</td>
<td>-19.0</td>
<td>5.13</td>
</tr>
<tr>
<td>0.63</td>
<td>-6.0</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Table 4.4: Effective diffusion coefficients calculated from the diffusion-only controlled models at short and long time limits for Dynax DX1030, Dynax DX2200 and Capstone 1157. The CMC data for the FC surfactants is presented in Table 4.3.

Comparable $D_{eff}$ values for both Dynax DX1030 and Capstone 1157 would be expected due to the similarities in both molecular weight and chemical structure. At the short time diffusion limit, when Dynax DX1030 is at a concentration of 0.63 x CMC, similarities are observed between the two FC surfactants. At this concentration, as $t \to 0$, $\gamma(t)$ gets the closest to the solvent tension, therefore providing a more realistic value for $D_{eff}$ compared to the higher concentration samples. Previously reported $D$ values for similar sized ionic HC\textsuperscript{33} and FC\textsuperscript{34} surfactants are on the order of 10$^{-10}$ m$^2$ s$^{-1}$, therefore providing agreement with the results presented here.
As expected, the $D_{\text{eff}}$ values for the higher molecular weight Dynax DX2200 are lower than for the small molecule surfactants (disregarding the high concentration Dynax DX1030 data). This is the expectation due to the observed slower DST behaviour (Figure 4.3b). As previously mentioned, even though the data for Dynax DX2200 does not pass through $\gamma_{\text{eq}}$ as $t \to \infty$, it was possible to fix the fitted function to the $\gamma_{\text{CMC}}$, however this was not possible for the 0.63 x CMC sample, hence the anomalous $D_{\text{eff}}$ value. It should be noted that for similar high molecular weight surfactants, $D_{\text{eff}}$ values on the order of $10^{-11}$ m$^2$ s$^{-1}$ have been shown.$^{27}$

The short time diffusion coefficients allow for theoretical modeling of DST data at both short and long times to determine whether surfactant adsorption is a diffusion-only process (more information in Chapter 1). The short time $D_{\text{eff}}$ values in Table 4.4 and $\Gamma$ data presented in Section 4.5 were used for data modeling. Figure 4.5 shows the data and theoretical models for all of the FC surfactants.
Figure 4.5: DST curves for Dynax DX1030, Dynax DX2200 and Capstone 1157 at concentrations of 1.25 x CMC, 1.25 x CMC and 0.63 x CMC, respectively. The red lines theoretical calculations using Equations 1.8 and 1.11, respectively. Note: the long time model has been used to predict the $\gamma(t)$ of Dynax DX2200 at longer times than measured.

For all of the FC surfactants, good agreement between the theoretical and experimental results are generally observed at short times, with the $\gamma(t)$ decay being well described by the model. This is a clear indication of the diffusion-controlled nature of the short time $\gamma(t)$ decay, as has been commonly observed in both FC and HC surfactants.27, 30, 32, 34–36 The short time diffusion controlled mechanism is due to initial low $\Gamma$ values, more vacant sites are available for adsorption and less back diffusion is expected. However, now considering the end of the decay, when $\Gamma$ is approaching $\Gamma_{eq}$, there is now less agreement between theoretical and experiment results, with the theoretical models generally predicting lower tensions than have been measured. This behaviour is consistent with the presence of a weak adsorption barrier, and the process is therefore no longer diffusion controlled at long times.27, 30, 35

These results have therefore provided important insight into the DST behaviour of the three FC surfactants, with results showing generally consistent behaviour with previous literature on both FC and HC surfactants.27, 30, 32, 34–36 In Chapter 5, the DST behaviour of FC: HC surfactant mixtures is investigated, and these results will therefore act as a reference point for the analysis.
4.5 Neutron reflectivity

Using NR to study FC surfactants on null reflecting water (NRW, i.e. \( \rho_{\text{NRW}} = 0 \, \text{Å}^{-2} \)), the surface coverages can be determined directly from analyses of the reflectivity profiles \( R(Q) \).\textsuperscript{26, 37} Data were modeled in terms of a single uniform layer to fit for monolayer thicknesses, \( \tau \), and scattering length densities \( \rho \). Attempts were made to model data using two layer models, leading to the same fitted parameters. Data are shown in the Appendix. Molecular areas and surface excesses were then calculated using Equations shown in Chapter 3. The normalised reflectivity curves for each studied FC surfactant in NRW can be found in the Appendix.

4.5.1 NaPFO

As for tensiometry, NaPFO was initially characterised to validate the method and ensuing analyses. For this reason, and to make the most efficient use of expensive beam time, only three data points were measured. The parameters from analysis of the NaPFO \( R(Q) \) data can be found in Table 4.5 and the \( \Gamma \) vs. concentration plot calculated can be seen below in Figure 4.6. Here, similar results have been reported when comparing to fitted parameters found in the literature.\textsuperscript{21, 22, 38}

![Figure 4.6: Surface excess of NaPFO obtained by analysis of neutron reflectivity data. Critical micelle concentration was taken as 25 mM. \( T = 25 \, ^\circ\text{C} \).]
## Table 4.5: Parameters from analysis of Neutron Reflection Data of NaPFO.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$\rho$/ (10^{-6} Å^{-2})</th>
<th>$\tau$/ (Å)</th>
<th>$\Gamma_{\text{CMC}}$/ (10^{-6} mol m^{-2})</th>
<th>$A_{\text{CMC}}$/ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaPFO (This Study)</td>
<td>2.50</td>
<td>15.0 ± 0.5</td>
<td>4.05 ± 0.10</td>
<td>41.0 ± 2.0</td>
</tr>
<tr>
<td>NaPFO (Literature)</td>
<td>1.80</td>
<td>18.0 ± 0.5</td>
<td>4.00</td>
<td>42</td>
</tr>
</tbody>
</table>

$\rho$ is the fitted scattering length density, $\tau$ the fitted monolayer thickness, $\Gamma_{\text{CMC}}$ is the surface excess concentration at the CMC and $A_{\text{CMC}}$ is the area per molecule at the CMC.

Comparisons can also be made between NR and surface tension data in terms of both $\Gamma_{\text{CMC}}$ and $A_{\text{CMC}}$. A high degree of agreement should be noted between these two complementary techniques: $\Gamma_{\text{CMC}} = 4.07 \pm 0.20 \times 10^{-6}$ mol m$^{-2}$ (ST) and $4.05 \pm 0.10 \times 10^{-6}$ mol m$^{-2}$ (NR), $A_{\text{CMC}} = 40 \pm 2$ Å$^2$ (ST) and $41 \pm 2$ Å$^2$ (NR). These results therefore show how using both standard tensiometric methods in conjunction with NR can provide directly comparable results, and are both therefore amenable for analysis of research-grade FC surfactants.

### 4.5.2 Technical Grade Surfactants

It was previously shown that using common tensiometric techniques did not allow accurate analysis of parameters such as $\Gamma_{\text{CMC}}$ and $A_{\text{CMC}}$ for the technical grade FC surfactants. Therefore, the basis of this section is to determine whether these important surfactant parameters can be obtained using NR. All surfactants studied in this section have been subject to the same analysis as previously shown for NaPFO. Presented in Table 4.6 are the fitted values for analyses of the NR data, and the $\Gamma$ vs. concentration plots for the three technical grade surfactants are shown in Figure 4.7.
Comparing the results for the technical grade surfactants with the NaPFO, it can be seen that as might be expected owing to the similarities in chemical structure (Table 4.1) Dynax DX1030 and NaPFO have similar values for both $A_{\text{CMC}}$ and $\Gamma_{\text{CMC}}$. Different thicknesses are expected due to Dynax DX1030 having the additional CH$_2$ groups. Dynax DX1030 and Capstone 1157 have very similar overall molecular size and tail structures, therefore as expected comparable values are observed for fitted layer thickness ($\tau$), 26.5 ±1.0 Å and 23.0 ±0.5 Å respectively. Although they are similar in size, differences are observed when considering both $A_{\text{CMC}}$ and $\Gamma_{\text{CMC}}$, because Dynax DX1030 is anionic and Capstone 1157 zwitterionic. Dynax DX1030 has a larger area per molecule and thus lower surface excess to Capstone 1157, due to charge repulsion between head groups. Comparing ST and NR for Capstone 1157, there are similarities between the values for both $\Gamma_{\text{CMC}}$ and $A_{\text{CMC}}$: $\Gamma_{\text{CMC}} = 5.80 \pm 0.1 \times 10^{-6}$ mol m$^{-2}$ (ST) and $5.22 \pm 0.10 \times 10^{-6}$ mol m$^{-2}$ (NR), $A_{\text{CMC}} = 28 \pm 1$ Å$^2$ (ST) and $31 \pm 1$ Å$^2$ (NR). Capstone 1157 was found to be the most amenable to tensiometric measurements and analysis, see Table 4.3. Another important comparison to make is between the cross-sectional area of a single FC chain, which is approximately 28 Å$^2$. Well packed FC surfactant monolayers generate a low limiting value of $\gamma_{\text{CMC}}$ of 15 mN m$^{-1}$. This value represents the physical limit at which these surfactant molecules can pack at an air-water interface, therefore leading to the lowest achievable value of $\gamma_{\text{CMC}}$. With this in mind, it is
interesting to observe the easy to follow trend between $A_{\text{CMC}}$ and limiting value of $\gamma_{\text{CMC}}$ between the technical surfactants in this study. The molecule with the largest $A_{\text{CMC}}$ (Dynax DX2200) has a $\gamma_{\text{CMC}}$ of $\sim 20$ mN m$^{-1}$ (Table 4.3). Capstone 1157 has the lowest $A_{\text{CMC}}$ of the three technical surfactants (comparable to that of a single fluorocarbon chain), explaining the low observed $\gamma_{\text{CMC}}$ of $\sim 16$ mN m$^{-1}$.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$\rho$ / $(10^{-6}$ Å$^{-2})$</th>
<th>$\tau$ / (Å)</th>
<th>$\Gamma_{\text{CMC}}$ / $(10^{-6}$ mol m$^{-2}$)</th>
<th>$A_{\text{CMC}}$ / (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td>1.35</td>
<td>26.5 ± 1.0</td>
<td>3.95 ± 0.20</td>
<td>42.5 ± 2.0</td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td>2.55</td>
<td>25.0 ± 2.0</td>
<td>2.50 ± 0.10</td>
<td>65.0 ± 0.5</td>
</tr>
<tr>
<td>Capstone 1157</td>
<td>2.00</td>
<td>23.0 ± 0.5</td>
<td>5.22 ± 0.10</td>
<td>31.0 ± 1.0</td>
</tr>
</tbody>
</table>

Table 4.6: Parameters from analyses of neutron reflectivity data of the three technical grade FC surfactants. $\rho$ is the fitted scattering length density, $\tau$ the fitted monolayer thickness. $\Gamma_{\text{CMC}}$ is the surface excess concentration at the CMC and $A_{\text{CMC}}$ is the area per molecule at the CMC.

Due to its larger relative size compared to the two other surfactants, it is expected that Dynax DX2200 will have a smaller surface excess and a larger area per molecule, as reflected in the findings. As previously mentioned, properties of a non-ionic surfactant of similar structure to Dynax DX2200 have been reported in the literature. Parameters derived from analysis of NR data provided comparable results for both $\Gamma_{\text{CMC}}$ and $A_{\text{CMC}}$: $\Gamma_{\text{CMC}} = 2.50 \pm 0.10$ mol x $10^{-6}$ m$^{-2}$ and 65.0 ± 0.5 Å$^2$ (Dynax DX2200), $\Gamma_{\text{CMC}} = 2.46 \times 10^{-6}$ mol m$^{-2}$ and 67 Å$^2$ (THAM-derived telomer).

Neutron reflectivity provides significant information on how these fire-fighting surfactants adsorb and pack at the air/water interface. Although this study has reported results on these FC surfactants as single surfactant systems, it provides a means for further investigations into more complex mixed systems, including FC: HC surfactant mixtures, as found in commercial formulations. Overall, it has been shown that NR can be used to achieve consistent and reliable results for studying both research-grade and technical-grade FC surfactants. For the pure NaPFO, the data from both NR and tensiometric techniques were directly comparable to literature data. In addition to this, the three technical grade FC surfactants followed expected trends in terms of $\tau$, $\Gamma_{\text{CMC}}$ and $A_{\text{CMC}}$, unlike the unexpected and erratic trends found using tensiometry.
4.6 Small-angle neutron scattering

SANS has been employed to investigate self-assembly of the FC surfactants over multiple concentrations above their respective CMCs (Table 4.3) at 25 °C in D₂O. The scattering profiles for the three FC surfactants are shown in Figures 4.8 and 4.9. The anionic surfactant, Dynax DX1030 (Figure 4.8a), and the non-ionic surfactant, Dynax DX2200 (Figure 4.8b), are well described by a form factor for oblate spheroids. Parameters for the oblate spheroid form factor are: equatorial radius ($R_{eq}$/ Å), polar radius ($R_{pol}$/ Å), aspect ratio ($X = R_{eq}/R_{pol}$) and charge ($Z$) for the anionic surfactant. The zwitterionic surfactant, Capstone 1157, displays scattering with a $Q^{-2}$ dependency and have been fit using a lamellar form factor as infinite sheets of thickness (T/ Å). The fitted structural parameters are given in Tables 4.7 and 4.8.

At low concentration (5 x CMC), Dynax DX1030 aggregates appear to be spherical in shape, whereas ellipsoidal aggregates are observed at 10 x CMC and above. The aspect ratio of the aggregates above 10 x CMC remain constant ($X = 1.71\pm0.01$), suggesting that the micelle shapes are not changing at these higher concentrations (Table 4.7). Another observation is that the structure factor $S(Q)$ peak for the anionic surfactant Dynax DX1030 which occurs at $Q_{\text{max}}$ shifts to higher $Q$ as the concentration is increased. At low concentrations, the $S(Q)$ peak is difficult to discern due to weaker interactions. The $Q_{\text{max}}$ peak provides a rough guide to the average distance between the micelles. This shift to higher $Q$ shows that there is a decrease in the average distance between the micelles with concentration. Similar results have been observed in studies of both anionic HC and FC surfactants.43, 44

Considering the molecular structure of non-ionic Dynax DX2200, with a fluorinated tail group and repeating acrylamide unit head group, a complex core-shell model fit was investigated. The model was set up to account for a fluorinated tail micelle core ($\rho \sim 3 \times 10^{-6}$ Å$^{-2}$) surrounded by a shell of acrylamide unit head-groups ($\rho \sim 1 \times 10^{-6}$ Å$^{-2}$) contrasted against a D₂O continuum ($\rho \sim 6 \times 10^{-6}$ Å$^{-2}$). Attempts to determine a model fit for the sytem using this approach provided unphysical values for parameters, suggesting that the internal structure of these micelles cannot be resolved by SANS in this case. Several reasons may explain this: (1) Perhaps because there is only effectively a relatively small contrast step across the interface; (2) Blurring of the contrast step at the headgroup/D₂O interface due to hydration by D₂O; (3) H-D exchange of NH₂ groups. This loss of interfacial contrast has been noted before in SANS studies of both HC and FC hydroxy surfactants and is therefore likely here considering the acrylamide groups bear labile amide protons.26, 45 Hence, analyses of the micelle structures formed by Dynax DX2200 have been only able to resolve an average contrast and an overall global fits have been conducted.
Figure 4.8: Small-angle neutron scattering profiles for Dynax DX1030 and Dynax DX2200, with fitted functions shown as lines. Critical micelle concentrations have been taken as 1.37 mM and 0.02 mM for Dynax 1030 and Dynax DX2200, respectively. T = 25 °C.
Table 4.7: Parameters obtained by fitting SANS data to structural models. The fitted background for all samples was 0.04. $R_{eq}$ is the equatorial radius of an ellipsoid, $R_{pol}$ is the polar radius of the ellipsoid, aspect ratio is defined as $X = R_{eq}/R_{pol}$, $N_{agg}$ is the aggregation number, $Z$ is effective charge, $\Phi_{Fitted}$ is fitted volume fraction and $\Phi_{Calculated}$ is calculated volume fraction based on sample composition. Critical micelle concentrations have been taken as 1.37 mM and 0.02 mM for Dynax 1030 and Dynax DX2200, respectively. Data taken on SANS2D.

The self-assembled structures adopted by non-ionic Dynax DX2200 at all studied concentrations are best described by oblate spheroids, or globular micelles, with no observable structure factor over these concentrations and $Q$ ranges. This has been seen in other studies of similar non-ionic FC surfactants.\textsuperscript{26, 46} From Table 4.7 it can be seen that on average the surfactant micelles have an equatorial radius of 65 Å and a polar radius of 28 Å. The calculated tip-to-toe length of this molecule is $\sim$ 63 Å, therefore suggesting that the molecule is fully extended at the extreme equatorial axis, but coiled at the extreme polar axis. This coiling has been previously observed using SANS in surfactants containing polyoxyethylene groups, therefore is likely to occur with the oligomeric acrylamide moieties.\textsuperscript{47}
The zwitterionic betaine surfactant, Capstone 1157 has been studied at four different concentrations above the CMC. At the studied concentrations, the solutions showed viscoelastic behaviour, suggesting the formation of large and/or entangled aggregates. Amphoteric betaines are known to exhibit viscoelastic behaviour in solution, and work by Kumar et al. showed by SANS/ TEM how a C22-amphoteric betaine surfactant generates worm-like micelles that lead to the observed rheological properties.\textsuperscript{48} 

Figure 4.9: Small-angle neutron scattering profiles for Capstone 1157, with fitted functions shown as lines. Data have been offset by multiplied by 4, 16 and 36 respectively for clarity. Critical micelle concentration has been taken as 0.23 mM. \( T = 25 ^\circ C \)

In the low-\( Q \) region, the scattering scales as \( I(Q) \approx Q^{-D} \), where \( D \) is a characteristic dimensionality of the dispersed colloids and the gradient of a log-log plot will be -\( D \).\textsuperscript{49} In the case of non-interacting spheres, \( D \) should be zero in the low-\( Q \) region, for cylinders, \( D=1 \), and for disks/ lamellar structure \( D = 2 \). Capstone 1157 generates scattering with a clear \( Q^{-2} \) dependency, as shown in Figure 4.9, and therefore can be attributed to large lamellar structures across the concentration range studied. Fitting the data to a lamellar model provides information on the thickness of the layers only. The average fitted thickness over all concentrations is \( \sim 25 \text{ Å} \), this value being roughly commensurate with the tip-to-toe length of two of the tail groups for this surfactant.
Table 4.8: Parameters obtained by fitting SANS data to a structural model for infinite lamellae. Critical micelle concentrations has been taken as 0.23 mM. T = 25 °C. Data taken on SANS2D.

The different aggregate structures can be explained by consideration of the surfactant packing parameter argument (Equation 4.1):

\[ P_C = \frac{v}{(a_o l_c)} \]  

where \( v \) is volume of the hydrophobic tails, \( a_o \) is head group area and \( l_c \) is the length of the hydrophobic chain. For each surfactant the tail volume and length effectively remains the same and the only factor changing is predominantly the head group area. As expected, the molecule with the largest headgroup (Dynax DX2200) formed ellipsoidal micelles, and the molecule with the smallest head group (Capstone 1157) formed larger lamellar aggregates. Overall, three different self-assembled structures were observed for the three different fluorinated surfactants, highlighting how a change of surfactant headgroup can vastly affect self-assembly structure.
There are clear incentives to move away from the use of industrial fluorocarbon (FC) surfactants. However, to practically achieve this, there must be an understanding of the important bulk and surface properties of these surfactants as both single and multi-component systems. Here, three typical industrial FC surfactants used in fire-fighting have been characterised by surface tension, fluorescence probe studies, neutron reflection (NR) and small-angle neutron scattering (SANS), so that links can be made between their structures and respective bulk and interfacial performance.

As expected, all surfactants have very low limiting surface tensions, with the lowest being observed for the zwitterionic FC surfactant ($\gamma_{\text{CMC}} = 15.6 \text{ mN m}^{-1}$). Comparisons in limiting surface tension and critical micelle concentrations (CMC) between partially fluorinated surfactants in this study and fully fluorinated surfactant sodium perfluorooctanoate (NaPFO) have been made (Tables 4.2 and 4.3), with clear differences being noted. It was interesting to note the differences in surface activity between the zwitterionic surfactant Capstone 1157 and the anionic surfactant Dynax DX1030. Although they both have the same tail structure, but only differ in head group, the zwitterionic surfactant has a CMC $\sim 6$ times lower and a $\gamma_{\text{CMC}}$ $\sim 4 \text{ mN m}^{-1}$ lower than the anionic surfactant. These results show how considerable changes in the interfacial properties of surfactants result from changes in surfactant chemical structure.

In depth analyses of surface tension data using the Gibbs adsorption isotherm was prevented due to possible contamination owing to the commercial nature of these surfactants. In an attempt to circumvent this problem, NR was used to gain understanding of the surface films, by determining parameters such as surface excess ($\Gamma_{\text{CMC}}$) and area per molecule ($A_{\text{CMC}}$). The range of surfactants used in this work provided an easy to follow expected trend, the largest $A_{\text{CMC}}$ was observed in the largest molecule, non-ionic Dynax DX2200, and smallest $A_{\text{CMC}}$ in the smallest molecule zwitterionic Capstone 1157. Again it is interesting to see the differences when comparing the zwitterionic to the anionic surfactant. The charge on the anionic surfactant feeds through to an increase of $\sim 12 \text{ Å}^2$ in $A_{\text{CMC}}$ and a $\sim 1.2 \times 10^{-6}$ mol m$^{-2}$ decrease in $\Gamma_{\text{CMC}}$. Another important observation was that the monolayer density of Capstone 1157 appears to be comparable to that of a single FC chain ($\sim 28 \text{ Å}^2$), suggesting that the molecules are reaching the limit at which they can physically fit at the air/water interface, further explaining why this molecule has such a low value of $\gamma_{\text{CMC}}$ ($\sim 15.6 \text{ mN m}^{-1}$).

Through the use of SANS it has been possible to explore self-assembly structures. The differences observed in aggregation and self-assembly could be understood in
terms of the packing parameter (Equation 4.1). Large head group surfactants (Dynax DX2200 and Dynax DX1030) resulted in scattering consistent with spherical or ellipsoidal form factors, whereas the small head group surfactant (Capstone 1157) was better described by a lamellar-type form factor. Capstone 1157 has been noted to be the only surfactant to display a noticeable increase of viscosity in solution, as previously reported by Kumar et al. with similar FC zwitterionic surfactants. 48 By having this understanding of how these surfactants self-assemble individually, more complex studies can be proposed to model systems closer to practical applications, i.e. mixed FC: HC surfactant systems.

This study has highlighted some of the important surfactant properties for firefighting applications, notably for aqueous film-forming foams (AFFFs). Surfactants with low surface tensions and CMCs are likely to perform better and provide a way of achieving the desired interfacial properties. As well as this, results have shown the sensitivity between the relationship of structure and performance between surfactants with similar tail groups but different head groups. This emphasises how changes in surfactant head group can feed through to a large difference in both bulk and surface behaviour. In addition, it has been shown how lab-based tensiometric techniques are not always reliable for analysis of technical grade FC surfactants. However, the utility of NR for systems and studies of this kind has been demonstrated. These results therefore provide important insight into structure-performance relationships in partially fluorinated surfactants, and will point towards new ways to design more environmentally benign and effective FC surfactants in the future.
References


Chapter 5

Solution properties of fluorocarbon hydrocarbon surfactant mixtures

5.1 Introduction

As discussed in the previous Chapters, fluorocarbon (FC) surfactants often exhibit superior surface properties compared to their hydrocarbon (HC) counterparts.\textsuperscript{1, 2} The hydrophobic and oleophobic character of FC surfactants is unique and is exploited in a variety of industrial processes.\textsuperscript{1, 3} However, very often FC surfactants alone do not have all of the required properties for a given application.\textsuperscript{4} In aqueous film-forming foams (AFFFs) for example, FC surfactants are very effective at reducing aqueous (air/water) surface tension, but not interfacial tension between the foam and the burning fuel. This problem is commonly circumvented by producing FC/HC surfactant mixed systems, and adjusting the ratios to obtain specific properties.\textsuperscript{4-6} In addition to this, with growing concerns about the use of FC surfactants in industrial processes due to toxicity, bioaccumulation and persistence, the ability to produce mixtures that function well and contain less FC surfactants would be beneficial.\textsuperscript{7-12}

It is commonly known that mixtures containing FC and HC chains form non-ideal mixtures that separate into two liquid phases below a critical solution temperature.\textsuperscript{1, 13, 14} For example, when perfluoro-\textit{n}-heptane and \textit{n}-heptane are mixed at room temperature, they separate into two layers at equilibrium up to a temperature of \( \sim 50 \) °C.\textsuperscript{13} Miscibility studies on different chain length FC and HC solvent mixtures showed that the free energies of transfer of a CH\textsubscript{2} group into a FC solvent and \textit{vice versa} are approximately 1.1 and 1.4 kJ mol\textsuperscript{-1} respectively.\textsuperscript{15} The values suggest that the antipathy between HC and FC chains is about \( 1/3 \) of the free energy of transfer of CH\textsubscript{2} groups from an alkane to water. With this in mind, it is unsurprising that mixtures of perfluorinated surfactants with HC surfactants have been reported to display the same antagonism, determined by the affect that
mixing has on the micellisation behaviour. This is usually characterised by a positive deviation away from the calculated ideal behaviour from regular solution theory (RST). RST has been discussed in detail in Chapter 1. For example, there have been many studies on the micellisation behaviour of the two anionic surfactants sodium perfluorooctanoate (SPFO) and sodium decylsulfate (SDeS). Critical micelle concentration (CMC) values of the FC and HC surfactants at 25 °C are 30 and 32 mM, respectively. Mukerjee et al. showed by conductance that the critical aggregation concentration (CAC) of the mixed FC: HC surfactant system was higher than that for ideal mixing at all studied mole fractions. In the region where the mole fraction of FC was equal to HC, the maximum CAC of ∼40 mM was observed. The positive deviation from ideal behaviour is a direct consequence of the lack of affinity/non-favourable interactions between the FC and HC surfactants. Much of the literature also suggests that due to the highly antagonistic behaviour observed between SPFO and SDeS that two populations of micelles are produced in solution, one being rich in FC surfactants and one being rich in HC surfactants. However, this will be discussed further in Chapter 7, where the bulk properties of FC: HC surfactant mixtures are investigated through the use of small-angle neutron scattering (SANS) measurements.

Interestingly, when non-ionic and zwitterionic HC surfactants are mixed with SPFO, negative deviations from ideal behaviour (synergistic behaviour) have been reported. Guo et al. studied mixtures of SPFO with the non-ionic HC surfactant N-triethoxylated heptanlamide (HEA8-3). The CACs for the different mole fractions were determined using surface tension, H and F NMR measurements. All of the methods produced consistent results which showed a negative deviation from ideal mixing behaviour. A reduction in the repulsive interactions between the head groups of SPFO due to the insertion of the non-ionic surfactant molecules, and hydrogen bonding between amide groups in the non-ionic surfactant and the carboxyl group in SPFO are reasons why synergism is observed. In general, when mixing anionic FC surfactants with non-ionic HC surfactants, a combination of interactions are taking place that lead to the observed synergism. There is the common positive deviation from ideal behaviour associated with mixing FC and HC tail groups. The interaction of the anionic and non-ionic headgroups, however, lead to a considerable negative deviation from ideal behaviour. Thus, for these mixed systems, both positive and negative deviations from ideal behaviour compensate each other leading to the overall slight synergism. Further studies on mixtures of SPFO with non-ionic HC surfactants have been reported that display the same synergistic behaviour.

Stronger negative deviations from ideal behaviour are observed for mixtures of zwitterionic HC and SPFO. Guo et al. studied the interaction of 3-(decyldimethy lammonino)-1-propanesulfonate (DEDIAP) with SPFO. DEDIAP bears both sul-
fonate and tetraalkylammonium groups and although zwitterionic surfactants have no overall net charge, the surfactants have the ability to either donate or accept protons, allowing it to bear an overall negative or positive charge. Therefore, the interaction between the HC and FC surfactant is dominated by the strong Coulombic attraction between the carboxylate head group on the SPFO and the positive charge on the DEDIAP. There are many comprehensive reviews on the subject of perfluorinated surfactant mixtures with HC surfactants, for example, but not limited to.

This Chapter is concerned with determining the mixed micellisation behaviour of partially fluorinated surfactants (anionic, non-ionic and zwitterionic) with a common HC surfactant, SDS. After an extensive literature search only a few articles were found that were relevant for discussion. Jackson et al. carried out a systematic study on the composition and structure of many different partially fluorinated cationic surfactants (different degrees of fluorination) with the cationic HC surfactant CTAB, reporting unusual behaviour in terms of micellisation. The first observation was that as the degree of fluorination was increased (between C4 and C8), the behaviour went from synergistic to antagonistic. In addition to this, ideal micellisation behaviour was observed at low mole fractions of FC surfactant, but antagonism was displayed at high mole fractions of FC. Esumi et al. carried out an investigation on the behaviour of partially fluorinated zwitterionic surfactants mixed with lithium dodecyl sulfate (LiDS) in which ideal behaviour was observed. The ideal behaviour was reported as being caused by two effects. The first effect is the repulsive interaction commonly displayed when mixing HC and FC chains, which is unfavourable/antagonistic. The other, as discussed above, is due to the electrostatic attraction between the cationic portion of the FC and the anionic portion of the HC surfactants, which is favourable. There is therefore a compensation between these two effects that leads to the ideal mixed micellisation behaviour.

In this Chapter, partially fluorinated surfactants bearing different head groups have been mixed with SDS and have been studied in terms of micellisation and dynamic surface tension (DST) behaviour. Initially, the critical aggregation concentrations (CACs) of the mixed systems at different mole fractions were determined using both surface tension measurements and UV-Vis, with the two methods generally providing comparable results. For each mixed system, regular solution theory (RST) has been used to calculate the ideal CAC behaviour and compared to the experimentally determined results. Different behaviour in terms of deviations from the ideal CACs were observed for each mixed system. DST measurements were carried out on all of the FC: HC surfactant mixtures at different mole fractions and compared with data for the individual FC surfactants in Chapter 4. The results generally showed that the DST behaviour was dictated by the more hydrophobic FC surfactants at all investigated mole fractions, even when the HC was the majority component within the mixture. The aim is to gain an understanding on how the surface properties are...
affected by mixing a typical anionic HC surfactant with different head group FC surfactants.

5.2 Materials and Methods

5.2.1 Materials

The preparation of the partially fluorinated surfactants has been described in Chapter 2. Sodium dodecylsulfate (CAS 151-21-3) (Sigma-Aldrich, ≥ 98.5 %), Orange OT (IUPAC name: 1-(o-Tolylazo)-2-naphthol, CAS 2646-17-5) (Sigma-Aldrich, ≥ 75 %) and deuterium oxide (Sigma-Aldrich, 99.9 %) were used as received.

<table>
<thead>
<tr>
<th>Surfactant Name</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td>![Dynax DX1030 Chemical Structure]</td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td>![Dynax DX2200 Chemical Structure]</td>
</tr>
<tr>
<td>Capstone 1157</td>
<td>![Capstone 1157 Chemical Structure]</td>
</tr>
<tr>
<td>Sodium Dodecylsulfate</td>
<td>![Sodium Dodecylsulfate Chemical Structure]</td>
</tr>
</tbody>
</table>

Table 5.1: Surfactants used in this Chapter

5.2.2 Methods

Surface Tension Measurements

Surface tension measurements were carried out on a Krüss K100 force tensiometer using the Wilhemy plate method as described in Chapter 2. Stock solutions containing mixtures of FC and HC surfactants were prepared at concentrations higher than the CMCs of the individual surfactants. Measurements were taken using the Krüss automatic dosing unit, whereby ultra pure water is automatically added to the stock solutions.
solution until a predefined concentration is reached. Surface tension measurements were taken after every aliquot of water, and measurements were repeated over a period of up to 30 minutes to ensure equilibration. Between measurements, the solutions were stirred for a period of 5 minutes to ensure thorough mixing. It is important to study the mixtures at different compositions, therefore each FC: HC surfactant mixture was studied at five different mole fractions (0.90: 0.10, 0.75: 0.25, 0.50: 0.50, 0.25: 0.75, 0.10: 0.90).

UV-Vis

UV-Vis measurements were carried out as described in Chapter 2 using an Evolution 300 UV-Vis spectrophotometer. Measurements were carried out on all of the FC: HC surfactant mixtures at the same concentrations studied in the surface tension measurements.

Dynamic Surface Tension

Dynamic surface tension (DST) measurements were carried out on a Krüss BP100 bubble pressure tensiometer using the method as described in Chapter 2. Stock solutions containing the FC: HC surfactant mixtures at different mole fractions were prepared at the respective CACs as determined from the surface tension and UV-Vis measurements. Before the measurement, the solutions were left to equilibrate to temperature for 10 minutes. The measurements were all repeated three times to ensure reproducibility, and the mole fractions studied were all the same as above.
5.3 Critical aggregation concentrations for fluoro-carbon hydrocarbon surfactant mixtures at different mole fractions

The individual critical micelle concentrations (CMC) of the fluorocarbon (FC) surfactants have already been determined in Chapter 4, the CMC of sodium dodecylsulfate (SDS) has been reported numerous times in the literature but has been reproduced in this work for completeness. Here mixtures of SDS with three FC surfactants, each bearing a different headgroup, are under investigation. In order to identify relationships between critical aggregation concentrations (CAC) and surfactant structure for a mixed system, it is important to measure CACs at a variety of bulk compositions. As mentioned above, five different mole fractions were measured so that a full range of compositions could be realised. Tensiometry and UV-Vis were chosen for CAC measurements because they both rely on different methods for determination of this parameter, tensiometry relies on changes in surface tension (a surface property), whereas UV-Vis relies on the incorporation of a hydrophobic dye into a micelle core (a bulk property). In the Appendix the analysis used to determine the CAC using the above methods has been explained in detail and will therefore be omitted here. Before complex mixed systems can be studied, it is firstly instructive to make sure the experimental technique provides results that are comparable to those found in the literature.

5.3.1 Validating the UV-Vis method

The critical micelle concentration (CMC) determination of Sodium dodecylsulfate (SDS) using UV-Vis has been reported many times in the literature, for example but not limited to. The procedure by Dominguez et al. has been followed here. Below in Figure 5.1, the raw data from the UV-Vis experiments, along with the determination of CMC is shown.

From Figure 5.1a, it is possible to see the effect of increasing the surfactant concentration on the UV-absorption of Orange OT at 1 x 10^{-3} mM. Below the CMC, no changes are observed in the presence of surfactant monomers and the maximum absorption stays relatively stable. Above the CMC of SDS, the maximum absorption at $\lambda \sim 496$ nm increases as the hydrophobic dye begins to become incorporated into the micellar cores. These changes in maximum absorption at increasing SDS concentrations are shown in Figure 5.1b. Two lines were fit to the data at concentrations above and below the CMC; the intersecting point, hence CMC, was determined to be $8.5 \pm 0.4$ mM (Lit = 7.8 mM).
(a) Raw UV-Vis data for SDS at increasing concentrations.

(b) Maximum absorbance vs. concentration of SDS. Dashed lines serve as a guide for the eye to show determination of the CMC.

Figure 5.1: Showing the CMC determination of SDS from UV-Vis measurements. T = 21 °C.

5.3.2 Fluorocarbon hydrocarbon surfactant mixtures

Measurements of equilibrium $\gamma$ vs. concentration were carried out for all mixed systems: Dynax DX1030 (Anionic) with SDS, Dynax DX2200 (non-ionic) with SDS and Capstone 1157 (zwitterionic) with SDS. In Figure 5.2a, data for the Capstone 1157: SDS mixed systems are provided as an example of the experimental surface tension behaviour, which display clear break points in the data at the respective CACs. Experimental $\gamma$ vs. concentration for the remaining FC: HC surfactant mixtures are shown in the Appendix. Figure 5.2b shows the maximum absorption
vs. total concentration data from the UV-absorption experiment for the Capstone 1157: SDS mixed system at a mole fraction of 0.50: 0.50. As shown above in Section 5.3.1 (Figure 5.1b), a break in the data for the max absorption vs. concentration represents the CMC. A clear break point can be observed in this data, suggesting that the CAC has been reached. Experimental CAC results for both methods are given below in Table 5.2 where they are compared with the calculated ideal values from regular solution theory (RST) using Equation 1.22.

![Surface Tension vs. ln(Concentration) for Capstone 1157: SDS mixed system at varying mole fractions.](image)

![Maximum absorbance vs. total concentration for Capstone 1157: SDS mixed system at a mole fraction of 0.50:0.50.](image)

Figure 5.2: The two methods utilised for CAC determination.

As previously mentioned, the ideal CAC behaviour is calculated from knowledge of both the bulk compositions of each FC: HC surfactant mixture (at each mole fraction), as well as the CMCs of the pure surfactants. The ideal CAC values are
a qualitative indicator of the interactions taking place between the two surfactants within the mixed system. For example, if the experimentally obtained CAC value is lower than that calculated assuming ideal mixing, a synergism is indicated, with the opposite being indicative of antagonism. In the case of mixing fully fluorinated surfactants with hydrocarbon surfactants, antagonism is observed, this can often be explained due to the immisibility of the surfactant hydrophobic tail groups. In the case of partially fluorinated surfactants, however, it has been shown that the degree of ideality can differ depending on the composition of the mixture. In general, the data presented in Table 5.2 show that the FC: HC surfactant mixtures studied in this work display CACs that are either close to ideal or antagonistic. Each mixed system, however, displays slightly different behaviour and individual discussions are therefore required.

<table>
<thead>
<tr>
<th>Mole fraction/Fluorocarbon</th>
<th>CAC (Surface Tension)/ (mM)</th>
<th>CAC (UV-Vis)/ (mM)</th>
<th>Ideal CAC/ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030: SDS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>1.37</td>
<td>1.50</td>
<td>-</td>
</tr>
<tr>
<td>0.90</td>
<td>2.00</td>
<td>1.70</td>
<td>1.50</td>
</tr>
<tr>
<td>0.75</td>
<td>2.43</td>
<td>1.73</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>2.53</td>
<td>2.90</td>
<td>2.35</td>
</tr>
<tr>
<td>0.25</td>
<td>3.35</td>
<td>-</td>
<td>3.65</td>
</tr>
<tr>
<td>0.10</td>
<td>3.85</td>
<td>3.50</td>
<td>5.47</td>
</tr>
<tr>
<td>0.00</td>
<td>8.30</td>
<td>8.50</td>
<td></td>
</tr>
<tr>
<td>Dynax DX2200: SDS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.90</td>
<td>0.01</td>
<td>0.70</td>
<td>0.02</td>
</tr>
<tr>
<td>0.75</td>
<td>0.02</td>
<td>0.85</td>
<td>0.03</td>
</tr>
<tr>
<td>0.50</td>
<td>0.05</td>
<td>2.05</td>
<td>0.04</td>
</tr>
<tr>
<td>0.25</td>
<td>0.04</td>
<td>4.10</td>
<td>0.08</td>
</tr>
<tr>
<td>0.10</td>
<td>0.05</td>
<td>7.51</td>
<td>0.20</td>
</tr>
<tr>
<td>0.00</td>
<td>8.30</td>
<td>8.50</td>
<td></td>
</tr>
<tr>
<td>Capstone 1157: SDS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.90</td>
<td>0.15</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>0.75</td>
<td>0.15</td>
<td>-</td>
<td>0.30</td>
</tr>
<tr>
<td>0.50</td>
<td>0.53</td>
<td>1.00</td>
<td>0.45</td>
</tr>
<tr>
<td>0.25</td>
<td>1.06</td>
<td>-</td>
<td>0.85</td>
</tr>
<tr>
<td>0.10</td>
<td>1.68</td>
<td>2.50</td>
<td>1.84</td>
</tr>
<tr>
<td>0.00</td>
<td>8.30</td>
<td>8.50</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2: Critical aggregation concentration results from mixed surface tension measurements of Dynax DX1030, Dynax DX2200 and Capstone 1157 with SDS. Ideal CACs were calculated using Equation 1.22.
Dynax DX2200: SDS

The first mixed system to be discussed is the non-ionic FC surfactant with SDS. From the data presented in Figure 5.3, it is clear that the results obtained from using surface tension and UV-Vis measurements are not complementary. The surface tension data suggests that the mixed system is essentially ideal for all studied mole fractions, showing CAC values which are very similar to that of Dynax DX2200 individually. The UV-Vis data, however, suggests that the interaction between the surfactants is highly antagonistic, as would be expected in mixtures containing long chain FC surfactants with HC surfactants. The two different methods used to measure the CACs rely on probing different properties; surface tension measurements probe changes in the surface tension over a range of concentrations (surface property), whereas the UV-Vis measurements rely on the incorporation of a hydrophobic dye into the core of a micelles (bulk property).

Figure 5.3: Critical aggregation concentration vs. mole fraction of SDS for the Dynax DX2200: SDS mixed systems. Red circles are data from surface tension measurements (T= 25 °C), blue circles are data from UV-Vis measurements (T= 21 °C) and black circles are calculated ideal values using RST.

Unlike the other two FC surfactants investigated in this work, Dynax DX2200 has a C8 fluorinated tail group with a relatively large head group, which feeds through to an $A_{CMC}$ of 65 Å² compared to 44 Å² for SDS. In addition to this, there is less polarity in the molecule compared to the other two FC surfactants, due to the lack of carbonyl or amide groups (see structures in Table 5.1). It is therefore possible that the bulky head group and very hydrophobic C8 tail group could lead to the air/water interface being essentially dominated by the non-ionic FC surfactant, causing the surface tension data measurements to produce apparent CACs that are
CHAPTER 5. SOLUTION PROPERTIES OF FLUOROCARBON HYDROCARBON SURFACANT MIXTURES

in line with the CMC for the FC surfactant individually (refer to Table 5.2). By determining the CACs from the UV-Vis measurements (bulk measurement), however, a larger sample of molecules are being studied compared to the surface measurements and for these reasons, the CACs are likely to be better represented by these bulk (UV-Vis) measurements.

There have been many reports on the CAC behaviour in mixtures containing non-ionic HC surfactant and anionic FC surfactants,\textsuperscript{5, 6} however reports on mixtures containing non-ionic FC surfactant with anionic HC surfactants are hard to come by. When the non-ionic surfactant is HC, ideal or sometimes synergistic CACs have been observed.\textsuperscript{6} For example, in a mixed system composed of sodium perfluorooctanoate (SPFO) and a N-triethoxylated heptanlamide non-ionic HC surfactant, the synergistic interaction were explained in the following way:

1. A reduction in the repulsive interaction between the anionic surfactant head groups, due to the insertion of the non-ionic surfactant molecules

2. Interactions through hydration between the hydrophilic part of the anionic surfactant head group and the ether oxygens of the non-ionic surfactant

In this work, although the tail group of Dynax DX2200 is partially fluorinated and some polarity is present between the CF$_2$CH$_2$ groups, there is no other polarity in the tail group which would allow for favourable interactions with the SDS.\textsuperscript{35} It is therefore possible that the observed antagonistic behaviour between SDS and the non-ionic FC surfactant can be best understood by assuming the FC surfactant is fully fluorinated, and antagonism is therefore to be expected.

**Capstone 1157: SDS**

Although zwitterionic surfactants have no overall net charge, mixtures of zwitterionic surfactants with anionic surfactants are known to produce weak synergistic interactions.\textsuperscript{6, 17, 21} This being due to the ability of the zwitterionic surfactant to either accept or donate a proton, allowing it to acquire a net positive or negative charge.\textsuperscript{21} Taking the example of an alkyl betaine (\textit{cf.} Capstone 1157) containing both a quaternary ammonium group and a carboxylate group, it is clear that the surfactant would only be able to accept a proton onto the carboxylate group due to the stability of the quaternary ammonium group. This would therefore render the surfactant with a small positive charge, allowing for favourable interactions with an anionic surfactant. Similar behaviour has been observed in both HC: HC\textsuperscript{36, 37} and even FC: HC\textsuperscript{5, 6, 17} mixed surfactant systems. Below in Figure 5.4 the results from Capstone 1157: SDS mixed systems can be seen, with good overlap being observed for the two different experimental methods.
Figure 5.4: Critical aggregation concentration vs. mole fraction of SDS for the Capstone 1157: SDS mixed systems. Red circles show data from surface tension measurements (T = 25 °C), blue circles show data from UV-Vis measurements (T = 21 °C) and black circles show calculated ideal results from RST.

Apparently, ideal behaviour is observed in the FC: HC surfactant mixtures at all studied mole fractions. Similar ideal behaviour has been previously reported for partially fluorinated zwitterionic surfactants mixed with anionic HC surfactants.\textsuperscript{24} Esumi et al. argued that the reason for the ideal behaviour was caused by two effects. One due to the weaker interaction between the HC and FC chains in these systems, compared to between HC and FC chains individually, resulting in an apparent increase in the CAC, and the second due to the electrostatic attraction between the positive charge of the zwitterionic FC surfactant and anionic portion of the FC surfactant, this being a favourable interaction. These two effects were found to compensate each other and lead to the overall observed ideal behaviour. In this work, as previously discussed, an attraction between the anionic HC head group and the positive charge on the FC quaternary ammonium group (due to the protonation of the carboxylate group) is expected. In addition to this, the slight polarity in the FC due to the CF₂CH₂ group and the presence of the sulfonamide group may further offset the repulsive behaviour usually experienced when mixing FC and HC surfactants.\textsuperscript{35}

Dynax DX1030: SDS

The final mixture to be discussed is the anionic FC: anionic HC surfactant system. Unlike the other two mixed systems discussed above, three different behaviours are observed in this FC: HC mixed surfactant system with reference to the calculated
ideal CAC predictions. These behaviours are as follows: at low mole fractions of SDS (0.10 - 0.25), i.e. when the mole fraction of SDS is lower than the FC surfactant, antagonism is displayed, when the mole fraction of SDS is higher than than the FC surfactant (mole fractions of 0.75 - 0.90), synergism is apparently displayed and at the intermediate mole fraction (0.50: 0.50), close to ideal behaviour is displayed. Figure 5.5 shows the CAC vs. mole fraction of SDS data and good agreement between the two experimental methods is observed, providing additional reliability in the results.

Figure 5.5: Critical aggregation concentration vs. mole fraction of SDS for the Dynax DX1030: SDS mixed systems. Red circles show data from surface tension measurements (T= 25 °C), blue circles show data from UV-Vis measurements (T= 21 °C) and black circles show calculated ideal results from RST.

To make sense of this change, it is instructive to make links to both the relevant literature and the structures of the respective surfactants (Table 5.1). Firstly, if one considers the interaction between two HC surfactants of similar tail lengths bearing the same headgroup, it is easy to consider that these systems will obey the thermodynamics of ideal mixing, with many reports demonstrating this behaviour.5, 38–40 Conversely, mixtures of anionic perfluorinated surfactants with anionic HC surfactants are known to show positive deviation from ideal behaviour (antagonism), which can be easily understood due to the lack of affinity between the FC and HC tail groups.5, 31, 41 Here, a partially fluorinated anionic surfactant has been mixed with an anionic HC surfactant, which both bear the same head group.

After an extensive literature search, few comparable reports were available. Jackson et al. carried out a systematic characterisation, in terms of the composition and structure of many different mixed systems containing cationic FC surfactants (changing the degree of fluorination in the chain) and a cationic HC surfactant
Results showed that as the degree of fluorination increased from C4 to C8, the mixed system behaviour went from synergistic to antagonistic, respectively, i.e. the more fluorination in the surfactant chain, the less favourable the interactions are between the FC and HC surfactants. In addition to this, the mixtures were also found to display unsymmetrical CAC behaviour between the different investigated mole fractions. At low mole fractions of FC, the results showed approximately ideal behaviour, but antagonism was displayed when the mole fraction of FC was high. This was attributed to a gain in energy from a reduced immersion of the FC chain, brought about by screening of the FC from water by the HC surfactant. At high mole fractions of FC, however, there was thought to be no space at the air/water interface for further screening between the FC and HC surfactant chains therefore leading to the expected antagonism.

Although in this work both Dynax DX1030 and SDS are anionic surfactants (Table 5.1) and bear the same headgroup, a similar justification can be made. The two surfactants have very similar structures in terms of chain length: C15 and C12 for the FC and HC, respectively. This similarity in chain length is reflected in comparable surface density parameters, area per molecule ($A_{\text{CMC}}$) and surface excess ($\Gamma_{\text{CMC}}$): \( \sim 42 \, \text{Å}^2 \) and \( \sim 3.9 \times 10^{-6} \, \text{mol m}^{-2} \) for the FC surfactant and \( \sim 44 \, \text{Å}^2 \) and \( \sim 3.8 \times 10^{-6} \, \text{mol m}^{-2} \) for the HC surfactant. In addition to this, partially fluorinated surfactants, unlike perfluorinated surfactants, have strong dipole moments at the CF$_2$CH$_2$ linkage and this dipole moment could well cause interactions to occur between FC and HC surfactants, and could account for both the ideal and synergistic behaviour reported here.

Understanding how these FC: HC mixed surfactant systems interact is important for further investigations into the important surface and bulk properties. Results have shown that when partially fluorinated surfactants are mixed with anionic HC surfactants, the interactions are not always easy to predict and different trends can be observed. FC surfactants and HC are known to have very different surface activities and it is therefore of interest to determine how changes in the composition of FC: HC surfactant mixed systems can affect the reductions in aqueous surface tension.
5.4 Dynamic surface tension of fluorocarbon hydrocarbon surfactant mixtures

In industrial applications that rely on time-dependent processes, the dynamic surface tension (DST or $\gamma(t)$) of a surfactant or mixed surfactant system is an important property to consider. Here, the DST behaviour of three binary mixed systems containing the three FC surfactants with SDS are under investigation. The CAC data for all of the mixed systems are shown above in Table 5.2. Due to the known differences in surface activities between FC and HC surfactants, it is important to understand the relationship between DST behaviour and composition of the FC/HC mixed surfactant systems.1,2

As with the above UV-Vis method for determining the CACs of the mixed systems, it is firstly important to make sure that the DST experimental technique provides results that are comparable with the relevant literature.

5.4.1 Dynamic surface tension of water: ethanol mixtures

When measuring the DST of complex mixed systems, it is important to validate the method as well as accuracy and reproducibility of the instrument (Krüss BP100). A common and well reported system in which comparisons can easily be made is a water: ethanol mixed system, which spans a range of surface tension values from 72.0 mN m$^{-1}$ to 22.0 mN m$^{-1}$ for water and ethanol, respectively. Vazques et al. carried out an in-depth analysis on the DST of water: alcohol mixed systems at multiple temperatures and here comparisons have been made.42 A plot of surface tension vs. mole fraction of ethanol is shown below in Figure 5.6, the raw data can be found in the Appendix.

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>$\gamma$/ (mN m$^{-1}$)</th>
<th>Literature $\gamma$/ (mN m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>72.6</td>
<td>72.0</td>
</tr>
<tr>
<td>0.25</td>
<td>37.5</td>
<td>35.3</td>
</tr>
<tr>
<td>0.50</td>
<td>29.0</td>
<td>28.0</td>
</tr>
<tr>
<td>0.75</td>
<td>25.1</td>
<td>25.0</td>
</tr>
<tr>
<td>1.00</td>
<td>21.6</td>
<td>21.8</td>
</tr>
</tbody>
</table>

Table 5.3: Water: ethanol mixed system dynamic surface tension data, compared to literature results.42 (T= 25 °C).
From the data presented in Figure 5.6, good agreement is observed between the experimental and literature data for all studied mole fractions, suggesting that the method used in this work is accurate. Results have been summarised in Table 5.3.

5.4.2 Fluorocarbon hydrocarbon surfactant mixtures

The DST of the mixed systems was investigated at five different mole fractions so that a full range of behaviour could be realised. The DST of SDS has been previously reported, but for completeness has been reproduced in this work (data in Appendix).\textsuperscript{43} In Chapter 4, the DST behaviour of the three FC surfactants were investigated. The two small molecule surfactants, Dynax DX1030 and Capstone 1157, displayed quick DST behaviour, reaching $\gamma_{eq}$ within $\sim$ 1 s. As might be expected, the higher molecular weight surfactant Dynax DX2200 had much slower dynamics and did not reach $\gamma_{eq}$ within the time frame of the experiment, i.e. longer than 100 s. Slow DST behaviours are often reported for high molecular weight surfactants and polymers.\textsuperscript{44–47}

The effective diffusion coefficients ($D_{eff}$) of the individual FC surfactants were also determined using the diffusion-only adsorption model determined by Ward and Tordai\textsuperscript{48} and extended by Miller et al.\textsuperscript{49} Determination of these $D_{eff}$ values requires the use of the diffusion-only adsorption model at short and long time limits (Equations 1.8 and 1.11 in Chapter 1) and can be used when $\gamma(t)$ is close to either the tension of the solvent ($\gamma_0$) or $\gamma_{eq}$ as $t \to 0$ or $\infty$, respectively. This then
allows comparisons to be made between the theoretical predictions and experimental results to determine whether the adsorption is a diffusion controlled process.\textsuperscript{49} As is commonly reported for both FC and HC surfactants, at short times good agreement was observed between the theoretical predictions and experimental results for all FC surfactants, indicating that the adsorption is diffusion-controlled.\textsuperscript{44, 50–54} At long times, however, the adsorption was no longer diffusion controlled and the data were consistent with the presence of a weak adsorption barrier.\textsuperscript{44, 50, 51}

This section investigates how the addition of SDS affects the DST behaviour of the three FC surfactants. As mentioned above, five mole fractions were studied for each mixture and DST measurements were carried out at the CAC (Table 5.2). Different behaviours are observed in each mixed system and individual discussions are therefore necessary. Figures shown in this section are representative runs with values of $\gamma_t$ reproducible to $\pm 2 \text{ mN m}^{-1}$.

**Dynax DX1030: SDS**

DST curves for the Dynax DX1030: SDS mixed systems at different mole fractions are shown below in Figure 5.7a. At all different mole fractions an initial $\gamma_t$ value below the tension of the solvent ($\gamma_0$) is seen. This behaviour was shown for Dynax DX1030 individually (Chapter 4) due to the high surface activity of the surfactant. Table 5.4 shows both the $\gamma_{eq}$ results for both the individual surfactants and mixtures as well as the $\gamma_{t=100 \text{s}}$, i.e. the $\gamma_t$ reached at the end of the DST measurement. When the mole fraction of the FC surfactant is higher than the HC surfactant, the $\gamma_{eq}$ values are reached during the timescale of the experiment, however at high mole fractions of HC surfactant, $\gamma_{eq}$ values are not reached. This suggest that the concentration/mole fraction of the FC within the mixture has a large effect on the $\gamma(t)$ decay.

<table>
<thead>
<tr>
<th>Mole fraction/</th>
<th>$\gamma_{t=100 \text{s}}$ (mN m$^{-1}$)</th>
<th>$\gamma_{eq}$ (mN m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>21.0</td>
<td>19.2</td>
</tr>
<tr>
<td>0.90</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>0.75</td>
<td>19.5</td>
<td>20.5</td>
</tr>
<tr>
<td>0.50</td>
<td>21.5</td>
<td>21.0</td>
</tr>
<tr>
<td>0.25</td>
<td>24.8</td>
<td>23.2</td>
</tr>
<tr>
<td>0.10</td>
<td>32.5</td>
<td>23.5</td>
</tr>
<tr>
<td>0.00</td>
<td>35.7</td>
<td>35.0</td>
</tr>
</tbody>
</table>

Table 5.4: $\gamma_{t=100 \text{s}}$ values from DST measurements and $\gamma_{eq}$ values from surface tension measurements for the Dynax DX1030: SDS mixed system at different mole fractions. Data for the individual surfactants are also reported.
(a) Dynamic surface tension of Dynax DX1030: SDS mixtures. The key to the right displays the mole fractions in the ratio of FC: HC.

(b) Normalised dynamic surface tension of the above data for Dynax DX1030: SDS.

Figure 5.7: Raw and normalised dynamic surface tension plots of the Dynax DX1030: SDS mixed systems. The key shown in (a) represents the data in both graphs. All samples measured at respective CACs (see Table 5.2). Note: in log scale $3 = 10^3$ ms. $T = 25\, ^\circ\mathrm{C}$.

The initial $\gamma_t$ values produced by the mixtures at mole fractions of both 0.90: 0.10 and 0.75: 0.25 (Dynax DX1030: SDS) are lower than those at the other mole fractions, where initial $\gamma_t$ values similar to Dynax DX1030 are seen. FC surfactants are generally more surface active than HC surfactants, and it is therefore likely that the initial part of the $\gamma(t)$ decay will be dominated by the FC surfactant adsorption, hence the concentration of FC surfactant in the solution will determine the initial $\gamma_t$ value.$^{1, 2}$ As shown in Table 5.2, the mixed CAC increases as the mole fraction of SDS increases in the mixtures, and the mixed CAC at mole fractions of 0.90: 0.10 and 0.75: 0.25 are 2.00 and 2.43 mM respectively. Dynax DX1030 has a CMC of 1.37 mM and therefore within these mixed systems is present at a concentration higher
than its CMC, and lower initial $\gamma_t$ values are to be expected. This behaviour was previously shown in Chapter 4 for Dynax DX1030 and been reported previously.\textsuperscript{54} The concentration of Dynax DX1030 within the other mole fraction samples is either lower or similar to its CMC and the initial values of $\gamma_t$ are expected to be similar to that of Dynax DX1030 individually. Data have also been normalised (Figure 5.7b) so that the $\gamma(t)$ decays be observed in a similar scale. The data were normalised using the following Equation:

$$\text{Normalisation} = \frac{(\gamma_t - \gamma_{\text{min}})}{(\gamma_{\text{max}} - \gamma_{\text{min}})}$$  \hspace{1cm} (5.1)

where $\gamma_t$ is the surface tension at time $t$, $\gamma_{\text{min}}$ is the minimum recorded surface tension and $\gamma_{\text{max}}$ is the maximum surface tension measured. From the normalised data it can be seen that the $\gamma(t)$ decay is faster than Dynax DX1030 individually at all mole fractions until there is a majority of SDS present in the mixed system, i.e. 0.25: 0.75 (Dynax DX1030: SDS). The increase in the $\gamma(t)$ decay for the mole fractions where Dynax DX1030 is the majority component could be explained by either an increase in the concentration of Dynax DX1030 as stated above, or due to the presence of SDS within the mixed systems. To determine whether this is likely to be a concentration effect, comparison can be made between the DST data of both the mixed systems and Dynax DX1030 individually. By comparing the time it takes for the normalised $\gamma(t)$ to decay to a surface tension of 0.50 ($t_{50\%} = 50\%$), it will be possible to determine whether the DST curves are following a similar decay rate. In addition to this, effective diffusion coefficients ($D_{\text{eff}}$) of both Dynax DX1030 individually and the mixed systems can be compared.

As introduced in the Chapter 1, the $D_{\text{eff}}$ values can be determined through the diffusion-controlled short and long time limiting laws determined by Miller \textit{et al.}\textsuperscript{49} (see Equations 1.8 and 1.11). Plots of $\gamma(t)$ vs. $t^{1/2}$ and $t^{-1/2}$ result in linearity as $t \to 0$ or $\infty$, respectively, allowing determination of $D_{\text{eff}}$ values at short and long times. Accurate employment of this analysis requires $\gamma(t)$ data to tend to either the tension of the solvent ($\gamma_0$) or the equilibrium surface tension $\gamma_{\text{eq}}$ as $t \to 0$ or $\infty$. As shown in Figure 5.7, the DST curves do not begin at $\gamma_0$ and for this reason the solvent tension variable has been allowed to float in the fit, thus become linear as $\gamma(t)$ approaches "$\gamma_0$". This method has been used previous within the literature for analysis of highly surface active FC surfactants.\textsuperscript{54} Using this approach is likely to cause inconsistencies in the calculated $D_{\text{eff}}$ results, but will nonetheless provide a means for comparison between the different mole fraction data. Figure 5.8 shows the long and short time limit plots for all of the mole fractions and the associated data is presented in Table 5.5.
A general trend is observed whereby increasing the mole fraction of SDS in the mixed system causes an increase in the $t_{\gamma=50\%}$ reduction. Although the $t_{\gamma=50\%}$ reduction at mole fractions of 0.90: 0.10 and 0.75: 0.25 are lower than that of Dynax DX1030 individually, it should be noted that the concentration of Dynax DX1030 within the mixed system is $\sim 1.8$ mM and hence higher than its CMC. The $t_{\gamma=50\%}$ reduction for Dynax DX1030 at $\sim 2 \times$ CMC is $\sim 0.25$ s and therefore aligns well with mixed system results. In the 0.10: 0.90 mixture, the concentration of Dynax DX1030 is $\sim 0.4$ mM and the $t_{\gamma=50\%}$ reduction for Dynax DX1030 below the CMC is $\sim 1.60$ s. This is again comparable to the mixed system data, further indicating that the FC surfactant is dominating the $\gamma(t)$ decay.

Considering the $D_{\text{eff}}$ data, there is a large disparity between the calculated and literature value for SDS at short times. From the data in Figure 5.7, it can be
seen that SDS has very fast DST behaviour and the calculated value of $0.01 \times 10^{-10}$ m$^2$s$^{-1}$ would suggest slow DST behaviour similar to that of a high molecular weight surfactant.\textsuperscript{50} For this reason, these discussions are using the quoted literature value for SDS for comparative purposes. When Dynax DX1030 is the majority component in the mixed system, the calculated $D_{\text{eff}}$ values are similar between the mixed systems and Dynax DX1030 individually at both long and short times, and $D_{\text{eff}}$ becomes smaller when SDS is the majority component. These data are therefore comparable with the $t_{\gamma=50\%}$ reduction data, suggesting both that the $\gamma(t)$ decay is essentially dominated by the FC surfactant and the diffusion of surfactants to the air/water interface is slowed down as the mole fraction of SDS is increased.

**Dynax DX2200: SDS**

Raw and normalised DST plots for the Dynax DX2200: SDS mixed systems are shown below in Figure 5.9 and the $\gamma_{\text{eq}}/\gamma_t = 100$ s data for both the individual and mixed systems are shown in Table 5.6. The data in Table 5.6 shows upon increasing the mole fraction of SDS in the mixed system, the $\gamma_t = 100$ s value reached in the DST experiment becomes closer to the $\gamma_{\text{eq}}$ value.

<table>
<thead>
<tr>
<th>Mole fraction/ Dynax DX2200</th>
<th>$\gamma_{t=100}$ s / (mN m$^{-1}$)</th>
<th>$\gamma_{\text{eq}}$/ (mN m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>54.0</td>
<td>19.6</td>
</tr>
<tr>
<td>0.90</td>
<td>45.4</td>
<td>20.0</td>
</tr>
<tr>
<td>0.75</td>
<td>32.7</td>
<td>21.3</td>
</tr>
<tr>
<td>0.50</td>
<td>25.5</td>
<td>22.0</td>
</tr>
<tr>
<td>0.25</td>
<td>30.0</td>
<td>25.0</td>
</tr>
<tr>
<td>0.10</td>
<td>28.4</td>
<td>27.0</td>
</tr>
<tr>
<td>0.00</td>
<td>35.7</td>
<td>35.0</td>
</tr>
</tbody>
</table>

Table 5.6: $\gamma_{t=100}$ values from DST measurements and $\gamma_{\text{eq}}$ values from surface tension measurements for the Dynax DX2200: SDS mixed system at different mole fractions. Data for the individual surfactants are also reported.

The DST of the mixed systems display slow behaviour similar to that of Dynax DX2200 individually (see Chapter 4), also commonly observed for both FC and HC high molecular weight surfactants.\textsuperscript{50, 56, 57} In addition to this, initial $\gamma_t$ values decreases as the mole fraction of SDS is increased. This behaviour cannot be explained as above for the Dynax DX1030: SDS mixed system by an increase in the concentration of Dynax DX2200 within the mixture, because the DST data for Dynax DX2200 individually produced initial $\gamma_t$ values of water ($\sim 72$ mN m$^{-1}$) at all concentrations. As discussed above, lack of polarity in Dynax DX2200 in addition to the C8 fluorinated tail group led to the highly antagonistic behaviour observed in this mixed system. The antagonism within the mixed systems could conceivably speed up
the rate at which the most hydrophobic component (FC surfactant) adsorbs to the 
air/water interface, hence explaining the decrease in initial $\gamma_t$ value and faster $\gamma(t)$ 
decay shown in the normalised Figure (5.9b). The extent to which the SDS increases 
the rate of $\gamma(t)$ decay can be considered by comparing both the $t_{\gamma=50\%}$ reduction 
results as well as the short and long time $D_{\text{eff}}$ values. These data are summarised 
below in Table 5.7 and the plots of $\gamma(t)$ vs. $t^{1/2}$ and $t^{-1/2}$ are shown in Figure 5.10.

![Graphs showing surface tension decay over time](image)

Figure 5.9: Raw and normalised dynamic surface tension plots of the Dynax DX2200: SDS mixed systems. The key shown in (a) represents the data in both graphs. All samples measured at respective CACs (see Table 5.2). $T = 25$ °C.
RESULTS CLEARLY SHOW THAT AS THE MOLE FRACTION OF SDS IS INCREASED WITHIN THE MIXTURE, THE $t_{\gamma=50\%}$ REDUCTION DECREASES SIGNIFICANTLY COMPARED TO DYNAX DX2200. FOR ADDITIONAL REFERENCE, DYNAX DX2200 AT 40 x CMC ($\sim$ 0.8 mM) TAKES 25 s TO REACH $t_{\gamma=50\%}$. ALTHOUGH A GENERAL DECREASE IS BEING OBSERVED, THERE IS STILL A MARKED DIFFERENCE IN $t_{\gamma=50\%}$ REDUCTION COMPARED TO SDS INDIVIDUALLY, SHOWING THAT THE $\gamma(t)$ DECAY OF SDS IS SUBSTANTIALLY HINDERED BY THE PRESENCE OF A SMALL AMOUNT OF THE FC SURFACTANT. MIXED SYSTEMS IN WHICH THE SDS IS THE DOMINANT COMPONENT STILL DISPLAY AN ORDER OF MAGNITUDE DIFFERENCE IN $t_{\gamma=50\%}$ VALUES COMPARED TO SDS INDIVIDUALLY, SUGGESTING THAT THE DOMINANT COMPONENT, EVEN WHEN PRESENT AT LOW MOLE FRACTIONS IS THE NON-IONIC FC SURFACTANT.

THE CALCULATED $D_{\text{eff}}$ VALUES ALLOW FOR FURTHER QUANTIFICATION OF THE EXTENT TO WHICH THE SDS IS INCREASING THE $\gamma(t)$ DECAY. UNLIKE THE DYNAX DX1030: SDS MIXED SYSTEMS, FOR SOME OF THE DYNAX DX2200: SDS MIXED SYSTEMS IT WAS POSSIBLE TO FIX THE $\gamma_0$
at the tension of water, allowing for accurate determination of $D_{\text{eff}}$ values as $t \to 0$. At short times, the gradients, and hence $D_{\text{eff}}$ values are very small for the mixed systems that contain Dynax DX2200 as the majority component, emphasising that the Dynax DX2200 is dominating the DST behaviour. At mole fractions when SDS is the majority component, the gradients are shown to increase significantly, although no marked difference in $D_{\text{eff}}$ values are observed. An increase in the $D_{\text{eff}}$ would be expected over the range of mole fractions from consideration of the $t, \gamma=50\%$ data, however the magnitude of $D_{\text{eff}}$ are directly affected by both the gradient and bulk concentration. This could therefore influence the calculated value of $D_{\text{eff}}$ and will be considered when using these values to theoretically predict whether the adsorption process is diffusion-controlled in Section 5.4.3.

**Capstone 1157: SDS**

The final mixed system to be discussed is the zwitterionic: anionic mixture of Capstone 1157: SDS. The mixtures were found to obey ideal behaviour in terms of mixed aggregation concentrations, which was understood by considering the formation of a small effective positive charge on the zwitterionic surfactant. The charge could be introduced by the carboxylate group accepting a proton, therefore rendering the favourable interaction with anionic SDS possible, as has been seen previously in FC: HC mixed systems.\textsuperscript{5, 6, 17} Out of the three FC surfactants studied in this work, Capstone 1157 is the most surface active and has a $\gamma_{\text{CMC}}$ of 15.6 mN m$^{-1}$. Below in Table 5.8, both the $\gamma_{\text{eq}}$ and $\gamma_{t=100\ s}$ values are shown for the individual surfactants and mixtures.

<table>
<thead>
<tr>
<th>Mole fraction/ Capstone 1157</th>
<th>$\gamma_{t=100\ s}$ / (mN m$^{-1}$)</th>
<th>$\gamma_{\text{eq}}$ / (mN m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>17.5</td>
<td>15.6</td>
</tr>
<tr>
<td>0.90</td>
<td>18.1</td>
<td>18.0</td>
</tr>
<tr>
<td>0.75</td>
<td>18.2</td>
<td>18.0</td>
</tr>
<tr>
<td>0.50</td>
<td>18.4</td>
<td>17.9</td>
</tr>
<tr>
<td>0.25</td>
<td>17.6</td>
<td>17.5</td>
</tr>
<tr>
<td>0.10</td>
<td>18.7</td>
<td>17.5</td>
</tr>
<tr>
<td>0.00</td>
<td>35.7</td>
<td>35.0</td>
</tr>
</tbody>
</table>

Table 5.8: $\gamma_{t=100\ s}$ values from DST measurements and $\gamma_{\text{eq}}$ values from surface tension measurements for the Capstone 1157: SDS mixed system at different mole fractions. Data for the individual surfactants are also reported.

For each mole fraction, very low $\gamma_{t}$ are reached in both DST and tensiometry measurements, even when SDS is the dominant component. This behaviour is unlike the other FC: HC surfactant mixtures whereby the $\gamma_{t}$ value were found to increase as the mole fraction of SDS was increased. Esumi \textit{et al.} reported analogous behaviour.
Results showed that the FC: HC mixed surfactant system gave $\gamma_{eq}$ of 16.5 mN m$^{-1}$ at all mole fractions; $\gamma_{eq}$ values for the FC and HC surfactants are 20 mN m$^{-1}$ and 44.2 mN m$^{-1}$, respectively. Mixtures therefore reduced values of $\gamma_{eq}$ to below that of the FC surfactant and resulted from electrostatic attractions between the two surfactants. Although no overall reduction in $\gamma_{eq}$ is shown here, it is clear that similar logic can be employed and this is therefore the first indication that the $\gamma(t)$ decay is highly influenced by the presence of Capstone 1157. Raw and normalised DST data for the mixed systems can be seen below in Figure 5.11.

Figure 5.11: Raw and normalised dynamic surface tension plots for the Capstone 1157: SDS mixed systems. The key shown in (a) represents the data in both graphs. All samples measured at respective CACs (see Table 5.2). $T = 25^\circ C$.

Similarities are observed in the general shape of the raw DST curves in Figure 5.11a, further highlighting that the DST/ short time interfacial behaviour is predominately dictated by the FC surfactant. Linear DST behaviour is seen for SDS individually at the CMC (8.3 mM) and unlike the other investigated mixed systems, there is no trend towards linear behaviour even at high SDS mole fractions.
CHAPTER 5. SOLUTION PROPERTIES OF FLUOROCARBON HYDROCARBON SURFACTANT MIXTURES

To emphasise differences in rates of $\gamma(t)$ decay between the studied mole fractions, normalised data has been plotted in Figure 5.11b and shows a trend whereby the $\gamma(t)$ decay is slower as the SDS mole fraction is increased. Slower $\gamma(t)$ decays in both the 0.90: 0.10 and 0.75: 0.25 (FC: HC) mole fractions samples can be understood by the noted high viscosity of the FC surfactant. In Chapter 4, small-angle neutron scattering showed that elongated structures are formed in solution, which have been shown previously to lead to increased viscoelastic behaviour in zwitterionic surfactants. Both the 0.90: 0.10 and 0.75: 0.25 mole fraction samples contain the highest concentrations of Capstone 1157 and increasing the viscosity will slow down the rate at which surfactants diffuse to the surface, leading to slower $\gamma(t)$ decays. The concentration of Capstone 1157 in the mixtures increases up to the 0.50: 0.50 mole fraction sample, at which point the $\gamma(t)$ decay increases. As previously stated, electrostatic attractions occur in mixtures containing zwitterionic FC and anionic HC surfactants and this favourable interaction between the FC and HC surfactants may occur only when the concentration/mole fraction of HC surfactant is sufficiently high. If complexation takes place between the two surfactants, both the aggregation structures and viscosity of the solution would conceivably change. As the mole fraction of HC is increased to 0.10: 0.90, further complexation may take place leading to molecules with apparent higher molecular weights which would diffuse slower than the individual components. Quantifying these rates of $\gamma(t)$ decay over the range of mole fractions has been carried out in the same way as previously shown. Plots are shown in Figure 5.12 and the associated data is presented in Table 5.9.

Figure 5.12: Dynamic surface tension of the Capstone 1157: SDS mixed systems plotted vs. $t^{1/2}$ and $t^{-1/2}$ for analysis of short and long time $D_{\text{eff}}$ values. Data for the individual surfactants are also shown. The lines are least square fits to the data. The concentrations and mole fractions are the same as in Figure 5.11. $T = 25 \, ^{\circ}\text{C}$. 

(a) Capstone 1157: SDS as $t \to 0$

(b) Dynax DX2200: SDS as $t \to \infty$
CHAPTER 5. SOLUTION PROPERTIES OF FLUOROCARBON HYDROCARBON SURFACTANT MIXTURES

<table>
<thead>
<tr>
<th>Mole fraction/ Capstone 1157</th>
<th>Short time diffusion</th>
<th>Long time diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gradient/ s</td>
<td>$D_{\text{eff}}/ \text{mN m}^{-1} \text{s}^{-1/2}$</td>
</tr>
<tr>
<td>1.00 0.90</td>
<td>-6.0 2.05</td>
<td>15.5 1.66</td>
</tr>
<tr>
<td>0.90 1.23</td>
<td>-8.0 2.15</td>
<td>22.0 1.37</td>
</tr>
<tr>
<td>0.75 3.16</td>
<td>-17.0 2.73</td>
<td>33.0 0.28</td>
</tr>
<tr>
<td>0.50 1.12</td>
<td>-27.0 1.53</td>
<td>8.0 1.63</td>
</tr>
<tr>
<td>0.25 2.00</td>
<td>-22.0 1.01</td>
<td>26.0 0.15</td>
</tr>
<tr>
<td>0.10 6.31</td>
<td>-9.0 0.10</td>
<td>47.0 0.02</td>
</tr>
<tr>
<td>0.00 0.15</td>
<td>-              4.50*</td>
<td>38.0 0.0002</td>
</tr>
</tbody>
</table>

Table 5.9: Time taken for the normalised $\gamma(t)$ to decay to a surface tension of 0.50 and effective diffusion coefficients calculated from the diffusion-only controlled models at short and long time limits for the Capstone 1157: SDS mixed systems. * Literature value for the SDS diffusion coefficient.  

The previous argument regarding the initial increase in viscosity between the 0.90: 0.10 and 0.75: 0.25 mole fractions samples, and subsequent decrease in viscosity due to the complexation between the two surfactants is further emphasised from the $t_{\gamma=50\%}$ reduction data. From the data in Figure 5.12a, it is clear that the $\gamma(t)$ decays for all of the studied mole fractions do not begin at $\gamma_0$, and issues are therefore expected in the calculations of $D_{\text{eff}}$ at both long and short times. Although issues are expected, the $D_{\text{eff}}$ data at short times follows the correct trend and fit well with the above argument. The only anomalous results is that for the 0.10: 0.90 mole fractions sample, whereby the short time $D_{\text{eff}}$ value reduces by an order of magnitude compared to the 0.25: 0.75 sample. This value of $0.10 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ is similar to that of a high molecular weight surfactant and is a much lower value than expected from observations of the normalised data. As previously mentioned, the magnitude of $D_{\text{eff}}$ is directly affected by both the gradient in $\gamma(t)$ vs. $t^{1/2}$ plot and bulk concentration. If the DST behaviour is essentially dominated by the FC surfactants, the concentration used to calculate the $D_{\text{eff}}$ value at high mole fractions of SDS will therefore be too high, leading to $D_{\text{eff}}$ values being underestimated. This is considered in the following section whereby the $D_{\text{eff}}$ values are used to in the diffusion-only adsorption model to produce theoretical DST curves.

In all of the mixed systems, it has been shown that the DST behaviour is essentially dominated by the more surface active FC surfactants. The extent to which the air/water interface is dominated by the FC surfactant cannot be determined by this DST method, and only trends regarding how the $\gamma(t)$ decay is affected by the increasing the mole fraction of SDS can be compared and discussed. In Chapter 6, neutron reflectivity (NR) has been used to investigated the composition of the air/water interface for these different FC: HC surfactant mixtures. Although the NR experiments are being carried out over time periods much longer than a DST measurement, an idea of how the surface is populated at these fast times can be understood.
5.4.3 Modeling of mixed system dynamic surface tension data

As in Chapter 4, the short time $D_{\text{eff}}$ values can be used to theoretically model the DST data and determine whether the mixed system adsorption is a diffusion-only mechanism.$^{44, 49-51}$ To appropriately employ the diffusion-only model requires the short and long time limits to be used when $\gamma(t)$ is close to either the tension of the solvent ($\gamma_0$) or $\gamma_{\text{eq}}$ as $t \to 0$ or $\infty$, respectively. From the short time plots of $\gamma(t)$ vs. $t^{1/2}$ (Figures 5.8, 5.10 and 5.12), it was shown that as $t \to 0 \neq \gamma_0$ for the majority of the samples due to the high surface activity of the respective surfactants, and errors associated with the determined $D_{\text{eff}}$ are expected. The above results for the FC: HC mixed surfactant systems showed that the $\gamma(t)$ decay behaviour is dominated by the FC surfactants. As a comparison, the theoretical models have therefore been calculated using both the mixed system and individual surfactants $D_{\text{eff}}$ values. Figure 5.13 shows the data and theoretical models for the 0.50: 0.50 mole fractions mixtures for the three mixed surfactant systems. Due to the large volume of data, the remaining models can be found in the Appendix.

(a) Dynax DX1030: SDS 0.50: 0.50 mole fraction model
Figure 5.13: DST for the FC: HC mixed systems at a mole fraction of 0.50: 0.50. All concentrations are at respective CACs (Table 5.2). The red, dark blue and cyan lines are theoretical calculations using Equations 1.8 and 1.11, respectively. Note: the long time model has been used to predict the $\gamma(t)$ of the Dynax DX2200: SDS mixed system at longer times than measured.

Within the relevant literature, it is common that the diffusion-only controlled mechanism accurately accounts for the $\gamma(t)$ decay at short times, whereas at long times less agreement is observed.$^{44, 50–54}$ Agreement at short times is due to the initial availability of ‘vacant’ adsorption sites and low $\Gamma$ value, however at long times ($\Gamma$ approaches $\Gamma_{eq}$) less adsorption sites are available and more back diffusion is likely, leading to behaviour which is consistent with the presence of a weak adsorption barrier and is therefore no longer a diffusion-only controlled mechanism.$^{44, 50, 51}$
Calculations using the $D_{\text{eff}}$ value for SDS were carried out for completeness, but in all cases poorly account for the $\gamma(t)$ decays at both short and long times. Although the use of both the mixed and FC surfactants $D_{\text{eff}}$ values account well for $\gamma(t)$ decay in the Dynax DX1030: SDS and Dynax DX2200: SDS mixed systems (Figure 5.13a and 5.13b) at short times, the FC surfactants $D_{\text{eff}}$ values provide a better description of the data compared to the mixed $D_{\text{eff}}$. This therefore provides further evidence that the short times $\gamma(t)$ is dictated by the FC surfactants. In the Capstone 1157: SDS mixed system there is very poor agreement between the theoretical and experimental results at short times, with the theoretical models greatly overestimating the rate of $\gamma(t)$ decay. This therefore shows that diffusion/adsorption in the mixed system is slower than that for the FC surfactant individually. As discussed above, antagonistic FC: HC interactions and attractive interactions between the positive charge of the zwitterionic FC surfactant and anionic portion of the HC surfactant lead to the overall ideal behaviour in the Capstone 1157: SDS mixed systems. The attractive interaction could lead to complexation between the two surfactant molecules and hence formation of a larger molecular weight species, which would therefore be expected to slow down the diffusion process and hence explain the lack of agreement in the theoretical model prediction.

Considering the long time data for all of the mixed systems, the lack of agreement between the theoretical and experimental $\gamma(t)$ decays is consistent with the presence of a weak adsorption barrier, a behaviour that is commonly observed for both FC and HC surfactants. This typical long time behaviour is seen in both the Dynax DX1030: SDS and Dynax DX2200: SDS mixed systems, whereby a lower tension is predicted compared the experimental results, hence the adsorption is no longer diffusion-controlled. Upon reaching $\gamma_{\text{eq}}$ in the Capstone 1157: SDS mixed system, the theoretical prediction is shown to compare well with the experimental results, with no disparity between the tension values. However, as with the short time diffusion, the model overestimates the $\gamma(t)$ decay rate, plateauing at $\gamma_{\text{eq}}$ much quicker than the experimental results.

Comparing the diffusion-only controlled adsorption predictions for the three mixed surfactant systems at different mole fractions (Figure 5.13 and the Appendix), a general trend was observed that when SDS is the major component within the mixture, the theoretical models tend to fall apart and not agree well with the experimental data. As the mole fraction of SDS is increased within the mixed system, additional interactions between the two surfactant molecules that would need to be considered to accurately describe the diffusion process, which are not taken into account when using the diffusion-only adsorption model.
CHAPTER 5. SOLUTION PROPERTIES OF FLUOROCARBON HYDROCARBON SURFACTANT MIXTURES

5.5 Conclusions

Literature associated with the micellisation properties/ dynamic surface tension behaviour of mixtures containing partially fluorinated surfactants (with different head groups) and a common hydrocarbon (HC) surfactant are hard to come by.\textsuperscript{23, 24} This is despite the multitude of literature on anionic perfluorinated surfactant mixtures with different head group HC surfactants.\textsuperscript{1, 3, 6, 13, 14, 16, 17, 20} In general, the interaction between HC and FC tail groups are unfavourable and lead to antagonistic behaviour when considering mixtures of anionic perfluorinated surfactants with anionic HC surfactants. This has been shown not to be the case with mixtures of non-ionic and zwitterionic HC surfactant mixtures with perfluorinated surfactants, due to a reduction in repulsion between head groups in the non-ionic and strong Columbic attractions in the zwitterionic, leading to synergistic behaviour.

In this Chapter, the solution properties of mixtures containing partially fluorinated surfactants bearing different head groups (anionic, non-ionic and zwitterionic) and an anionic HC surfactant, SDS, have been studied. Mixed CACs were determined using both surface tension and UV-Vis measurements, generally displaying comparable values. The experimental values were also compared to calculated ideal values using regular solution theory (RST). Large differences between the two techniques were observed in the mixed system containing the non-ionic FC surfactant and SDS. The reason for this was thought to be due to the large area per molecule observed for the non-ionic surfactant compared to the SDS (65 Å\textsuperscript{2} and 44 Å\textsuperscript{2} respectively), essentially causing the air/water interface to be dominated by the FC surfactant, as was also observed in the dynamic surface tension (DST) behaviour. For this reason, the UV-Vis data was used for discussion as a larger sample of molecules are taken into account during the measurement. Antagonistic behaviour was observed for this mixed system and is expected due to the presence of the C8 fluorinated tail group and lack of polarity within the molecule. The zwitterionic FC surfactant mixtures with SDS displayed ideal behaviour, with good overlap between the two different employed methods. Ideal behaviour between partially fluorinated surfactants and SDS have been reported previously.\textsuperscript{24} Zwitterionic surfactants are able to accept or donate a proton, allowing the production of a net positive or negative charge.\textsuperscript{21} The zwitterionic betaine surfactant used in this study, Capstone 1157, bears both a quaternary ammonium group and carboxylate group. The surfactant is more likely to accept a proton onto the carboxylate group due to the stability of the quaternary ammonium group group, leading to a small positive charge on the FC surfactant. The combination of the favourable interaction between the positive charge on the FC surfactant and the negative charge on the HC surfactant and the unfavourable interaction between the FC and HC chains compensate one another, leading to the observed ideal behaviour. Mixtures containing the anionic FC and anionic HC
surfactants produced unusual behaviour. At high mole fractions of FC surfactant, antagonism was observed, ideal behaviour was shown at equal mole fractions and synergism was displayed at low mole fractions of FC surfactant. Similar trends were shown previously for mixtures of partially fluorinated cationic surfactants mixed with the cationic HC surfactant CTAB.\(^{23}\)

The surface tensions (\(\gamma\)) of partially fluorinated surfactants and HC surfactants can differ greatly.\(^{1, 2}\) DST measurements were therefore carried out to determine how the addition of an anionic HC surfactant (SDS) at different mole fractions can affect the \(\gamma(t)\) decay of the FC surfactants. SDS shows fast initial dynamics followed by a linear decay in \(\gamma(t)\), whereas the FC surfactants generally show a slightly slower decay in \(\gamma(t)\) over the duration of the DST measurements. By comparing the DST curves for the different FC: HC surfactant mixtures at the range of mole fractions, it was possible to determine that the DST behaviour is generally dictated by the presence of FC surfactants in all of the investigated mixtures. In addition to this, in some cases it was shown that the FC: HC surfactant mixtures led to faster \(\gamma(t)\) decays and also reached \(\gamma_{eq}\) values similar to the FC surfactants. This therefore shows that the FC: HC surfactant mixtures in some cases can display superior surface properties compared to the individual components.

It has therefore been shown that mixtures containing partially fluorinated surfactants and an anionic HC surfactant (SDS) can often interact favourably in terms of micellisation behaviour and \(\gamma\) reduction. It is clear in some mixed systems that even at low mole fractions of FC surfactant, both low CACs and \(\gamma_{eq}\) values can be reached. This is an important insight in terms of using FC surfactants in industrial formulations, as it has been shown that the desired solution properties of a formulation can still be achieved at both low concentrations/ compositions of FC surfactants.
References


REFERENCES


Chapter 6

Investigations into the surface compositions of fluorocarbon hydrocarbon surfactant mixtures

The previous Chapter was concerned with determining the solution properties of mixed systems containing partially fluorinated surfactants with an anionic hydrocarbon (HC) surfactant. Three different partially fluorinated surfactants were investigated, all of which had different headgroups, and were mixed in different mole fractions with SDS. Critical aggregation concentration (CACs) and dynamic surface tension (DST) measurements showed that some mixed systems, namely the zwitterionic fluorocarbon (FC) and SDS mixture, displayed favourable properties upon mixing (low CACs and surface tension) even at high mole fractions of SDS. This Chapter will therefore build upon the results in Chapter 5 by using neutron reflectivity (NR) to investigate the surface compositions and surface density parameters of FC: HC surfactant mixed systems at multiple bulk compositions and concentrations.

6.1 Introduction

Contrast variation NR has been used extensively for detailed analysis of both the surface properties and compositions of complex mixed surfactant systems.\textsuperscript{1–11} The technique exploits the large differences in scattering length density (SLD) between hydrogen and deuterium containing materials through the use of h/d isotopic substitution in null reflecting water (NRW, SLD $\sim 0 \times 10^{-6}$ Å$^{-2}$). For HC: HC surfactant mixtures in NRW, if one surfactant is deuterated and the other is hydrogenated, the reflectivity of the deuterated surfactant (SLD $\sim 6 \times 10^{-6}$ Å$^{-2}$) is highlighted, whilst the hydrogenated surfactant will be contrast matched out (SLD $\sim 0 \times 10^{-6}$ Å$^{-2}$). This method allows for the surface excess of each surfactant within
the mixed system to be determined individually and hence providing information on surface compositions. Early work by Penfold et al. used this method to determine the surface composition of an equimolar mixture containing two non-ionic HC surfactants at multiple concentrations. The data were compared to surface composition results from both surface tension measurements and analysis using regular solution theory (RST), showing good agreement between the two methods.

The use of RST to describe the composition of mixed surfactant monolayers was put forward by Rosen and was an extension of the model used for describing the composition of mixed micelles by Rubingh (discussed further in Chapter 1). Since then, RST has been used in conjunction with NR to provide detailed theoretical and experimental descriptions of the solution properties and surface compositions of mixed surfactant systems. Most of the studies comparing theoretical and experimental surface compositions have been investigated using ideal and non-ideal HC: HC surfactant mixtures. Hines et al. used NR and RST to carry out extensive investigations into different HC: HC surfactant mixtures displaying ideal and non-ideal behaviours, comparing the experimentally and theoretically determined surface composition values. Comparable surface compositions were reported in the non-ideal surfactant system containing a mixture of C12Maltoside (non-ionic) and SDS (anionic), whereas differences in the surface compositions were shown in the ideal mixed surfactant system containing C12Maltoside and C12betaine (zwitterionic). The large difference in CMC between the non-ionic and zwitterionic surfactant explained the observed differences between the theoretical and experimental surface compositions, which in the non-ideal mixture was offset due to the strong synergistic interactions between the two surfactants. Li et al. investigated the surface compositions and interactions of synergistic mixtures containing ionic and zwitterionic surfactants by NR at concentrations both above and below the mixed CACs. For all studied mixtures, the surface compositions were found to be directed towards the more surface active component within the mixture at all mole fractions. In addition to this, the strong synergy displayed between the mixed systems fed through to synergy in the total surface excess at concentrations above the mixed CAC, showing enhancements of the components by \( \sim 45 \% \). Many more studies have been carried out comparing the theoretical and experimental surface compositions of HC: HC surfactant mixtures, often showing good agreement between the two methods.

There is much literature regarding the micellisation of mixtures containing perfluorinated surfactants mixed with HC surfactants, especially concerning the possible segregation in micelle populations, but papers examining surface adsorption in FC: HC surfactant mixtures are harder to come by. Villeneuve et al. summarised the earlier studies whilst carrying out novel investigations using surface tension measurements to determine the miscibility of mixtures containing non-ionic FC and HC surfactants at the surface and in micelles. To determine the
extent of non-ideal mixing, estimations were made using the Gibbs-Duhem method to determine the excess free energy of mixing ($G^E$). At the surface, positive values of $G^E$ were observed at all studied mole fractions, with a maximum of $\sim 0.12$ RT at a FC surfactant mole fraction of 0.60, a smaller interaction than determined for the micelles ($\sim 0.30$ RT). The results therefore show an enhancement in non-ideal interactions in the micelles compared to at the surface for the FC: HC surfactant mixtures, suggesting that the antagonism between FC and HC surfactants is stronger in the micelles than at the surface.

More recently, contrast variation NR along with determination of $G^E$ values has been used to investigate the surface compositions of mixtures containing partially fluorinated and HC cationic surfactants. Three FC surfactants with differing FC tail lengths (C4 - C8) were studied. Direct measurements of the surface compositions showed that even when the bulk composition was majority HC surfactant, the FC surfactants were present at higher surface compositions, this likely being due to lower surface activity of the HC surfactants compared to the FCs. In addition to this, for all of the studied mixed systems, $G^E$ was shown to be highly asymmetrical, being close to ideal at FC surface compositions $< 0.50$, but increasing with FC content to a maximum in the range of 0.2 - 0.3 RT. In depth NR experiments using isotopic contrasts of both the FC and HC surfactants allowed for detailed analyses of the different surfactant arrangements in the mixed monolayers. At low fractions of FC, any increase in the FC: HC antagonism was compensated by a reduction in the immersion of the FC surfactants in water, which in turn is caused by screening by the small amount of HC surfactant. This compensation, however, is lost as the concentration of HC surfactant increases to $\sim 0.50$ and the FC: HC surfactant antagonism cannot be avoided.

In this Chapter, the surface composition ($\chi'$) of mixtures containing partially fluorinated surfactants bearing different head groups mixed with SDS at varying bulk mole fractions and concentrations have been studied by NR and compared to theoretical predictions by RST. The NR data have been analysed by two different methods to determine the experimental $\chi'$ values. The first uses the assumption that the fitted SLD ($\rho_{\text{fitted}}$) of the mixed monolayer can be described by the ratio of $\rho_{\text{fitted}}$ for the two constituent components within the mixtures, the second uses h/d-SDS isotopic contrast variation experiments to determine the surface density parameters of the mixed systems and hence compositions of the monolayers. For all of the FC: HC surfactant mixtures, results show that the surface is dominated by the FC surfactants, even at high SDS bulk composition. Good agreement between the experimental and theoretical $\chi'$ values has been shown at high FC surfactant mole fractions, but less agreement at high mole fractions of SDS.
CHAPTER 6. INVESTIGATIONS INTO THE SURFACE COMPOSITIONS OF FLUOROCARBON HYDROCARBON SURFACTANT MIXTURES

6.2 Materials and Methods

6.2.1 Materials

The preparation of the partially fluorinated surfactants has been described in Chapter 2. Sodium dodecylsulfate (CAS 151-21-3) (Sigma-Aldrich, ≥ 98.5 %) and deuterium oxide (Aldrich, 99.9 %) were used as received. Deuterated sodium dodecylsulfate was prepared and supplied by the ISIS deuteration facility at the Rutherford Appleton laboratory, Didcot, UK. All surfactant structures are shown below in Table 6.1.

<table>
<thead>
<tr>
<th>Surfactant Name</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td><img src="image" alt="Dynax DX1030 Chemical Structure" /></td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td><img src="image" alt="Dynax DX2200 Chemical Structure" /></td>
</tr>
<tr>
<td>Capstone 1157</td>
<td><img src="image" alt="Capstone 1157 Chemical Structure" /></td>
</tr>
<tr>
<td>Sodium Dodecylsulfate</td>
<td><img src="image" alt="Sodium Dodecylsulfate Chemical Structure" /></td>
</tr>
</tbody>
</table>

Table 6.1: Surfactants used in this Chapter
6.2.2 Methods

Neutron Reflection

Neutron reflection (NR) measurements were carried out on the SURF beam-line on Target Station 1 at the ISIS facility (Rutherford Appleton Laboratory, Didcot, UK)\textsuperscript{31} and the FIGARO beam-line at the Institut Laue-Langevin (ILL, Grenoble, France).\textsuperscript{32} On FIGARO, a chopper pair gives a neutron $\lambda$ range between 2 and 30 Å. The incident beam is at 0.62$^\circ$ and the angle can be altered to 3.8$^\circ$ to produce a possible Q range of 0.0045 to 0.42 Å$^{-1}$. On SURF, the incident beam is inclined at 1.51$^\circ$ from the horizontal, which can be varied to either 0.35$^\circ$ and 0.65$^\circ$ using either a computer-controlled goniometer, or a 3 x demagnifying curved supermirror for liquid surfaces. SURF has incident wavelengths of 0.55 - 6.8 Å at 50 Hz and an associated Q range of 0.048 - 1.1Å$^{-1}$. The NR experiments were carried out using null reflecting water (NRW; 8 mol\% D$_2$O in H$_2$O with an SLD of $\sim 0 \times 10^{-6}$ Å$^{-2}$). A pippette was used on each sample to suck off any air bubbles and also to remove the initial surface layer in case any hydrophobic impurities were present. The data were fit using MOTOFIT, written for IGOR Pro.\textsuperscript{33}
6.3 Using neutron reflectivity to determine the composition and surface density parameters of mixed monolayers

Neutron reflectivity (NR) is the most direct approach for investigating the compositions of mixed surfactant monolayers at the air/water interface and as such has attracted much interest within the literature.\textsuperscript{1-9} For example, studies on mixed HC surfactants take advantage of the large difference in SLD between deuterated and hydrogenated surfactants in NRW. The reflected signal of a deuterated surfactant in NRW will be strong, however a hydrogenated surfactant in NRW will produce only a very small reflected signal, if any. Hence, the reflectivity of mixtures can be measured with one surfactant deuterated and the other hydrogenated in NRW, allowing the surface excess, $\Gamma$, and composition of the mixed systems to be determined in the usual way:

$$A = \frac{1}{\Gamma N_a} = \frac{b}{\rho \tau}$$  \hspace{1cm} (6.1)

where $\rho$ (Å$^{-2}$) is the fitted scattering length density of the layer, $\tau$ (Å) is the fitted thickness of the layer, $b$ (Å) is the scattering length of the molecule, $A$ (Å$^2$) is the area per molecule, $\Gamma$ (mol m$^{-2}$) is the surface excess and $N_a$ (mol$^{-1}$) is Avogadro’s number. Ideally, the evaluation of the adsorbed amounts are made with the protonated component having zero scattering length, then Equation 6.1 can be used.\textsuperscript{5} However, if the SLD of the hydrogenated surfactant is not zero, simple manipulation allows Equation 6.1 to be expanded to account for both components in the mixture:

$$\rho = \frac{b_1}{A_1 \tau} + \frac{b_2}{A_2 \tau}$$  \hspace{1cm} (6.2)

where the superscripts 1 and 2 refer to the two components within the mixture. This Equation therefore gives $\Gamma$ values for the overall mixed system. Using the example of a FC: HC surfactant mixture, the $\Gamma$ of the second component (SDS) can then be easily determined from:

$$\Gamma_{\text{mixed}} = \Gamma_{\text{f-surf}} + \Gamma_{\text{SDS}}$$  \hspace{1cm} (6.3)

In addition to this previously developed method, a method based on fitted $\rho$ values has been used to calculate the surface compositions. Having studied all of the FC surfactants individually by NR (Chapter 4) above and below the respective CMCs, the fitted NR parameters have been determined. This is also true for SDS,
which will be presented in Section 6.4. Therefore, the fitted SLD \( \rho_{\text{fitted}} \) of a FC: HC surfactant mixture can be compared to the calculated SLD \( \rho_{\text{calc}} \) in the following way:

\[
\rho_{\text{calc}} = (\alpha_{\text{f-surf}} \cdot \rho_{\text{f-surf}}) + ((1 - \alpha_{\text{f-surf}}) \cdot \rho_{\text{SDS}})
\]

(6.4)

where \( \rho_{\text{calc}} \) is the calculated SLD of the mixture, \( \alpha \) is the mole fraction of each component in the mixture and \( \rho_{\text{f-surf}}/\rho_{\text{SDS}} \) are the fitted SLDs of the FC surfactant and SDS individually at the CMC. The values for \( \rho_{\text{f-surf}}/\rho_{\text{SDS}} \) are already known from previous individual measurements, hence the \( \alpha \) term can be adjusted until \( \rho_{\text{calc}} = \rho_{\text{fitted}} \), and the composition of the mixed monolayers can be determined. To properly apply this Equation relies on having NR data for the constituent components at the concentrations present within the mixture. This has not been possible for every mixed system, therefore \( \rho \) values above the CMC of the constituent components have been used. To back up these initial calculations, the contrast match experiments described above have been employed.

It is clear that the d/h contrast variation experiment described above can be used in mixed FC: HC surfactant systems. For clarity, the investigated contrasts are shown pictorially below:

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{contrast_variations.png}
\caption{Showing the two contrasts used in this Chapter. In (a) h-SDS is of low contrast and so reflection from FC surfactant is highlighted, Equation 6.1 is then applied. (b) The reflection of the overall layer is seen, Equations 6.2 and 6.4 are then be applied.}
\end{figure}

Manipulation of the SDS contrast therefore makes it possible to highlight the scattering of interest, allowing for determination of the important compositions/surface density parameters. To be able to apply Equation 6.4, it is necessary to have determined the reflection parameters associated with d-SDS at the air/NRW interface at concentrations above and below the CMC. These data are presented next with direct comparisons to the relevant literature.
6.4 Neutron reflectivity of sodium dodecylsulfate

To ensure confidence in the determination of the mixed FC: HC surface compositions, it is important that the analysis of the standard SDS individually is correct and comparable to the literature. SDS is a relatively simple, albeit expensive, molecule to deuterate, hence has been the subject of many NR studies, for example but not limited to.\textsuperscript{2, 5, 34} Early studies utilised NR as a way of directly comparing surface density parameters ($\Gamma_{CMC}$ and $A_{CMC}$) from both surface tension and NR methods. The normalised reflectivity profiles as well as the $\Gamma$ vs. concentration plot are shown below in Figure 6.2, and the surface density parameters associated with modeling of the normalised data are shown in Table 6.2.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$\rho$/ (10^{-6} Å^{-2})</th>
<th>$\tau$/ (Å)</th>
<th>$\Gamma_{CMC}$/ (10^{-6} mol m^{-2})</th>
<th>$A_{CMC}$/ (Å^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-SDS (This Study)</td>
<td>3.55</td>
<td>20.0 ± 1.0</td>
<td>4.25 ± 0.20</td>
<td>40.0 ± 2.0</td>
</tr>
<tr>
<td>d-SDS (Literature)</td>
<td>3.54</td>
<td>19.0 ± 2.0</td>
<td>4.10 ± 0.40</td>
<td>41.0 ± 4.0</td>
</tr>
</tbody>
</table>

Table 6.2: Parameters associated with modeling the d-SDS neutron reflectivity data. $\rho$ is the fitted scattering length density, $\tau$ the fitted monolayer thickness. $\Gamma_{CMC}$ is the surface excess concentration at the CMC and $A_{CMC}$ is the area per molecule at the CMC. The data from literature have been taken from ref.\textsuperscript{2}
Figure 6.2: (a) Neutron reflectivity profiles of d-SDS at concentrations above and below the CMC (8.2 mM) in NRW. Fitted functions shown as lines. (b) Surface excess vs. concentration plot as determined by analysis of the neutron reflectivity data. Data from Lu et al. also shown.\(^2\) Dashed line is a guide to the eye. \(T = 25\,^{\circ}\)C.

From Figure 6.2b, the \(\Gamma\) vs. conc graph shows the expected plateau behaviour associated with the saturation of the air/water interface above the CMC of d-SDS. Although having additional data points on this graph would be beneficial, it was necessary to be sparing with the use of d-SDS throughout the experiments. From Table 6.2, results determined from analysis of the NR data has been presented, showing more good agreement with the literature\(^2,\,5,\,34\). Therefore, going forward with the analysis of the complex FC: HC surfactant mixtures, it is now known that the analysis of d-SDS is both correct and comparable to the literature, providing further confidence in the following results Sections.
6.5 Compositions and surface density parameters of fluorocarbon hydrocarbon surfactant mixtures

As previously mentioned, NR is a very useful technique for determining both the compositions and surface density parameters of mixed surfactant systems. This is due to the sensitivity of the technique to small changes in the scattering length density within the monolayer. Therefore, through the use of careful contrast variation experiments, these of which have been described above, specific components within a mixed monolayer can be contrast matched out, leaving the reflectivity signal of the surfactant of interest being highlighted. It is instructive to make sure the fitted parameters associated with both the individual FC surfactants and SDS have been determined correctly. Data for the individual FC surfactants were presented in Chapter 4 as well as in ref \textsuperscript{35} and have been summarised below in Table 6.3.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$\rho$ / ((10^{-6} \text{ Å}^{-2}))</th>
<th>$\tau$ / (Å)</th>
<th>$\Gamma_{\text{CMC}}$ / ((10^{-6} \text{ mol m}^{-2}))</th>
<th>$A_{\text{CMC}}$ / ((\text{Å}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td>1.35</td>
<td>26.5 ± 1.0</td>
<td>3.95 ± 0.20</td>
<td>42.5 ± 2.0</td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td>2.55</td>
<td>25.0 ± 2.0</td>
<td>2.50 ± 0.10</td>
<td>65.0 ± 0.5</td>
</tr>
<tr>
<td>Capstone 1157</td>
<td>2.00</td>
<td>23.0 ± 0.5</td>
<td>5.22 ± 0.10</td>
<td>31.0 ± 1.0</td>
</tr>
<tr>
<td>d-SDS</td>
<td>3.55</td>
<td>20.0 ± 0.5</td>
<td>4.25 ± 0.10</td>
<td>40.0 ± 1.0</td>
</tr>
</tbody>
</table>

Table 6.3: Parameters from analysis of neutron reflectivity data for Dynax DX1030, Dynax DX2200, Capstone 1157 and d-SDS. $\rho$ is the fitted scattering length density, $\tau$ the fitted monolayer thickness. $\Gamma_{\text{CMC}}$ is the surface excess concentration at the CMC and $A_{\text{CMC}}$ is the area per molecule at the CMC.

These data have been used in conjunction with Equation 6.4 to determine the compositions of the mixed FC: HC surfactant monolayers at concentrations above and below the critical aggregation concentrations (CACs). The problems associated with employing this Equation have been highlighted above and will be addressed throughout the discussion.

The first set of analyses will provide the compositions of the mixed FC: HC monolayers (structure of surfactants can be seen in Table 6.1). Each mixture has been studied at three mole fractions, 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 and concentrations above and below the respective CACs so that a full range of compositions can be realised. The CAC data were presented in Chapter 5. The second set of analyses will use the contrast variation experiments described above to determine the surface density parameters and hence compositions of the mixed monolayers. This will then be compared with the initial method as well as RST.\textsuperscript{12–15} All of the reported data have been modeled using a single layer model.
6.5.1 Surface compositions above and below critical aggregation concentrations

The initial measurements of the FC surfactant surface compositions ($\chi'_{f-surf}$) in the FC: HC surfactant mixtures were carried out using the FC surfactant: d-SDS: NRW contrast. The reflected signals are therefore from both the FC and HC surfactants at the air/water interface. Above the respective CMCs, the individual FC surfactants all have lower fitted $\rho$ values than d-SDS (Table 6.3). Measurements of the reflected signal will therefore increase as the composition of d-SDS is increased i.e. from 0.90: 0.10 to 0.10: 0.90 (FC: HC). For example, a fully saturated layer of Dynax DX1030 has a $\rho_{fitted}$ value of $\sim$1.35 x $10^{-6}$ Å$^{-2}$, whereas d-SDS has $\rho_{fitted}$ value of $\sim$3.55 x $10^{-6}$ Å$^{-2}$. The reflected signal of mixed systems above the CAC should therefore never go below that of Dynax DX1030 or above that of d-SDS, and the compositions can therefore be determined using Equation 6.4. This behaviour can be seen in Figure 6.3.

Experiments reported here and in the following Section were carried out on several instruments (SURF, ISIS and FIGARO, ILL) over multiple experiments. The data shown in Figure 6.3 was measured on SURF and the data for the same experiments on FIGARO can be found in the Appendix. The calculated FC surfactant surface composition ($\chi'_{f-surf}$) values are averaged over both multiple fits and multiple experiments. The fits were carried out until $\chi^2 \leq 0.01$ and an error of $\sim$ 5 % for $\rho_{fitted}$ was generally found. These errors have been included in the calculations of $\chi'_{f-surf}$. The $\rho_{fitted}$ values for the mixed systems along with the calculated values of $\chi'_{f-surf}$ are presented below in Table 6.4.
Figure 6.3: Neutron reflectivity profiles of FC: d-SDS mixed systems at three mole fractions: 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 (FC: d-SDS) in NRW. All data are at 2.00 x CAC to ensure monolayer saturation. The neutron reflectivity profiles of each component at concentrations above the CMC are also shown. The overall concentrations in the mixture are shown in Table 6.4. Fitted functions shown as lines. T = 25 °C.
## CHAPTER 6. INVESTIGATIONS INTO THE SURFACE COMPOSITIONS OF FLUOROCARBON HYDROCARBON SURFACTANT MIXTURES

<table>
<thead>
<tr>
<th>Mole fraction/Fluorocarbon</th>
<th>Concentration/ mM (x CAC)</th>
<th>$\rho_{\text{fitted}}/ (10^{-6} \text{Å}^{-2}) \pm 5%$</th>
<th>Surface composition/ ($\chi'_{f-surf}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dynax DX1030: SDS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>4.00 (2.00)</td>
<td>1.35</td>
<td>0.97 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>0.50 (0.25)</td>
<td>1.26</td>
<td>0.97 ± 0.03</td>
</tr>
<tr>
<td>0.50</td>
<td>5.06 (2.00)</td>
<td>1.51</td>
<td>0.92 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>0.63 (0.25)</td>
<td>1.39</td>
<td>0.90 ± 0.04</td>
</tr>
<tr>
<td>0.10</td>
<td>7.70 (2.00)</td>
<td>2.23</td>
<td>0.60 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>0.96 (0.25)</td>
<td>1.73</td>
<td>0.83 ± 0.04</td>
</tr>
<tr>
<td><strong>Dynax DX2200: SDS (Surface tension CAC)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>0.020 (2.00)</td>
<td>2.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.003 (0.25)</td>
<td>1.40</td>
<td>1.00</td>
</tr>
<tr>
<td>0.50</td>
<td>0.100 (2.00)</td>
<td>2.40</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.013 (0.25)</td>
<td>2.30</td>
<td>1.00</td>
</tr>
<tr>
<td>0.10</td>
<td>0.100 (2.00)</td>
<td>2.30</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.013 (0.25)</td>
<td>2.00</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Dynax DX2200: SDS (UV-Vis CAC)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>1.40 (2.00)</td>
<td>2.52</td>
<td>0.95 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>0.18 (0.25)</td>
<td>2.45</td>
<td>0.98 ± 0.02</td>
</tr>
<tr>
<td>0.50</td>
<td>4.10 (2.00)</td>
<td>2.55</td>
<td>0.94 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>0.51 (0.25)</td>
<td>2.60</td>
<td>0.85 ± 0.15</td>
</tr>
<tr>
<td>0.10</td>
<td>15.00 (2.00)</td>
<td>3.07</td>
<td>0.51 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>1.88 (0.25)</td>
<td>3.00</td>
<td>0.55 ± 0.15</td>
</tr>
<tr>
<td><strong>Capstone 1157: SDS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>0.30 (2.00)</td>
<td>2.00</td>
<td>0.97 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>0.04 (0.25)</td>
<td>1.85</td>
<td>0.96 ± 0.04</td>
</tr>
<tr>
<td>0.50</td>
<td>1.06 (2.00)</td>
<td>2.20</td>
<td>0.87 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>0.13 (0.25)</td>
<td>1.92</td>
<td>0.93 ± 0.07</td>
</tr>
<tr>
<td>0.10</td>
<td>3.36 (2.00)</td>
<td>2.80</td>
<td>0.49 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>0.42 (0.25)</td>
<td>2.30</td>
<td>0.60 ± 0.10</td>
</tr>
</tbody>
</table>

Table 6.4: Surface compositions determined by modeling of the mixed FC: HC surfactant systems neutron reflectivity data. $\rho_{\text{fitted}}$ is the fitted scattering length density of the layer, $\chi'_{f-surf}$ is the calculated surface composition of the FC surfactants within the mixtures (calculated using Equation 6.4). The total concentration along with the relative (x CAC) concentrations have been included.

From Figure 6.3 it can be seen that the data generally follows the discussed trend, i.e. the mixed systems NR profiles lie inbetween the NR data of the constituent components (these have been included in the Figures to show this observation). The only FC: HC surfactant mixture that does not follow this trend is Dynax DX2200: d-SDS (in particular the 0.90: 0.10 mole fraction sample), shown in Figure 6.3b. The concentration of the 0.90: 0.10 mole fraction sample was made up incorrectly (x 10 factor out), explaining the lower than expected reflected signal. With this being the only full set of data for this mixture, however, it has been left in the main text.
The surface compositions are dominated by the FC surfactants in all of the mixed systems, even when the HC surfactant is the major component. In this work (Chapters 4 and 5) the investigated FC surfactants were found to be very surface active, much more so than SDS. In Chapter 5 for example, the dynamic surface tension (DST) of the FC: HC surfactant mixtures were found to be directed by the FC surfactants at all compositions. This is expected due to the highly surface active nature of these FC surfactants. The same behaviour feeds through in terms of the $\chi_{f-surf}'$ values reported here. Similar results were found in a study by Jackson et al.\textsuperscript{9} In their work, three partially fluorinated cationic surfactants with differing lengths of FC tail were mixed with a cationic HC surfactant, with NR being used to study both the compositions and structures at the air/water interface. A suppression in the incorporation of the HC surfactant at the air/water was reported, especially at high FC surfactant compositions. At low FC surfactant compositions, the interactions between the FC and HC surfactants were found to be compensated by a reduction of the FC surfactant tail group in the water. However, this compensation was lost above 50 % HC surfactant and antagonism could not be avoided, therefore leading to a suppression in the HC surfactant surface compositions. These experiments by Jackson et al. involved extensive contrast variation, including deuteriation of both the partially fluorinated and HC surfactants.\textsuperscript{9} This has not been possible in this work, but nonetheless provides an interesting comparison to the presented results.

Unusual behaviour was displayed in the anionic Dynax DX1030: SDS mixed systems in Chapter 5. The mixtures exhibited antagonism at high mole fractions of FC, synergism at high mole fractions of HC surfactant, and ideal behaviour in the equimolar region. The same is not true when making reference to the $\chi_{f-surf}'$ values, whereby the surface is shown to be dominated by Dynax DX1030 at all compositions. Dynax DX1030 (anionic) and Capstone 1157 (zwitterionic) share similarities in chemical structure (see Table 6.1) and instructive comparisons can be made between these two mixed systems. Favourable interactions between the positive charge on the zwitterionic FC surfactant and the anionic headgroup of SDS\textsuperscript{36, 37} could account for the observed ideal behaviour for the Capstone 1157: SDS mixed systems. From this, it would be expected that the surface composition of HC surfactant would be higher in the Capstone 1157: SDS mixed systems compared to the Dynax DX1030: SDS mixtures, however similar $\chi_{f-surf}'$ values are observed for all compositions. Of the three FC surfactants, Capstone 1157 packs the most efficiently at the air/water interface and results in the lowest $\gamma_{\text{CMC}}$ ($\Gamma_{\text{CMC}} = 5.22 \times 10^{-6} \text{ mol m}^{-2}$, $\gamma_{\text{CMC}} = \sim 15.6 \text{ mN m}^{-1}$). This very high surface activity could suppress the favourable interactions between Capstone 1157 and SDS at the air/water interface, explaining the similarities in the $\chi_{f-surf}'$ to the Dynax DX1030: SDS mixtures. For strongly interacting mixed HC surfactant systems displaying synergism, the composition of the surface layers has been found to follow more closely with the bulk composition. For
example, the adsorption of synergistic mixtures of zwitterionic: ionic HC surfactants at the air/water interface were studied by Li et al. using NR. The least surface active species (ionic surfactant) was shown to have a lower surface composition at all studied mole fractions, but was nonetheless closer to the bulk composition than in the FC: HC surfactant mixtures studied here. This bias in terms of surface composition towards the more surface active component in mixed surfactant systems has been previously reported. 5, 9, 12 Therefore, with the large difference in surface activities between the FC and HC surfactants, it is not surprising that a strong suppression in the surface compositions of the less hydrophobic material are observed.

In Chapter 5 a large discrepancy in the experimentally determined CAC values between surface tension (SFT) and UV-Vis measurements was seen in the Dynax DX2200: SDS mixed systems. This mixed system has therefore been studied at the experimentally determined CAC values for both measurements. The data presented in Figure 6.3b was measured using the SFT determined CAC values. From the data, it can be seen that the reflected signal is dependent upon the concentration of Dynax DX2200 in the mixed system, and increasing the mole fraction of d-SDS has no effect. The concentration of d-SDS in these mixtures is very low and therefore expected to have limited influence on the overall reflected signals, hence explaining the $\chi_{f-surf}'$ values of 1.00 (FC). Considering the higher concentration samples (CACs determined by UV-Vis), with concentrations similar to the other mixed systems, changes in the $\chi_{f-surf}'$ values are seen. Dynax DX2200 is a much larger molecule than SDS with an area per molecule of 65 Å$^2$ compared to 40 Å$^2$ for SDS. More space will therefore be taken up at the air/water interface by Dynax DX2200, and this along with the antagonism experienced between the two surfactants, (see Chapter 5) leads to the observed suppression of SDS at the air/water interface.

Results have shown that the surface compositions of the FC: HC surfactant mixtures are highly influenced by the presence of the FC surfactants. The highly surface active nature of the FC surfactants suppresses any previously observed favourable interactions in the bulk between the FC and HC surfactants, leading to the composition of the surface being majority FC surfactants. Through the use of contrast match NR experiments, changes in the surface density parameters of the mixed systems will be considered.
6.5.2 Surface density parameters

Contrast variation NR is commonly used to determine the compositions of mixed monolayers.\textsuperscript{1, 2, 4, 5, 8, 9, 11, 12} Most of the literature associated with these experiments are concerned with HC: HC surfactant mixtures but more recently FC: HC surfactant mixtures have been studied.\textsuperscript{9} By deuterating each surfactant in the mixture in turn, leaving one surfactant hydrogenated, it is possible to contrast match out the hydrogenated surfactant (in NRW) so that the surface excess ($\Gamma$) can be calculated through the use of Equations 6.1 - 6.3. Here, however, in depth contrast variation experiments were not possible due to the difficulty in producing deuterated versions of the FC surfactants. Experiments were carried out using d/h-SDS contrast variation, allowing the $\Gamma$ value of the FC surfactants to be determined. The total $\Gamma$ and hence $\Gamma$ of SDS could then be calculated.

Below in Figure 6.4, data for the FC: d/ h-SDS mixed systems in NRW are shown. In the h-SDS samples, the reflected signal is just from the FC surfactant. The trend in the data is that the samples containing d-SDS produce larger reflected signals than that of the individual FC surfactants (included in the plotted data), and the opposite for the h-SDS samples. There was too much overlap in the d/ h-SDS data for the Dynax DX2200: SDS mixed system making observations difficult, therefore the h-SDS containing samples are shown below, and the d-SDS data is in Figure 6.3b.
Figure 6.4: Neutron reflectivity profiles of FC: d/h-SDS mixed systems at three mole fractions: 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 (FC: d/h-SDS) in NRW. All data are at 2.00 x CAC to ensure monolayer saturation. The neutron reflectivity profiles of each component at concentrations above the CMC are also shown. The overall concentrations in the mixture are shown in Table 6.4. Fitted functions shown as lines. T = 25 °C.
The data show clear differences between the d/ h-SDS samples. Both the Dynax DX1030 and Capstone 1157 mixed systems (Figures 6.4a and 6.4c) show a lowering of the reflected signal in h-SDS containing samples compared to d-SDS. The similarity in SLD between h-SDS and NRW means that no reflected signal will be produced from the h-SDS, hence only the FC surfactant is probed. It is therefore clear from the contrast matching experiments that mixed monolayers are being formed. Data for the Dynax DX2200: h-SDS mixed system (Figure 6.4b) is the same until the 0.10: 0.90 sample, suggesting that mixed monolayers are only formed when h-SDS is the major component. To calculate $\Gamma$ requires modeling of the data to determine thicknesses ($\tau$) of the layers and fitted SLDs (see Table 6.4). Fitted $\tau$ values were used to calculate the area per molecules (A) through the use of Equation 6.1 and are presented in Table 6.5.

<table>
<thead>
<tr>
<th>Mole fraction/Fluorocarbon</th>
<th>Concentration/ (x CAC)</th>
<th>$\tau_{\text{FC}}$/ (Å)</th>
<th>$A_{\text{FC}}$/ (Å²)</th>
<th>$\tau_{\text{Total}}$/ (Å)</th>
<th>$A_{\text{Total}}$/ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dynax DX1030: SDS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>2.00</td>
<td>25.5 ± 1.5</td>
<td>45.0 ± 3.0</td>
<td>26.5 ± 1.0</td>
<td>42.0 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>26.0 ± 1.0</td>
<td>46.0 ± 2.0</td>
<td>26.0 ± 2.0</td>
<td>48.5 ± 3.5</td>
</tr>
<tr>
<td>0.50</td>
<td>2.00</td>
<td>27.5 ± 2.0</td>
<td>44.0 ± 3.0</td>
<td>26.0 ± 1.0</td>
<td>38.5 ± 1.5</td>
</tr>
<tr>
<td>0.10</td>
<td>2.00</td>
<td>27.0 ± 3.0</td>
<td>81.0 ± 9.0</td>
<td>25.0 ± 2.0</td>
<td>38.0 ± 3.0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>30.0 ± 2.0</td>
<td>50.5 ± 3.5</td>
<td>21.0 ± 1.0</td>
<td>42.0 ± 2.0</td>
</tr>
<tr>
<td><strong>Dynax DX2200: SDS (UV-Vis CAC)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>2.00</td>
<td>27.0 ± 2.0</td>
<td>63.5 ± 4.5</td>
<td>25.0 ± 1.0</td>
<td>59.0 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>25.0 ± 2.0</td>
<td>75.0 ± 6.0</td>
<td>23.0 ± 1.0</td>
<td>67.0 ± 3.0</td>
</tr>
<tr>
<td>0.50</td>
<td>2.00</td>
<td>30.0 ± 2.0</td>
<td>60.0 ± 4.0</td>
<td>24.0 ± 1.0</td>
<td>56.0 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>30.0 ± 2.0</td>
<td>66.5 ± 4.5</td>
<td>23.0 ± 1.0</td>
<td>59.5 ± 2.5</td>
</tr>
<tr>
<td>0.10</td>
<td>2.00</td>
<td>25.0 ± 2.0</td>
<td>75.0 ± 6.0</td>
<td>26.0 ± 1.0</td>
<td>49.5 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>29.0 ± 2.0</td>
<td>75.5 ± 5.5</td>
<td>25.0 ± 1.0</td>
<td>52.0 ± 2.0</td>
</tr>
<tr>
<td><strong>Capstone 1157: SDS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>2.00</td>
<td>23.0 ± 1.0</td>
<td>32.0 ± 1.0</td>
<td>23.0 ± 1.0</td>
<td>32.0 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>22.0 ± 1.0</td>
<td>37.5 ± 1.5</td>
<td>26.5 ± 1.0</td>
<td>37.0 ± 1.0</td>
</tr>
<tr>
<td>0.50</td>
<td>2.00</td>
<td>25.0 ± 1.0</td>
<td>33.5 ± 1.5</td>
<td>25.0 ± 1.0</td>
<td>27.0 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>25.0 ± 0.5</td>
<td>35.5 ± 0.5</td>
<td>24.0 ± 1.0</td>
<td>32.0 ± 1.0</td>
</tr>
<tr>
<td>0.10</td>
<td>2.00</td>
<td>25.0 ± 2.0</td>
<td>41.0 ± 3.0</td>
<td>19.5 ± 2.0</td>
<td>30.0 ± 3.0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>25.0 ± 2.0</td>
<td>38.0 ± 3.0</td>
<td>22.0 ± 2.0</td>
<td>30.5 ± 2.5</td>
</tr>
</tbody>
</table>

Table 6.5: Structural parameters from model fitting of FC: h/ d-SDS mixed system neutron reflectivity data. $\tau_{\text{FC}}$ and $A_{\text{FC}}$ represent the thickness and area per molecule of the FC only, i.e. h-SDS contrast. $\tau_{\text{Total}}$ and $A_{\text{Total}}$ represent the total thickness and area per molecule, i.e. d-SDS contrast. Relative (x CAC) concentrations have been given, total concentrations are in Table 6.4.

The measured $\tau$ values of the mixed layers were found to be roughly the same, within experimental error, at all concentrations, compositions and contrasts, indicating no significant segregation of either adsorbing component. However, considering the structural parameters for the FC only samples (i.e. FC: h-SDS in NRW), it can
be seen that there is an increase in $A_{FC}$ as the mole fraction of h-SDS is increased, which is more pronounced at the low composition of FC, i.e mole fraction of 0.10: 0.90 (FC: HC). As expected, the samples below the CAC have a larger $A_{FC}$ than above the CAC, due to a reduction in the surfactant packing efficiency at the air/water interface as the concentration is reduced, leading to a larger separation. This is true for the samples at mole fractions of 0.90: 0.10 and 0.50: 0.50 but not at 0.10: 0.90, whereby at low concentrations there is a decrease in $A_{FC}$ for all mixtures. This indicates that dilution of the 0.10: 0.90 mole fraction samples leads to a reduction in the composition of SDS at the surface but an increase in the FC surfactants. The $\chi'_{f-surf}$ data is Table 6.4 also indicate this. Interestingly, although the $\chi'_{f-surf}$ values indicate higher surface compositions of FC surfactants compared to SDS at a mole fraction of 0.10: 0.90, the $A_{FC}$ data suggests that there is a suppression in the adsorption of the FC surfactants, especially for the Dynax DX1030: SDS (both anionic) mixed system. It is therefore likely that the increase in the SDS surface composition leads to an increase in the antagonism between FC and HC surfactant tails at the air/water interface, and as the system is diluted less antagonism allow the FC surfactants to populate the surface.

Comparable surface density parameters were shown for both Dynax DX1030 and SDS in the individual studies (Table 6.3), hence the values obtained for $A_{Total}$ (FC surfactant, d-SDS, NRW) are all very similar and within experimental error. NR studies on mixtures containing partially fluorinated cationic surfactants with a cationic HC surfactant studied by Jackson et al. showed this same behaviour, whereby comparable area per molecule values of the individual surfactants fed through to similarities in mixtures.\textsuperscript{9,38} $A_{Total}$ data for the Capstone 1157: SDS mixed systems show similarities to that of the Capstone 1157 individually (see Table 6.3) at a mole fraction of 0.90: 0.10, however a slight decrease in $A_{Total}$ is seen in the 0.50: 0.50 and 0.10: 0.90 mole fraction mixtures, indicating a higher surface concentration. Capstone 1157 is the most surface active of the three FC surfactants and was found to pack very efficiently at the air/water interface. This, coupled with the slight attraction between the FC and HC surfactants explains this observation and has been reported previously.\textsuperscript{10} Li et al. showed that mixtures of both ideal and non-ideal (synergistic) zwitterionic: ionic HC surfactants displayed enhancements in the surface concentrations at concentrations above the CAC, compared to the individual components.

Further evidence for formation of mixed monolayers in FC: HC mixed surfactant systems has therefore been shown through the use of contrast variation experiments and analysis of $A_{FC}/A_{Total}$ data. The similarities between $A_{FC}$ and $A_{Total}$ values for the 0.90: 0.10 and 0.50: 0.50 mole fractions mixtures show that the interfacial area is essentially occupied by the FC surfactant, and it is only when SDS is the major component within the mixtures that changes are observed. Significant differences
between \(A_{\text{FC}}\) and \(A_{\text{Total}}\) in the 0.10: 0.90 mole fraction mixtures indicates that both the SDS and FC surfactants are present at the air/water interface and that there is a reduction in the packing efficiency of the FC surfactants within the mixture. From the fitted parameters in Tables 6.4 and 6.5, it is possible to calculate \(\Gamma_{\text{FC}}, \Gamma_{\text{Total}}\) and \(\Gamma_{\text{SDS}}\) values through the use of Equations 6.1 - 6.3, allowing for a different method of calculating \(\chi_{f-surf}'\). These data are summarised below in Table 6.6. Comparisons of \(\chi_{f-surf}'\) values determined in Section 6.5.1 as well as surface composition predictions by RST will be discussed next.\(^{12-15}\)

<table>
<thead>
<tr>
<th>Mole fraction/Fluorocarbon</th>
<th>Concentration/(x\ CAC)</th>
<th>(\Gamma_{\text{FC}}/\Gamma_{\text{Total}}/\Gamma_{\text{SDS}})</th>
<th>(\chi_{f-surf}')</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>((x 10^{-6} \text{ mol m}^{-2}))</td>
<td></td>
</tr>
<tr>
<td><strong>Dynax DX1030: SDS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>2.00</td>
<td>3.7 ± 0.2</td>
<td>4.0 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>3.6 ± 0.1</td>
<td>3.5 ± 0.3</td>
</tr>
<tr>
<td>0.50</td>
<td>2.00</td>
<td>3.8 ± 0.3</td>
<td>4.3 ± 0.1</td>
</tr>
<tr>
<td>0.10</td>
<td>2.00</td>
<td>2.1 ± 0.2</td>
<td>4.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>3.3 ± 0.2</td>
<td>3.9 ± 0.2</td>
</tr>
<tr>
<td><strong>Dynax DX2200: SDS (UV-Vis CAC)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>2.00</td>
<td>2.6 ± 0.2</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>2.2 ± 0.2</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>0.50</td>
<td>2.00</td>
<td>2.8 ± 0.2</td>
<td>3.0 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>2.5 ± 0.2</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>0.10</td>
<td>2.00</td>
<td>2.2 ± 0.2</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>2.2 ± 0.2</td>
<td>3.2 ± 0.1</td>
</tr>
<tr>
<td><strong>Capstone 1157: SDS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>2.00</td>
<td>5.2 ± 0.2</td>
<td>5.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>4.5 ± 0.2</td>
<td>4.5 ± 0.2</td>
</tr>
<tr>
<td>0.50</td>
<td>2.00</td>
<td>5.0 ± 0.2</td>
<td>6.1 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>4.7 ± 0.1</td>
<td>5.3 ± 0.2</td>
</tr>
<tr>
<td>0.10</td>
<td>2.00</td>
<td>4.1 ± 0.3</td>
<td>5.6 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>4.4 ± 0.4</td>
<td>5.5 ± 0.5</td>
</tr>
</tbody>
</table>

Table 6.6: \(\Gamma\) values from analysis of contrast variation NR data for the FC: h/ d-SDS mixed systems. Where \(\Gamma\) values represent the total surface excess and the surface excess of the individual components. \(\chi_{f-surf}'\) is the calculated surface composition of the FC surfactant within the mixture. Relative (x CAC) concentrations have been given, total concentrations are shown in Table 6.4.
6.6 Surface composition comparisons

Two separate methods of analyses have been used to characterise the surface compositions of the FC: HC surfactant mixed systems from the NR data. Regular solution theory (RST) provides an addition approach for calculating surface properties and compositions of surfactant mixtures.\textsuperscript{13–15} The theory, which was described in Chapter 1, uses surface tension data of both the individual surfactants and mixtures to determine $\chi$ values. The surface tension data are presented in both Chapter 5 and the Appendix. RST therefore provides an opportunity to compare the experimentally determined values of $\chi_{f-surf}$ from NR measurements to theoretically determined values over a wide range of compositions. Values of $\chi_{f-surf}$ for the three different methods are summarised below in Table 6.7 for the 2.00 x CAC samples.

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>Fluorocarbon</th>
<th>$\chi_{f-surf}$/ From $\rho_{fitted}$</th>
<th>$\chi_{f-surf}$/ From contrast matching</th>
<th>$\chi_{f-surf}$/ From RST</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>Dynax DX1030: SDS</td>
<td>0.97 ± 0.03</td>
<td>0.92 ± 0.08</td>
<td>0.90</td>
</tr>
<tr>
<td>0.50</td>
<td>Dynax DX2200: SDS (UV-Vis CAC)</td>
<td>0.92 ± 0.04</td>
<td>0.89 ± 0.09</td>
<td>0.85</td>
</tr>
<tr>
<td>0.10</td>
<td>Capstone 1157: SDS</td>
<td>0.60 ± 0.05</td>
<td>0.46 ± 0.08</td>
<td>0.67</td>
</tr>
<tr>
<td>0.90</td>
<td>Dynax DX1030: SDS</td>
<td>0.95 ± 0.05</td>
<td>0.92 ± 0.08</td>
<td>0.93</td>
</tr>
<tr>
<td>0.50</td>
<td>Dynax DX2200: SDS (UV-Vis CAC)</td>
<td>0.94 ± 0.06</td>
<td>0.92 ± 0.08</td>
<td>0.88</td>
</tr>
<tr>
<td>0.10</td>
<td>Capstone 1157: SDS</td>
<td>0.51 ± 0.16</td>
<td>0.65 ± 0.08</td>
<td>0.78</td>
</tr>
<tr>
<td>0.90</td>
<td>Dynax DX1030: SDS</td>
<td>0.97 ± 0.03</td>
<td>0.97 ± 0.03</td>
<td>0.99</td>
</tr>
<tr>
<td>0.50</td>
<td>Dynax DX2200: SDS (UV-Vis CAC)</td>
<td>0.87 ± 0.07</td>
<td>0.82 ± 0.06</td>
<td>0.78</td>
</tr>
<tr>
<td>0.10</td>
<td>Capstone 1157: SDS</td>
<td>0.49 ± 0.09</td>
<td>0.74 ± 0.12</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Table 6.7: Surface compositions of the FC: HC surfactant mixtures at 2.00 x CAC from analysis of neutron reflectivity data and regular solution theory.

The two experimental methods used to determine $\chi_{f-surf}$ values from the NR data provide comparable results, within experimental error, for both the 0.90: 0.10 and 0.50: 0.50 (FC: HC) mixed systems. As previously discussed, determination of the experimental values of $\chi_{f-surf}$ rely on different methods of analysis of the NR data, from $\rho_{fitted}$ values and from $d/h$-SDS contrast variation experiments. An assumption is made when using the $\rho_{fitted}$ method along with Equation 6.4, this being that the mixed surface can be described by a ratio of the $\rho_{fitted}$ values of the individual components as fully saturated layers. At these two mole fractions, the FC surfactants are all present at concentrations above the CMC, whereas SDS is not. The more surface active FC surfactants are more likely to dominate the surface layer, making both the $\rho_{fitted}$ values similar to that of the fully saturated FC layers and Equation 6.4 is therefore valid at these two mole fractions.\textsuperscript{9, 10}
Disagreement between the two experimental methods is seen at high mole fractions of SDS, i.e. at a mole fraction 0.10: 0.90. The d/ h-SDS contrast variation experiments exploit the similarities in SLD between NRW and h-SDS to highlight the reflection of the FC surfactants only. Using this method allows determination of both the total coverage and coverage of the FC surfactants only, and has been used extensively to provide detailed descriptions of surface compositions.\textsuperscript{1, 2, 4, 5, 8, 9, 11, 12} It is likely that the assumption used when calculating $\chi_{f \text{-surf}}^{'}$ using $\rho_{\text{fitted}}$ values is not valid at this mole fraction due to a relatively large degree of mixing at the surface. When neither of the surfactants in the mixtures are present at concentrations above the CMC, as is the case in some of the mixtures at this mole fraction, the assumption that the mixed layer can be described as a ratio of the two constituent components as full saturated layers is not true, therefore making Equation 6.4 not valid. To accurately describe the surface compositions using this method requires further experiments to determine the $\rho_{\text{fitted}}$ values of the constituent components at the solution concentrations within the mixture.

As previously discussed, most of the studies comparing theoretically and experimentally determined surface compositions have been investigated using ideal\textsuperscript{5, 10, 12} and non-ideal\textsuperscript{5, 10} HC: HC mixed surfactant systems, often showing good agreement between the two methods. Here, comparable $\chi_{f \text{-surf}}^{'}$ values between RST and experimental data are shown for the FC: HC surfactant mixtures at mole fractions of 0.90: 0.10 and 0.50: 0.50, with less agreement displayed for the 0.10: 0.90 mixtures. In particular, the largest difference in experimental and theoretical $\chi_{f \text{-surf}}^{'}$ values is seen in the Dynax DX2200: SDS mixed system, $\sim$ 0.65 and 0.78, respectively. There are several possible explanations for why RST does not accurately describe this specific surface composition. It has been previously shown in HC: HC surfactant mixtures that large differences in the CMC in ideal systems results in marked differences in RST and experimental surface compositions.\textsuperscript{5} Although the Dynax DX2200: SDS mixed system does not display ideal behaviour (see Chapter 5), it has the largest difference between the CMCs of the individual surfactants, 0.02 mM to 8.3 mM, respectively. As the mole fraction of SDS is increased within the mixture, the model is going to be more affected by this large difference in CMCs. Another is that there is an assumption that the surface is made up of the two surfactants only, therefore not taking into account any changes in hydration that can occur on mixing.\textsuperscript{10}
6.7 Conclusions

In this Chapter, the surface compositions of mixed surfactant systems containing partially fluorinated surfactants bearing different head groups (anionic, non-ionic and zwitterionic) and an anionic HC surfactant, SDS, have been investigated using NR and RST. Two methods of analysing the NR data were used to determine the FC surfactant surface compositions ($\chi'_{f-surf}$) in the mixed systems: one using the assumption that the fitted scattering length density ($\rho_{fitted}$) of the mixed systems can be described by a weighted sum of the $\rho_{fitted}$ of the individual components, and the other method utilises common d/ h-SDS contrast variation experiments to determine the surface density parameters and hence $\chi'_{f-surf}$.\(^{1-9}\)

The two experimental methods for determining $\chi'_{f-surf}$ showed good agreement at high concentrations/ mole fractions of FC surfactant, however at high mole fractions of HC surfactant, less agreement was observed. Lack of agreement at high mole fractions of SDS was argued as being due to the breakdown of the $\rho_{fitted}$ model. The model uses the assumption that the mixed surfaces can be described by fully saturated layers of the two constituent surfactants. However, due to the relatively high degree of surface mixing at high mole fractions of SDS, this is not possible and it would be more accurate to use data commensurate with the individual surfactant solution concentrations. At high concentrations/ mole fractions of FC surfactants, the higher surface activity of the FC surfactants compared to SDS made the surface essentially dominated by the FC surfactants; dynamic surface tension (DST) results in Chapter 5 also showed this. At high SDS bulk compositions, the $\chi'_{f-surf}$ values were still shown to favour the FC surfactants which could be enhanced further through dilution of the bulk solution. Surface density parameters were investigated through the use of contrast variation experiments with h/ d-SDS isotopic substitution. Very comparable results for both the FC only and total surface excess, $\Gamma_{FC}$ and $\Gamma_{Total}$ were shown at high FC surfactant mole fractions. For example, at high mole fractions of Dynax DX2200, the $\Gamma_{FC}$ and $\Gamma_{Total}$ values were $2.6 \times 10^{-6}$ Å\(^{-2}\) and $2.8 \times 10^{-6}$ Å\(^{-2}\) for the 0.90: 0.10 mole fraction mixture, respectively and $2.8 \times 10^{-6}$ Å\(^{-2}\) and $3.0 \times 10^{-6}$ Å\(^{-2}\) for the 0.50: 0.50 mole fraction mixture, respectively. These mixed systems have the largest difference in individual $\Gamma$ between Dynax DX2200 and SDS, $2.55 \times 10^{-6}$ Å\(^{-2}\) and $4.25 \times 10^{-6}$ Å\(^{-2}\), respectively and therefore demonstrates this.

RST was used to determine whether the experimentally determined $\chi'_{f-surf}$ values were comparable with those determined through theoretical treatment of previously determined surface tension data (see Chapter 5 and Appendix). Results from RST showed good agreement with the experimental results at high FC surfactant mole fractions, but less so at high mole fractions of SDS. Large differences between the constituent surfactant CMCs, along with non-ideal behaviour have both been shown to lead to problems when employing RST to describe mixed surfactant systems.\(^{5}\) The
largest differences between RST and experimental $\chi'_{\text{f-surf}}$ was in the Dynax DX2200: SDS mixed system, which displays both non-ideal behaviour (antagonism) and has the largest difference in CMC, 0.02 mM and 8.3 mM, respectively. The experimental results showed that the surface is dominated by the FC when present in high mole fractions, however at a mole fraction of 0.10: 0.90 (FC: HC) a higher degree of surface mixing is observed. Jackson et al. reported the same behaviour, showing that at low fractions of FC surfactant, any increase in the FC: HC surfactant antagonism is compensated by a reduction in the immersion of the FC in the water, caused by the screening by the small amount of HC surfactant.\(^9\)

Overall these results show that the surface compositions of mixtures containing partially fluorinated surfactants and an anionic HC surfactant (SDS) are dominated by the more surface active FC surfactants, even when the bulk composition is majority SDS. This fits in well with the previous results in Chapter 5 whereby large surface tension reductions and low CACs were observed in the FC: HC surfactant mixtures at both low concentrations and bulk mole fractions of FC surfactants.
References


REFERENCES


Chapter 7

Composition and structure of mixed fluorocarbon hydrocarbon surfactant micelles

The previous Chapters have been concerned with determining both the solution properties and surface compositions of mixtures containing partially fluorinated surfactants, all of which have different headgroups, and an anionic hydrocarbon (HC) surfactant, SDS. From neutron reflectivity measurements, elucidation of the respective surfactant compositions in the mixed systems at different mole fractions and concentrations showed domination of the fluorocarbon (FC) surfactants at the air/water interface, even at high compositions of SDS. These data agreed well with the mixed FC: HC surfactant dynamic surface tension (DST) measurements, which were found to be dictated by the more surface active FC surfactants. This Chapter aims to probe the self-assembled structures of the FC: HC surfactant mixtures through the use of contrast variation small-angle neutron scattering (SANS), allowing for the composition, size and shape of the mixed system aggregates to be realised.

7.1 Introduction

SANS has proved to be a very powerful and widely employed technique for studying the aggregation and composition of complex mixed surfactant systems. It has been previously shown that SANS, in combination with h/d isotopic substitution, provides the opportunity to measure both structure and composition in mixed HC surfactant micelles.\textsuperscript{1–6} Work carried out by Penfold \textit{et al.} focused on using SANS to determine the composition of mixed micelles containing an anionic HC surfactant SDS, and a non-ionic HC surfactant $C_{12}E_6$.\textsuperscript{1, 2, 5, 6} The emphasis of the studies were on the variation in micelle composition and size in the context of regular solution theory.
(RST), with results showing good agreement between the two methods.\textsuperscript{7–9} Within the literature there are a wide range of studies on different surfactant mixtures, including non-ionic mixtures,\textsuperscript{10} cationic mixtures,\textsuperscript{11} as well as anionic: non-ionic,\textsuperscript{3, 4} anionic: cationic,\textsuperscript{12, 13} and anionic: zwitterionic.\textsuperscript{14, 15} In the context of this Chapter, however, there is more interest in the use of SANS to determine both the composition and structural changes for FC: HC surfactant micelles.

As mentioned in Chapter 5, non-ideal, antipathic interactions experienced in mixtures containing perfluoroalkanes and alkanes leads to segregation and phase separation below a critical solution temperature.\textsuperscript{16–18} This same idea, applied to demixing into two separate micelle populations in FC: HC surfactant mixtures, was first proposed by Mukerjee \textit{et al.}\textsuperscript{18} In this early study, electrical conductivity was used to measure the CMCs of mixtures containing sodium perfluorooctanoate with either sodium laurate or sodium decylsulfate, showing that hydrocarbon-rich and fluorocarbon-rich micelles coexisted in solution. The same conclusions were reported in several studies by Funasaki \textit{et al.} whereby the behaviour of non-ionic FC surfactants and anionic HC surfactants were investigated.\textsuperscript{19–21}

The theory regarding the coexistence of two micelle populations was first described using a pseudo-phase separation model by Mysels.\textsuperscript{22} The pseudo-phase model proved to be quite successful when assuming ideal mixing between surfactants.\textsuperscript{8} However, when there is significant non-ideal mixing within the mixed micelles (\textit{cf.} FC: HC surfactant mixtures), RST has been used and the interaction parameter $\beta$ allows for description of the the non-ideality of mixing.\textsuperscript{7–9} For example, Funasaki \textit{et al.} used surface tension measurements along with RST to determine the micellar compositions of non-ionic FC: anionic HC mixtures.\textsuperscript{19} Shinoda \textit{et al.} described the conditions for demixing using RST through measurements of the misibilities of FC and HC surfactants at the interface and in micelles, concluding that a FC surfactant with C7 fluorinated group will mix with a HC surfactant at all compositions, but only partially with a C8 fluorinated tail.\textsuperscript{23} Since these early studies, this area of research has received a lot of attention and the idea of demixing in FC: HC surfactant micelles has been a matter of debate within the literature.\textsuperscript{23–30}

Many different techniques have been utilised to verify demixing as well as the composition of mixed FC: HC surfactant micelles, with the majority of the literature focusing on NMR and SANS techniques which often provide complementary information.\textsuperscript{24, 26–29, 31–36} The use of $^{19}$F NMR has been shown to offer advantages to independently investigate the behavior of FC surfactants in mixtures, and is generally admitted to allow for both determination of the concentration at which the FC surfactants form micelles and provide information on the mixed micelle compositions.\textsuperscript{31} Kadi \textit{et al.} used NMR to determine the demixing experienced in a mixture containing a partially fluorinated cationic surfactant and a cationic
HC surfactant, with results indicating demixing into large FC-rich and small HC-rich micelles. The mole fraction of FC surfactants in the HC-rich micelles was calculated as $\sim 0.10$. Nordstierna et al., however, came to different conclusions upon investigations of an anionic FC surfactant and anionic HC surfactant. In this work, results showed neither demixing or complete mixing on the micellar level, instead favouring the formation of a single micelle population where the FC surfactants are preferentially coordinated to one another and the same for the HC surfactants.

As with the studies of HC: HC mixtures, SANS provides an ideal approach to study the composition of mixed FC: HC surfactant micelles through contrast variation experiments. One of the first studies of this type was carried out by Burkitt et al., in which SANS was used to investigate the composition of mixed micelles containing ammonium decanoate and ammonium perfluorooctanoate. Results showed formation of mixed micelles with good agreement in the calculated mixed micelle compositions between experimental techniques and use of an ideal mixing approach. It was also suggested speculatively that there was segregation in the mixed micelles between the FC and HC chains, which was also reported by Kadi et al. in mixed micelles containing a partially fluorinated cationic and a cationic HC surfactant. These in-depth contrast variation experiments were explained by the formation of mixed micelles, with no observed demixing, that had an inhomogeneous distribution of HC and FC surfactants present within the micelles. It was also reported that the FC surfactants were preferably located in the outer parts of the micelles and the HC surfactants within the cores. Further studies, on the same mixed system containing a partially fluorinated cationic: cationic HC surfactant mixture concluded that the micelle composition was best described as having a broad distribution of different mixed micelle compositions, not necessarily just one population of mixed micelles nor demixing into two populations. The broadness of the distribution decreased at higher temperature, and for an ideal system composed of h-SDS and d-SDS, very small distribution of micelles were observed.

In this Chapter, the composition and structural changes in mixtures containing partially fluorinated surfactants bearing different head groups and SDS have been investigated at varying bulk mole fractions through the use of SANS. Initially, contrast variation SANS was used to determine the composition of the mixed micelles by use of the models developed by Penfold et al. and compared to calculations using RST, showing mixed micelles formation with compositions generally favouring the FC surfactants. To minimise the effect of the structure factor $S(Q)$ and to make the modeling of the data easier, the compositional studies were carried out for each FC: HC surfactant mixture at multiples of the CAC (see Chapter 5). The structural studies, however, were carried out at fixed concentrations of either 50 or 100 mM to make sure that both surfactants are above their respective CMCs in the mixtures. Finally, alkane-induced swelling of mixed FC: HC surfactant micelles was investigated.
in a short SANS study. No swelling was observed upon addition of h-cyclohexane to the individual FC surfactants, however when present as mixed FC: HC micelles h-cyclohexane induced swelling was observed. These data provide further evidence for mixed FC: HC surfactant micelles, as the alkane can only be solubilised in the HC surfactant tails.

7.2 Materials and Methods

7.2.1 Materials

The preparation of the partially fluorinated surfactants has been described in Chapter 2. Sodium dodecylsulfate (CAS 151-21-3) (Sigma-Aldrich, ≥ 98.5 %) and deuterium oxide (Aldrich, 99.9 %) were used as received. Deuterated sodium dodecylsulfate was prepared and supplied by the ISIS deuteration facility at the Rutherford Appleton laboratory, Didcot, UK. All surfactant structures are shown below in Table 7.1.

<table>
<thead>
<tr>
<th>Surfactant Name</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td><img src="image" alt="Dynax DX1030" /></td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td><img src="image" alt="Dynax DX2200" /></td>
</tr>
<tr>
<td>Capstone 1157</td>
<td><img src="image" alt="Capstone 1157" /></td>
</tr>
<tr>
<td>Sodium Dodecylsulfate</td>
<td><img src="image" alt="Sodium Dodecylsulfate" /></td>
</tr>
</tbody>
</table>

Table 7.1: Surfactants used in this Chapter
7.2.2 Methods

Small-Angle Neutron Scattering

SANS measurements were performed using the SANS2D beam-line on Target station 2 at the ISIS facility (Rutherford Appleton Laboratory, Didcot, UK) and the LOQ beam-line on Target station 1 at the same facility. On SANS 2D, a simultaneous $Q$-range of $0.004 - 0.6 \text{ Å}^{-1}$ was achieved with a neutron wavelength range of $1.75 < \lambda < 15.5 \text{ Å}$ and a source-sample-detector distance $L_1 = L_2 = 4 \text{ m}$. On LOQ, a simultaneous $Q$ range of $0.008 - 0.254 \text{ Å}^{-1}$ was achieved with a neutron wavelength range of $1.75 < \lambda < 15.5 \text{ Å}$ and a source-sample-detector distance $L_1 = L_2 = 8 \text{ m}$. Raw SANS data were reduced by subtracting the scattering of the empty cell and the $\text{D}_2\text{O}$ background and normalised to an appropriate standard using the instrument-specific software. SANS data were fit using the analysis package SasView. The scattering length densities of all samples are shown below in Table 7.2.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$\rho$ / ($10^{-6} \text{ Å}^{-2}$)</th>
<th>$V_m$ / Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td>2.60</td>
<td>584</td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td>2.50</td>
<td>1547</td>
</tr>
<tr>
<td>Capstone 1157</td>
<td>2.60</td>
<td>563</td>
</tr>
<tr>
<td>h-SDS</td>
<td>-0.40</td>
<td>410</td>
</tr>
<tr>
<td>d-SDS</td>
<td>6.00</td>
<td>410</td>
</tr>
</tbody>
</table>

Table 7.2: Scattering length densities and molecular volumes of the surfactants studied in this Chapter.
7.3 Aggregation behaviour of fluorocarbon hydrocarbon surfactant mixtures

The individual aggregation behaviours of the partially fluorinated surfactants have been discussed in Chapter 4 and in the literature.\cite{37} The aggregation behaviour of sodium dodecylsulfate (SDS) has been previously reported but has also been reproduced here for consistency. In this section, three FC surfactants each bearing different headgroups are mixed with SDS and the aggregation behaviour is measured by use of SANS. The investigations are split into two separate studies:

- The first uses contrast variation experiments to determine the composition of the different surfactants in the FC: HC surfactant mixtures. For each mixed system comparisons are made composition predictions from regular solution theory (RST).\cite{9,38}

- The second investigation is into how the structure of the mixed FC: HC surfactant micelles changes as the bulk compositions are altered.

Before the mixed FC: HC surfactant systems can be studied, it is important to both examine and compare to the relevant literature, the aggregation behaviour of SDS at different concentrations.

7.3.1 Aggregation behaviour of sodium dodecylsulfate at different concentrations

SDS has been the subject of many SANS studies therefore comparisons can easily be made to ensure the data modeling is correct.\cite{13,39-44} Figure 7.1a shows the SANS profiles for h-SDS at three concentrations above the CMC in D$_2$O from this work. Initial approximation of the micelle sizes were determined using Porod plots (Figure 7.1b, but reliable Guinier approximations of the low Q data were not possible due to the presence of the structure factor (S(Q)) peak.

As has been previously reported by Hammounda, an increase in the fitted background is observed as the concentration of h-SDS is multiplied.\cite{40} The reason for this is due to an increase in the incoherent background as more H containing species are present within the system. A S(Q) is observed, which leads to the peak in the mid Q region and a depression in the low Q scattering as the concentration of SDS is increased. The S(Q) describes inter-particle interactions within the system (attractive, repulsive) and is typical behaviour for interacting charged micelles.\cite{43} Porod approximations have been used to provide an estimation of the particle radius,
Figure 7.1: (a) Small-angle neutron scattering profiles of sodium dodecylsulfate (SDS) in D$_2$O. The critical micelle concentration of SDS is 8.2 mM. The lines through the data are fitted functions. (b) Porod approximations from the above data. T = 25 °C.

$R$, through the relationship: $Q_{\text{max}} \approx 2.7/R$, where $Q_{\text{max}}$ is the first maximum peak in $Q$. From the Porod approximations, a maximum $Q$ peak of $\sim 0.14$ Å$^{-1}$ is observed at all concentrations. Using the relationship above, a $R$ of 19 Å is calculated for all concentrations, suggesting that the overall micelle size is not changing. Due to the assumptions that micelles are spherical and sufficiently dilute/ non interacting when using Porod approximations, a more detailed representation of the size and shape of the micelles can be determined using modeling software.
CHAPTER 7. COMPOSITION AND STRUCTURE OF MIXED FLUOROCARBON HYDROCARBON SURFACTANT MICELLES

The parameters used to model the data are displayed in Table 7.3. Here, the data were best described by an ellipsoidal form factor with the Hayter-Penfold mean spherical approximation (MSA) structure factor. It should be noted that in the fittings, the scattering length density (SLD) of SDS was kept fixed at \(-0.40 \times 10^{-6} \text{ Å}^{-2}\). In addition, when using the MSA structure factor, the following parameters are added to the model: salt concentration, charge, temperature and dielectric constant. Known values for salt concentration, temperature and dielectric constant were set at the correct values and only the charge parameter was allowed to float.

<table>
<thead>
<tr>
<th>SDS Concentration (x CMC)</th>
<th>Model</th>
<th>(R_{\text{eq}}) (Å) (±0.1)</th>
<th>(R_{\text{pol}}) (Å) (±0.1)</th>
<th>Aspect ratio</th>
<th>(N_{\text{agg}}) (± 1)</th>
<th>(Z)</th>
<th>(\Phi_{\text{Fitted}})</th>
<th>(\Phi_{\text{Calculated}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Ellipsoid</td>
<td>21.0</td>
<td>14.0 (±0.1)</td>
<td>1.5</td>
<td>65</td>
<td>10</td>
<td>0.008</td>
<td>0.012</td>
</tr>
<tr>
<td>10</td>
<td>Ellipsoid</td>
<td>22.0</td>
<td>15.0 (±0.1)</td>
<td>1.5</td>
<td>75</td>
<td>26</td>
<td>0.017</td>
<td>0.024</td>
</tr>
<tr>
<td>20</td>
<td>Ellipsoid</td>
<td>23.0</td>
<td>15.0 (±0.1)</td>
<td>1.5</td>
<td>82</td>
<td>24</td>
<td>0.038</td>
<td>0.048</td>
</tr>
</tbody>
</table>

Table 7.3: Parameters obtained by fitting SANS data to structural models. With increasing concentration, the fitted backgrounds are 0.005, 0.007 and 0.025 respectively. \(R_{\text{eq}}\) is the equatorial radius of an ellipsoid, \(R_{\text{pol}}\) is the polar radius of the ellipsoid, aspect ratio is defined as \(X = R_{\text{eq}}/R_{\text{pol}}\), \(N_{\text{agg}}\) is the aggregation number, \(Z\) is effective charge, \(\Phi_{\text{Fitted}}\) is fitted and \(\Phi_{\text{Calculated}}\) is calculated volume fraction based on sample composition. Critical micelle concentration has been taken as 8.2 mM.

From the above data, it can be seen that the aggregates are best described as oblate spheroids, with an average equatorial radius of 22.0 ± 0.1 Å and polar radius of 14.7 ± 0.1 Å. An aspect ratio of 1.5 is seen over all concentrations studied, suggesting that the shape of the micelles are not changing in the range of concentrations studied. The aggregation number was determined from the fitted equatorial and polar radii and the molecular volume of SDS (410 Å³). Aggregation numbers were found to increase with increasing concentration, due to the slight variations in the fitted radii. Separate SANS studies carried out by Zemb and Berström reported SDS to form ellipsoidal micelles, with average equatorial radii of 22.0 Å and 22.7 Å and polar radii of 17.9 Å and 13.1 Å being reported, respectively. These values lead to aspect ratios of 1.2 and 1.7, compared to the value of 1.5 in this work. Aggregation numbers were reported as 70 and 85 respectively and Zemb et al. reported an effective charge (Z) of 26. It is therefore possible to conclude that the results reported in this work are comparable to those found in the literature, suggesting that the model fitting procedure here, and for the ensuing analysis, is suitable.
CHAPTER 7. COMPOSITION AND STRUCTURE OF MIXED FLUOROCARBON HYDROCARBON SURFACANT MICELLES

7.3.2 Composition of micelles containing fluorocarbon hydrocarbon surfactant mixtures

As previously mentioned, the compositions of mixed micelles are most commonly calculated through evaluation of surface tension data with thermodynamic models developed by Rubingh. These thermodynamic models have been developed from regular solution theory (RST), as discussed in Chapter 1. More recently, however, SANS, in combination with H/D isotopic substitution has been shown to provide direct information on the composition of mixed micelles over a wide range of both concentrations and compositions, with results determined from SANS measurements providing good agreement with predictions from RST.

For mixed micelles dispersed in D$_2$O, the measured intensity (I(Q)) depends on the composition of the micelles via the square of the scattering length density ($\rho$$_{mixed} - \rho_s$)$^2$, or $\Delta \rho^2$. By making two different measurements on the same mixed system, one containing FC and h-HC (hydrogenated surfactant) and the second containing FC and d-HC (deuterated surfactant), the ratio of the two measured intensities, extrapolated to Q=0, gives directly an estimate of the micellar composition.

Taking for example the combination of a FC surfactant mixed with h/d-SDS, the volume fraction can be calculated in the following way:

$$\Phi_{SDS} = \frac{(\sqrt{R_1} - 1)(\rho_{f-surf} - \rho_{D_2O})}{(\rho_{h-SDS} - \rho_{f-surf}) - \sqrt{R_1}(\rho_{d-SDS} - \rho_{f-surf})} \quad (7.1)$$

where $\Phi_{SDS}$ is volume fraction of SDS, $R_1$ is $I(Q)_{h-SDS, f-surf} / I(Q)_{d-SDS, f-surf}$ and $\rho_{f-surf}$, $\rho_{D_2O}$, $\rho_{h/d-SDS}$ are the scattering length densities (Å$^{-2}$) of FC surfactant, D$_2$O and h/d-SDS, respectively. $\Phi_{SDS}$ can then be used to determine the mole fraction of SDS within the mixed micelles as follows:

$$\chi_{SDS} = \frac{\Phi_{SDS}/V_m(SDS)}{\Phi_{SDS}/V_m(SDS) + (1 - \Phi_{SDS})/V_m(f-surf)} \quad (7.2)$$

where $\chi_{SDS}$ is mole fraction of SDS in the mixed micelles and $V_m(SDS)$, $V_m(f-surf)$ are the molecular volumes (Å$^3$) of SDS and FC surfactant, respectively. It should be noted that an assumption that the micelle structure is unaffected by the amount of deuterated surfactant is made when carrying out this analysis.

Using the h/d-SDS isotopic substitution method described above, contrast variation SANS has been used to determine the composition of mixed micelles containing partially fluorinated surfactants with SDS (structures shown in Table 7.1) and compared to the calculated values using RST. For each of the studied mixtures, three mole fractions have been investigated at multiple concentrations...
above respective CACs. These low concentrations were chosen as a way to reduce the influence of the S(Q). Results from each mixed system will be presented and discussed separately. In this section, only the compositions of the mixed micelles are being evaluated and observed structural changes are discussed in Section 7.3.3.

**Dynax DX1030: SDS mixed micelle compositions above CAC**

As discussed above, the measured intensity of the mixed surfactant system depends on the composition of the micelles via $\Delta \rho^2$. By measuring the SANS profiles of the same mixture with two isotopic combinations, in this case h/ d-SDS, the intensity ratio ($R_1$) of the two measured intensities directly provides an estimate of the micelle composition. Below in Figure 7.2, this analysis is shown for the 0.90: 0.10 mole fraction Dynax DX1030: h/ d-SDS mixed systems at a concentration of 10 x CAC in D$_2$O. It should be noted that for all mole fractions, the same analysis has been carried out at multiple concentrations. The results have been included here, but the data can be found in the Appendix.
Figure 7.2: (a) SANS profiles of Dynax DX1030: d/ h-SDS mixed systems in D$_2$O at a mole fraction of 0.90: 0.10 and concentration of 10 x CAC. The critical aggregation concentration for this mole fraction is 2.0 mM. (b) Ratio of the SANS scattering intensities from the two above isotopic combinations (Dynax DX1030: h-SDS)/ (Dynax DX1030: d-SDS). T = 25 $^\circ$C.

Samples containing d-SDS were measured on both SANS2D and LOQ at separate times, providing comparable SANS profiles and intensity ratios as shown in Figures 7.2a and 7.2b. The mixed system containing h-SDS has a slightly higher intensity compared to the d-SDS containing sample in D$_2$O. This is expected because the intensity of the scattering scales with $\Delta \rho^2$, i.e. $\Delta \rho^2$ becomes smaller in the d-SDS containing sample. If there was no mixing/ formation of mixed micelles, a linear plot of $R_1$ vs. Q, extrapolated to Q = 0, would lead to a value of 1.00, hence the scattering intensity of the Dynax DX1030: h-SDS would be the same as Dynax DX1030: d-SDS. The $R_1$ vs. Q data shown in Figure 7.2b provides a linear relationship, leading to extrapolated $R_1$ values of 1.10 and 1.14 ± 0.05, respectively. An $R_1$ value greater than 1.00 indicates that the scattering intensity of the DX1030: h-SDS sample is higher than the Dynax DX1030: d-SDS sample. These samples have been measured at the same concentrations, therefore the only factor that can change the scattering intensity between these two samples is the value of $\Delta \rho^2$. Therefore for this value of $R_1$ to be achieved, the micelles must contain SDS, hence consistent with mixed micelle formation.
Figure 7.3 shows the SANS profiles for the 0.50: 0.50 mole fraction mixed system at a concentration of 10 x CAC. In this mixed system, the difference in scattering intensity due to the change in $\Delta \rho^2$ is much more pronounced, again suggesting the formation of mixed micelles containing both Dynax DX1030 and SDS.

Comparative results are observed between the measurements on both SANS2D and LOQ, indicating consistency in the sample preparation and SANS data normalisation procedures. The greater difference in intensity between the Dynax DX1030: h-SDS and Dynax DX1030: d-SDS samples indicates that a larger mole fraction of SDS is present within the mixed micelle, compared to the 0.90: 0.10 mole fraction sample. The calculated micelle compositions of FC surfactant ($\chi_{\text{f-surf}}$) have been calculated and are shown below in Table 7.4 by analysis of both the SANS data and RST iterative methods.\textsuperscript{7}


Table 7.4: Calculated values of $\chi_{f\text{-surf}}$ from using both SANS and iterative calculation for the 0.90: 0.10 and 0.50: 0.50 mole fraction mixtures (Dynax DX1030: SDS). Critical aggregation concentrations have been taken as 2.00 mM and 2.50 mM, respectively. The value of $\chi_{f\text{-surf}}$ from SANS measurements was averaged from the SANS2D and LOQ data.

Results show $\chi_{f\text{-surf}}$ values of $\sim 0.95$ for the FC: HC surfactant mixture at a mole fraction of 0.90: 0.10 (FC: HC), suggesting that the mixed micelle composition does not necessarily follow with the measured bulk mole fraction. In Chapter 5, it was shown that at high mole fractions of FC, the Dynax DX1030: SDS mixed system displayed antagonistic behaviour, i.e. the experimentally determined CACs were higher than predicted from ideal behaviour. If antagonism is displayed in a mixed system, this suggests that unfavourable interactions are taking place, likely due to the lack of affinity between the FC and HC tail groups. The higher overall concentration of FC surfactant and the lack of affinity between the two surfactants then explains the increased mole fraction of FC in the mixed micelles. It could be argued that micelles should therefore contain no SDS, however the strong dipole offered by the CF$_2$CH$_2$ group in Dynax DX1030 could allow for some favourable interactions, leading to the incorporation of a small amount of SDS. For the 0.50: 0.50 mole fraction mixed system, $\chi_{f\text{-surf}}$ values between the two methods of analysis were not comparable. The SANS data suggests that the $\chi_{f\text{-surf}}$ is roughly consistent with the bulk mole fraction, whereas the thermodynamic model calculations suggest that the FC surfactant makes up the majority of the micelles. The experimentally determined CAC for this mole fraction showed essentially ideal behaviour, i.e. the CAC was the same as the predicted ideal behaviour. Ideal behaviour is more consistent with the $\chi_{f\text{-surf}}$ calculated from the SANS data, due to the similarity between both the bulk mole fraction and $\chi_{f\text{-surf}}$ value.

Kadi et al. used SANS with contrast matching to investigate the composition of mixed micelles containing a partially fluorinated cationic and a cationic HC surfactant. The results were explained by the formation of mixed micelles (no
CHAPTER 7. COMPOSITION AND STRUCTURE OF MIXED FLUOROCARBON HYDROCARBON SURFACTANT MICELLES

demixing) with an inhomogeneous distribution of HC and FC surfactants present within the micelles. Results also suggested that the FC surfactants were preferably located in the outer parts of the micelles and the HC surfactant within the core. Although this study does not consider the mixing of a partially fluorinated anionic surfactant mixed with and anionic HC surfactant, both surfactants have the same head group and similar behaviours would therefore be expected. However, further investigations using in-depth contrast variation experiments would be required to characterise this.

Interestingly, the 0.10: 0.90 Dynax DX1030: SDS mixed system (Figure 7.4) showed no scattering profile for the d-SDS containing mixed system in D$_2$O. The similarities in SLD values of both d-SDS and D$_2$O (see Table 7.2) would suggest that either the micelles consist of only d-SDS or only a very small amount of FC surfactant is present in the mixed micelles. By measuring this sample in FC-contrast water, i.e. when the solvent $\rho_{\text{solvent}} = \rho_{f-\text{surf}} \left( \sim 2.50 \times 10^{-6} \text{ Å}^{-2} \right)$, the only observed scattering should appear from the d-SDS. The fitted structural parameters associated with the different contrast samples are shown below in Table 7.5.

![Figure 7.4](image-url)

Figure 7.4: SANS profiles of Dynax DX1030: d/h-SDS mixed system in different contrast solvents at a mole fraction of 0.10:0.90 at 10 x CAC. The CAC for this mole fraction is 3.85 mM. T = 25 °C.
CHAPTER 7. COMPOSITION AND STRUCTURE OF MIXED FLUOROCARBON HYDROCARBON SURFACTANT MICELLES

<table>
<thead>
<tr>
<th>Contrast</th>
<th>Model</th>
<th>$R_{eq}$/Å ($\pm 0.1$)</th>
<th>$R_{pol}$/Å ($\pm 0.1$)</th>
<th>Aspect ratio ($\pm 1$)</th>
<th>$Z$</th>
<th>$\Phi_{Fitted}$</th>
<th>$\Phi_{Calculated}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC: h-SDS in D$_2$O</td>
<td>Ellipsoid</td>
<td>23.0</td>
<td>14.6</td>
<td>1.6</td>
<td>19</td>
<td>0.022</td>
<td>0.024</td>
</tr>
<tr>
<td>FC: d-SDS in FC-contrast</td>
<td>Ellipsoid</td>
<td>22.0</td>
<td>14.5</td>
<td>1.5</td>
<td>19</td>
<td>0.017</td>
<td>0.024</td>
</tr>
</tbody>
</table>

Table 7.5: Parameters obtained by fitting the SANS data to structural models for the Dynax DX1030: SDS mixed system at a mole fraction of 0.10: 0.90 and concentration of 10 x CAC. CAC taken as 3.85 mM. $R_{eq}$ is the equatorial radius of an ellipsoid, $R_{pol}$ is the polar radius of the ellipsoid, aspect ratio is defined as $X = R_{eq}/R_{pol}$, $Z$ is effective charge, $\Phi_{Fitted}$ is fitted volume fraction and $\Phi_{Calculated}$ is calculated volume fraction based on sample composition.

As shown above in Table 7.3, SDS has $R_{eq}$ and $R_{pol}$ values of 22.0 $\pm$ 0.1 Å and 14.7 $\pm$ 0.1 Å, respectively and an aspect ratio of 1.5. On comparison with results in Table 7.5, it can be seen that there is a clear overlap between the structural parameters for both the mixed FC: HC surfactant system and SDS individually. This suggests that the main composition of the micelle at this composition of 0.10: 0.90 is SDS. The possibility of mixing cannot be concluded for this mole fraction, due to the lack of reliable data to sufficiently describe the micelles.

Dynax DX2200: SDS mixed micelle compositions above CAC

In Chapter 5, it was shown that mixing FC surfactant Dynax DX2200 with SDS produced an antagonistic affect, as would be expected for a long chain FC surfactant mixed with a HC surfactant. Investigations into the micelle composition would presumably show demixing into two distinct populations of FC and HC micelles due to the unfavourable interaction between the two surfactants. Below in Figure 7.5, the SANS profiles of Dynax DX2200 with h/d-SDS are shown.

(a) 0.90: 0.10 Mole fraction

(b) 0.50: 0.50 Mole fraction
Figure 7.5: SANS profiles of Dynax DX2200: SDS mixed systems in D₂O at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90. (a) shows the scattering profiles of the 0.90: 0.10 mole fraction samples at multiple concentrations, (b) and (c) are h/d-SDS contrast samples at 100 x CAC. The CAC used for these mole fractions were 0.01 mM, 0.05 mM and 0.05 mM, respectively. T = 25 °C.

No substantial scattering profiles were observed in the 0.90: 0.10 mole fraction sample (Figure 7.5a). The CACs used for these composition studies were those determined from surface tension measurements as presented in Chapter 5. For the Dynax DX2200: SDS mixed system, a large discrepancy between the CAC values determined from surface tension and UV-Vis measurements was observed, and it was argued that the UV-Vis method provided a more realistic value for the CAC due to sampling of a larger amount of molecules. As a result, the 100 x CAC scattering profile shown in Figure 7.5a is at a concentration of 1.00 mM, which is at the CAC determined from UV-Vis measurements, hence very little structural resolution would be expected at this concentration and compositional analysis could not be undertaken. For the other two mole fractions, 100 x CAC is above the CAC obtained from UV-Vis measurements, hence scattering profiles are expected.

Compositional analysis, using h/d-SDS contrast variation, was possible for the Dynax DX2200: SDS 0.50: 0.50 and 0.10: 0.90 mixed systems as can be seen in Figures 7.5a and 7.5b. Interestingly, for both mole fractions, a slight shift to low Q is seen when d-SDS is included in the sample compared to h-SDS. This slight shift to low Q is associated with an increase in $R_{eq}$ and $R_{pol}$ of 8 Å and 3 Å respectively for the 100 x CAC 0.50: 0.50 mole fraction sample. Analysis of $\chi_{surf}$ was difficult for this data set due to the low scattering intensities of some samples, Table 7.6 summarises the data.
CHAPTER 7. COMPOSITION AND STRUCTURE OF MIXED FLUOROCARBON HYDROCARBON SURFACTANT MICELLES

<table>
<thead>
<tr>
<th>Mole fraction/Dynax DX2200</th>
<th>Concentration (x CAC)</th>
<th>$\chi_{\text{f-surf}}$ SANS</th>
<th>$\chi_{\text{f-surf}}$ Iterative (±0.02)</th>
<th>$\rho_{\text{mixed}}$ $10^{-6}$ Å$^{-2}$ (Fitted)</th>
<th>$\rho_{\text{mixed}}$ $10^{-6}$ Å$^{-2}$ (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>25</td>
<td>1.00 ± 0.02</td>
<td>0.30</td>
<td>2.20 (h-SDS)</td>
<td>2.00 (d-SDS)</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.00 ± 0.01</td>
<td></td>
<td>2.80 (h-SDS)</td>
<td>2.48 (d-SDS)</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.94 ± 0.01</td>
<td></td>
<td>2.50 (h-SDS)</td>
<td>2.50 (d-SDS)</td>
</tr>
<tr>
<td>0.10</td>
<td>100</td>
<td>0.80 ± 0.20</td>
<td>0.10</td>
<td>2.60 (h-SDS)</td>
<td>-0.11 (h-SDS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.00 (d-SDS)</td>
<td>5.65 (d-SDS)</td>
</tr>
</tbody>
</table>

Table 7.6: Calculated values of $\chi_{\text{f-surf}}$ from using both SANS and iterative calculation for the 0.50: 0.50 and 0.10: 0.90 mole fraction mixtures (Dynax DX2200: SDS). Critical aggregation concentrations have been taken as 0.05 mM and 0.05 mM, respectively. The value of $\chi_{\text{f-surf}}$ from SANS measurements was averaged from the SANS2D and LOQ data. $\rho_{\text{mixed}}$ and $\rho_{\text{calc}}$ are the scattering length densities from fitting the data to structural models and calculated, assuming ideal mixing.

The data for both $\chi_{\text{f-surf}}$ and $\rho_{\text{mixed}}$ show that the FC surfactant is the dominant component within the micelles for both studied mole fractions, even when at high bulk compositions of SDS. Although there seems to be no significant incorporation of SDS into the mixed micelles, the slight shift to lower Q observed when changing h-SDS to d-SDS suggests a subtle affect on the overall size of the 0.50: 0.50 mole fraction mixture. This could suggest that SDS is being incorporated into the mixed micelles in very small amounts, leading to slight distortions in the overall micelle size. Large errors are associated with the $\chi_{\text{f-surf}}$ value in the 0.10: 0.90 mole fraction mixture, due to low volume fractions of sample ($\phi = 0.002$) causing low quality data.

Mixed systems containing non-ionic HC surfactants and anionic HC surfactants have been used extensively to investigate mixed micelles using SANS, often showing formation of mixed micelles.\textsuperscript{1, 2, 49} Guo \textit{et al.} also showed that mixing a non-ionic HC surfactant with a FC surfactant produced ideal mixing due to a decrease in the repulsion between anionic head groups due to the insertion of the non-ionic surfactant.\textsuperscript{50} The results here for the Dynax DX2200 (non-ionic): SDS (anionic) mixed system do not follow either of these studies and are more in keeping with what would be expected for FC/ HC mixtures, i.e. either complete demixing or a broad distribution of mixed micelles with a high population of FC containing micelles.\textsuperscript{27, 51} To gain more information on this mixed system, further experiments at higher concentrations and additional contrasts would be required.

**Capstone 1157: SDS mixed micelle composition above CAC**

Mixtures containing zwitterionic and anionic surfactants have been shown previously to associate to form complexes.\textsuperscript{52–58} The Capstone 1157: SDS mixed system produces essentially ideal behaviour over all studied mole fractions (see Chapter 5), which
was explained due to the combination of two interactions. One is a weak antipathy between HC and FC chains, resulting in an apparent increase in the CAC, and the second is due to the electrostatic attraction between the positive charge of the zwitterionic FC surfactant and anionic portion of the HC surfactant. These two effects were found to compensate each other to exhibit overall ideal behaviour. In addition to this, the slight polarity in the FC due to the CF$_2$CH$_2$ group and the presence of the sulfonamide group may further offset the antipathy usually experienced when mixing FC and HC surfactants. The scattering profiles for the Capstone 1157: SDS mixed systems are shown below in Figures 7.6 and 7.7.

Figure 7.6: SANS profiles of Capstone 1157: h/ d-SDS mixed systems in D$_2$O at mole fractions of 0.90: 0.10 and 0.50: 0.50 and concentration of 20 x CAC. The CAC used for these mole fractions were 0.15 mM and 0.53 mM respectively. T = 25 °C.
Although the scattering profiles of the 0.90: 0.10 and 0.50: 0.50 mixed systems look similar, differences were observed. The data were best modeled using a cylindrical form factor for the 0.90: 0.10 mixture and a lamellar model for the 0.50: 0.50 mixture, suggesting that interactions between the two surfactants in the mixture leads to the different aggregation structures. This will be discussed further in the following Section. Comparable data can be seen for both the SANS2D and LOQ data, showing consistency in preparation of the samples. Below in Table 7.7 the data for $\chi_{f-surf}$ are summarised.

<table>
<thead>
<tr>
<th>Mole fraction/ Concentration</th>
<th>$\chi_{f-surf}$</th>
<th>$\chi_{f-surf}$</th>
<th>$\rho_{mixed}$</th>
<th>$\rho_{mixed}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capstone 1157 (x CAC)</td>
<td>SANS</td>
<td>Iterative (±0.02) $10^{-6}$ Å$^{-2}$ (Fitted)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>10</td>
<td>0.98 ±0.01</td>
<td>2.20 (h-SDS)</td>
<td>2.20 (h-SDS)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.98 ±0.01</td>
<td>2.30 (d-SDS)</td>
<td>2.85 (d-SDS)</td>
</tr>
<tr>
<td>0.50</td>
<td>5</td>
<td>0.51 ±0.02</td>
<td>1.70 (h-SDS)</td>
<td>1.05 (h-SDS)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.63 ±0.01</td>
<td>1.65 (h-SDS)</td>
<td>4.00 (d-SDS)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.65 ±0.01</td>
<td>1.60 (h-SDS)</td>
<td>4.25 (d-SDS)</td>
</tr>
</tbody>
</table>

Table 7.7: Calculated values of $\chi_{f-surf}$ from using both SANS and iterative calculation for the 0.90: 0.10 and 0.50: 0.50 mole fraction mixtures (Capstone 1157: SDS). Critical aggregation concentrations have been taken as 0.15 mM and 0.53 mM, respectively. The value of $\chi_{f-surf}$ from SANS measurements was averaged from the SANS2D and LOQ data. $\rho_{mixed}$ and $\rho_{calc}$ are the scattering length densities from fitting the data to structural models and calculated, assuming ideal mixing.

Comparable $\chi_{f-surf}$ values can be seen for analysis from both SANS and iterative calculations. There is a slight deviation away from ideal behaviour in terms of $\chi_{f-surf}$, with a preference for the FC surfactants within the mixed FC: HC surfactant micelles. The $\rho_{mixed}$ (fitted) values can also be compared with the $\rho_{calc}$, calculated assuming ideal mixing, as well as the calculated $\rho$ values determined from $\chi_{f-surf}$. Using the experimental values of $\chi_{f-surf}$ to calculate the experimental $\rho$, leads to values for the 0.90: 0.10 mole fraction mixture of $2.44 \times 10^{-6}$ Å$^{-2}$ (h-SDS) and $2.57 \times 10^{-6}$ Å$^{-2}$ (d-SDS), and for the 0.50: 0.50 mole fractions mixture of $1.63 \times 10^{-6}$ Å$^{-2}$ (h-SDS) and $3.55 \times 10^{-6}$ Å$^{-2}$ (d-SDS). The same value of $\rho_{mixed}$ was fitted for the h-SDS and d-SDS samples at a mole fraction of 0.90: 0.10, showing that the composition of the micelles are essentially unchanged when the contrast is altered, providing further confidence in the value of $\chi_{f-surf}$. For the 0.50: 0.50 mixed system, the values of $\rho_{mixed}$ are comparable to those calculated using the experimental $\chi_{f-surf}$, again further showing that the micelle composition is consistent with the calculations.
The 0.10: 0.90 mixed system sample showed the possible formation of two populations of micelles, data shown below in Figure 7.7.

![Figure 7.7: SANS profiles of Capstone 1157: d/ h-SDS mixed systems in different contrast solvents at a mole fraction of 0.10: 0.90 at 20 x CAC. The CAC for this mole fraction is 1.70 mM. T = 25 °C.](image)

Different scattering profiles are observed when the FC surfactant and d-SDS are contrast matched out respectively. Similar scattering profiles are shown for both the FC: h-SDS: D\textsubscript{2}O sample and when the FC surfactant is matched out. However, when the d-SDS is contrast matched out, the scattering profile is similar to that of the other mole fraction samples, i.e. elliptical cylinders. All of the samples shown here are at the same concentration, with the only difference between them being the contrast. This is an interesting observation that is in keeping with previous experiments by Almgren et al., showing that instead of distinct populations of mixed micelles being formed, it is more likely that a broad distribution of different micelle compositions are present within this system.\textsuperscript{27, 29} This, however, can only be elucidated through further contrast variation experiments.

Overall, results have shown that mixtures containing partially fluorinated surfactants with different headgroups and an anionic HC surfactant leads to the formation of mixed FC: HC surfactant micelles, with a preference for FC surfacants within the mixed micelles. Clear conclusions, however, could not be drawn for the Dynax DX2200: SDS mixed system. The composition of the mixed micelles were calculated and compared using models developed by Penfold\textsuperscript{1, 2} and RST.\textsuperscript{7–9} For both
the Dynax DX1030 (anionic) and Capstone 1157 (zwitterionic): SDS mixtures, the values of $\chi_{f-surf}$ agreed well between SANS and RST at a mole fraction of 0.90: 0.10. Both of these FC:HC surfactant mixtures also had comparable $\chi_{f-surf}$ values at a mole fraction of 0.50: 0.50, again displaying a preference for FC surfactants in the mixed micelles. Although iterative calculations provided similar $\chi_{f-surf}$ values for the Capstone 1157: SDS mixed system: $\sim$ 0.60 and 0.65 for SANS and iterative calculations, respectively, the same was not observed for the Dynax DX1030: SDS mixed system: $\sim$ 0.57 and 0.85 for SANS and iterative calculations, respectively. Ideal behaviour was documented in Chapter 5 for the Dynax DX1030: SDS mixed system at a mole fraction of 0.50: 0.50, and it was argued that the $\chi_{f-surf}$ value obtained from analysis of the SANS data is a more realistic representation of this observed behaviour. In addition to this, the fitted SLDs of the FC:HC mixed surfactant systems gave good agreement with the $\chi_{f-surf}$ values determined using SANS measurements, hence showing that the fitted SLD matched the composition of the mixed micelles. Contrast variation SANS has therefore provided a direct/reliable measure of $\chi_{f-surf}$ values for sometimes unpredictable FC:HC mixed systems.

7.3.3 Structural changes in fluorocarbon hydrocarbon surfactant mixtures

Here the emphasis is on determining how mixing FC and HC surfactants affects the structure of the mixed micelles. Results from the micelle composition data showed formation of mixed micelles between the FC and HC surfactants, however the structure/fitting parameters were not addressed. In this section, the overall surfactant concentration was kept constant at either 50 mM or 100 mM to ensure formation of micelles, instead of low concentrations studies shown in Section 7.3.2. The structure of micelles are normally accounted for by use of the packing parameter:

$$P_C = v/(a_o l_c)$$

where $v$ is volume of the hydrophobic tail, $a_o$ is the head group area and $l_c$ is the length of the hydrophobic chain. The packing parameter has been used previously to justify the structure of mixed micelles, and the same will be applied here.$^{60,61}$

A matrix of experiments were carried out to investigate the structure of mixed FC:HC surfactant micelles; each mixed system was studied at three mole fractions: 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 in D$_2$O. In addition to this, the components of the mixed system at each composition were studied individually. The data reported here are of just the mixed systems, the individual data of each component are displayed in the Appendix.
Structural changes in mixed micelles containing Dynax DX1030: SDS

It has been shown that both Dynax DX1030 and SDS self-assemble in aqueous solution to form oblate spheroid shaped aggregates. This is unsurprising due to the similarities in both the surfactant headgroups and length of hydrophobic tails. Calculations of the individual packing parameters lead to values of \( \sim 0.31 \) and \( \sim 0.32 \) for the FC and HC, respectively, hence spherical or ellipsoidal micelles are expected. Upon mixing the FC and HC surfactants, changes in the packing parameter are unlikely to be observed and ellipsoidal shaped mixed micelles are expected. Despite this, SANS is an ideal tool to allow subtle structural changes of the micelles to be realised. Figure 7.8 shows the SANS profiles of the Dynax DX1030: SDS mixed surfactant system in D\(_2\)O.

![Normalised SANS profiles](image)

(a) Normalised SANS profiles

![Porod approximation](image)

(b) Porod approximation. Note, key is the same as in (a)

Figure 7.8: SANS profiles of Dynax DX1030: h-SDS mixed systems at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 and an overall concentration of 50 mM. Fitted functions shown as lines. Porod approximations of the high Q region of the same data set. \( T = 25 \, ^\circ\text{C} \).

By plotting all of the different mole fraction samples on the same graph, slight changes can be seen as the mole fraction of HC surfactant is increased. The first observation is that there is a small shift to higher Q as the mole fraction of HC surfactant is increased, which is indicative of a reduction in the overall micelle size. This is further emphasised by the changes shown in the Porod approximations in Figure 7.8b. The Porod approximations gave micelle radii of 25, 20 and 20 Å for the 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 mole fractions, respectively. Second, a slight increase in the intensity as the mole fraction of HC surfactant is increased is observed, which will stem from either a change in \( \Delta \rho^2 \) or volume fraction (\( \Phi \)). Calculations showed that \( \Phi \) decreases as the mole fraction of HC surfactant is increased within the mixture, therefore intensity increases is due to the change in \( \Delta \rho^2 \), i.e. as more HC surfactant is incorporated into the mixed micelles, the SLD of the micelles decreases,
leading to increases in $\Delta \rho^2$. Analyses by Guinier approximations proved difficult to carry out due to the S(Q) peak in the data and the micelle radii determined from the Porod approximations were therefore used as an estimate for the micelle size in the fitting process. The parameters used to model the data are shown below in Table 7.8.

<table>
<thead>
<tr>
<th>Mole fraction/ Dynax DX1030</th>
<th>Model</th>
<th>$R_{eq}$ /Å $(\pm 0.1)$</th>
<th>$R_{pol}$ /Å $(\pm 0.1)$</th>
<th>Aspect ratio</th>
<th>$N_{agg}$ (± 2)</th>
<th>Z</th>
<th>$\Phi_{\text{Fitted}}$</th>
<th>$\Phi_{\text{Calculated}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>Ellipsoid</td>
<td>29.0</td>
<td>16.1</td>
<td>1.8</td>
<td>97</td>
<td>7</td>
<td>0.021</td>
<td>0.025</td>
</tr>
<tr>
<td>0.90</td>
<td>Ellipsoid</td>
<td>29.0</td>
<td>16.1</td>
<td>1.8</td>
<td>97</td>
<td>10</td>
<td>0.021</td>
<td>0.028</td>
</tr>
<tr>
<td>0.50</td>
<td>Ellipsoid</td>
<td>25.0</td>
<td>15.0</td>
<td>1.7</td>
<td>76</td>
<td>12</td>
<td>0.017</td>
<td>0.022</td>
</tr>
<tr>
<td>0.10</td>
<td>Ellipsoid</td>
<td>22.5</td>
<td>15.0</td>
<td>1.5</td>
<td>78</td>
<td>13</td>
<td>0.012</td>
<td>0.016</td>
</tr>
<tr>
<td>0.00</td>
<td>Ellipsoid</td>
<td>21.0</td>
<td>14.0</td>
<td>1.5</td>
<td>65</td>
<td>10</td>
<td>0.008</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Table 7.8: Parameters obtained by fitting SANS data to structural models. $R_{eq}$ is the equatorial radius of an ellipsoid, $R_{pol}$ is the polar radius of the ellipsoid, aspect ratio is defined as $X = R_{eq}/R_{pol}$, $N_{agg}$ is the aggregation number, $Z$ is effective charge, $\Phi_{\text{Fitted}}$ is fitted volume fraction and $\Phi_{\text{Calculated}}$ is calculated volume fraction based on sample composition. The aggregation number was calculated using the value of $\chi_{f-surf}$ determined from the mixed micelle composition analysis. The concentration was fixed at 50 mM.

The data for two surfactants individually have been included in the table for completion (mole fractions of Dynax DX1030 = 1.00 and 0.00). For the two extremes in the mole fractions, i.e. 0.90: 0.10 and 0.10: 0.90 (FC: HC), the structural parameters tend to follow the parameters of the dominant component within the mixture, as was also seen in the results for the $\chi_{f-surf}$ determination. However, when the mole fraction is at 0.50: 0.50, the structure of the mixed micelles seems to be in an intermediate position between that of the FC and HC surfactants, respectively. The $\chi_{f-surf}$ at this mole fraction was $\sim$ 0.60: 0.40 (FC: HC), hence mixed micelles with different structural parameters are to be expected for this equivalent mixture.

**Structural changes in mixed micelles containing Dynax DX2200: SDS**

To ensure aggregation of the Dynax DX2200: SDS mixed system, the total concentration for all of the studied mole fractions was held at a high constant value of 100 mM. A change in packing parameter/structure is not unreasonable to envisage when studying mixtures of non-ionic and anionic surfactants. Addition of a non-ionic surfactant to an anionic surfactant has been shown to reduce the repulsion between the anionic head groups, even in mixtures containing FC and HC surfactants. This reduction in repulsion between surfactant headgroups would lead to a lower head group area, and thus an increase in packing parameter. The SANS profiles for the mixed system at the three mole fractions in $D_2O$ are shown below in Figure 7.9.
Figure 7.9: SANS profiles of Dynax DX2200: h-SDS mixed systems at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 and an overall concentration of 100 mM. Fitted functions shown as lines. T = 25 °C.

Headgroup area is known to have a strong influence on the surfactant packing parameter. Non-ionic surfactants generally have large head groups and relatively shorter hydrophobic tails, hence spherical or ellipsoidal micelles are expected. Ellipsoidal micelles have been previously reported for Dynax DX2200. The data for the mixed systems shown above in Figure 7.9 are consistent with ellipsoidal micelles, with strong intermicellar interactions. The strong S(Q) peak in the 0.90: 0.10 FC: HC mixture is due to the high concentration of the FC surfactant within the system. At 90 mM and a Φ of 0.140, the FC surfactant is at ∼ 4500 x CMC, whereas in Chapter 4, measurements of the FC surfactant were only carried out up to 80 x CMC, showing no S(Q) peak. The same can be said for the other two mixtures, although as the mole fraction of HC surfactant increases, the S(Q) is likely to be more dominated by the repulsive interactions between anionic surfactants.

A clear shift to high Q is observed as the mole fraction of HC surfactant is increased within the mixture, displaying a reduction in the overall size of the micelles. Strong S(Q) peaks lead to difficulties in obtaining reasonable analyses by Guinier and Porod approximations and the data were therefore initially modeled using the assumption that the structural parameters for the FC surfactant individually will provide a good approximation, and adjusted accordingly. The structural parameters for the different FC: HC surfactant systems, along with the individual surfactant parameters are shown below in Table 7.9.
Table 7.9: Parameters obtained by fitting SANS data to structural models. $R_{eq}$ is the equatorial radius of an ellipsoid, $R_{pol}$ is the polar radius of the ellipsoid, aspect ratio is defined as $X = R_{eq}/R_{pol}$, $N_{agg}$ is the aggregation number, $Z$ is effective charge, $\Phi_{\text{Fitted}}$ is fitted volume fraction and $\Phi_{\text{Calculated}}$ is calculated volume fraction based on sample composition. The concentration was fixed at 100 mM.

As was shown in the Dynax DX1030: SDS mixed system, at the two extremes in mole fraction, i.e. 0.90: 0.10 and 0.10: 0.90 (FC: HC), the fitted structural parameteres are similar to those of the dominant component within the mixture. In the 0.10: 0.90 FC: HC sample, however, a slight increase in size is seen when compared to the HC surfactant alone. In the equimolar region, the micelles are at an intermediate size between the two individual surfactants. Analysis of the composition data suggested that $\chi_{f-surf}$ was 1.00 for the 0.50: 0.50 mixed system, i.e. no HC surfactants present in the micelles. If this was the case, the parameters used to fit the FC surfactant alone should fit the mixed system at this composition. Hence, these results therefore emphasise the need for additional contrast experiments at higher concentrations to fully characterise the composition of this mixed system.

**Structural changes in mixed micelles containing Capstone 1157: SDS**

Above, it was shortly discussed that changes were observed in the aggregated structure of the Capstone 1157: SDS mixed systems across the range of studied mole fractions. The 0.90: 0.10 FC: HC surfactant micelles were best described as cylindrical with $Q^{-1}$ scattering, whereas the 0.50: 0.50 mixture indicated 2-D $Q^{-2}$ scattering, as has been shown for the FC surfactant alone (Chapter 4). Ellipsoidal micelles were observed for the 0.10: 0.90 mixture, however different structures were seen with contrast variation experiments, which could be indicative of multiple aggregation species. As a way to determine how altering the mole fraction within this mixture affects the aggregated structures, the mixed systems will be studied at both low (multiple of CAC) and high (50 mM) concentrations. The SANS profiles of the mixed FC: HC surfactant micelles at these concentrations in D$_2$O are shown below in Figure 7.10.
Figure 7.10: SANS profiles of Capstone 1157: h-SDS mixed systems at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 and an overall concentration of (a) 50 mM and (b) 10 x CAC. CACs used for the mole fractions were 0.15, 0.53 and 1.70 mM, respectively. CAC data shown in Chapter 5. Fitted functions shown as lines. T = 25 °C.

Considering the low concentration data in Figure 7.10b, there is a clear change in structure as the mole fraction of h-SDS is increased within the mixed system. In the low-\( Q \) region, the scattering scales as \( I(Q) \approx Q^{-D} \), where D is a characterisic dimensionality of the dispersed colloids and the gradient of a log-log plot will be \(-D\). The data show a \( Q^{-1} \) dependence for the 0.90: 0.10 mole fraction sample and a \( Q^{-2} \) dependency for the 0.50: 0.50 mole fraction sample. These exponents represent
CHAPTER 7. COMPOSITION AND STRUCTURE OF MIXED FLUOROCARBON HYDROCARBON SURFACTANT MICTELLES

formation of cylinder and discs/ lamellar, respectively. From this information, Guinier approximations using plots of ln[I(Q).Q] vs. Q^2 for the cylinder and ln[I(Q).Q^2] vs. Q^2 for the disc/ lamellar allowed approximations of the cylinder radius and disc thickness to be estimated. The cylinder radius was estimated to be 38 Å and the disc thickness was estimated to be 15 Å. Guinier approximations were not possible for the 0.10: 0.90 mixture due to the S(Q), however Porod approximations provided a radii of 20 Å. Data for the Guinier and Porod approximations are shown in the Appendix.

Interestingly, at high concentrations both the 0.90: 0.10 and 0.50: 0.50 mixed systems displayed a Q^-2 dependence, i.e. disc/ lamellar structure. Both of these SANS profiles could be fit to Guinier approximations using plots of ln[I(Q).Q^2] vs. Q^2, leading to apparent thickness values of 16 Å and 14 Å respectively. Porod approximations for the 0.10: 0.90 mixture produced radii of 21 Å. Although the low Q data for the 0.90: 0.10 mixture had a Q^-2 dependence, it was best fit using an elliptical cylinder model, as for the low concentration samples. The structural parameters for the three different mole fraction mixtures are presented separately below in Table 7.10.

<table>
<thead>
<tr>
<th>Mole fraction/ Capstone 1157</th>
<th>Concentration</th>
<th>Model</th>
<th>Guinier/ R_minor/(Å)</th>
<th>Aspect ratio</th>
<th>Φ_Fitted</th>
<th>Φ_Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>10 x CAC</td>
<td>Elliptical</td>
<td>38.0</td>
<td>20.0</td>
<td>3.0</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>50 mM</td>
<td>Elliptical</td>
<td>30.0</td>
<td>22.0</td>
<td>2.5</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>(a) 0.90: 0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>10 x CAC</td>
<td>Lamellar</td>
<td>15.0</td>
<td>35.0</td>
<td>0.001</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>50 mM</td>
<td>Lamellar</td>
<td>14.0</td>
<td>30.0</td>
<td>0.015</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>(b) 0.50: 0.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>10 x CAC</td>
<td>Ellipsoid</td>
<td>30.0</td>
<td>15.0</td>
<td>2.0</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>50 mM</td>
<td>Ellipsoid</td>
<td>25.0</td>
<td>15.0</td>
<td>1.7</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>(c) 0.10: 0.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.10: Parameters obtained by fitting SANS data to structural models. R_minor is the minor radius, aspect ratio is defined as X = R_eq/R_pol, thickness relates to layer of the lamellae, R_eq is the equatorial radius of an ellipsoid, R_pol is the polar radius of the ellipsoid, Z is effective charge, Φ_Fitted is fitted volume fraction and Φ_Calculated is calculated volume fraction based on sample composition. CACs used for the mixtures were 0.15, 0.53 and 1.70 mM for the 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 mole fractions, respectively. CAC data shown in Chapter 5.
The change in aggregated structure from cylinder to lamellar to ellipsoid would suggest an initial increase in the packing parameter and subsequent reduction. In Chapter 4, Capstone 1157 was shown to generate $Q^{-2}$ scattering consistent with lamellar structure at all studied concentrations above the CMC, i.e. has a packing parameter between 0.5 - 1.0. The composition data showed a $\chi_{f-surf}$ value of $\sim 1.00$ for the 0.90: 0.10 mixture, hence a similar packing parameter and aggregated structure is to be expected at this mole fraction. The formation of cylindrical micelles at this mole fraction therefore suggests that the presence of a small amount of anionic surfactant leads to an increase in packing parameter, possibly due to suppression of some charge repulsions experienced by the zwitterionic surfactant.

Although at high concentrations, data for the 0.90: 0.10 (FC: HC) mixed micelles were best fit by elliptical cylinders, the data at low $Q$ ($Q = 0.008 - 0.050$) could be modeled to a lamellar form factor, the thickness of which was $\sim 21$ Å in keeping with that of the individual surfactant. Following on from this, it can be seen that the 0.50: 0.50 mixture has a lamellar thickness of $\sim 30$ Å at 50 mM, hence as the mole fraction of SDS is increased so does the thickness. The $\chi_{f-surf}$ is $\sim 0.60$ for this mole fraction, hence the increase in thickness could be due to the incorporation of SDS into the lamellae, causing distortions in the size due to antagonism between the FC and HC tails. Following on from this, it can be seen that the 0.50: 0.50 mixture has a lamellar thickness of $\sim 30$ Å at 50 mM, hence as the mole fraction of SDS is increased so does the thickness. The $\chi_{f-surf}$ is $\sim 0.60$ for this mole fraction, hence the increase in thickness could be due to the incorporation of SDS into the lamellae, causing distortions in the size due to antagonism between the FC and HC tails. As the mole fraction of SDS is increased even further to 0.10: 0.90, a reduction in the packing parameters leads to the formation of ellipsoidal micelles, with a size roughly commensurate with that of the SDS. In Chapter 5, studies on the CAC behaviour of Capstone 1157: SDS mixed system were shown to display close to ideal behaviour in all studied mole fractions and favourable interactions between these two surfactants are possible. As the mole fraction of SDS is increased within the mixture, there will be a higher degree of charge from the anionic surfactant, hence repulsion between the surfactant headgroups is likely. This repulsion will lead to a larger headgroup area and thus reduction in packing parameter, explaining why a change from lamellar to ellipsoidal micelles are observed.

Reports on the structure of mixed micelles containing partially fluorinated zwitterionic surfactants with an anionic HC surfactant are hard to come by, but similar conclusions as reported here can be drawn with reference to HC: HC surfactant mixtures. Favourable interactions between zwitterionic and anionic surfactant can often lead to interesting structural changes in mixed micelles. Christov et al. reported spherical to rod-like structural changes in mixtures of SDS and cocoamidopropyl betaine as the mole fraction of zwitterionic surfactant was increased, with the reason for the transition being due to suppression of charge repulsion between the anionic surfactants, leading to a smaller headgroup area and thus higher packing parameter.
7.4 Alkane-induced swelling of mixed fluorocarbon hydrocarbon surfactant micelles

Here, a short investigation has been undertaken to determine whether addition of an alkane has a swelling affect on mixed FC: HC surfactant micelles. The structure of these mixed micelles have been reported above and act as a baseline to compare results with, i.e. any observed changes in the structure of the micelles are likely to be due to incorporation of alkanes into micelle cores. This is by no means an in-depth analysis of the phase behaviour of the mixed FC: HC systems, it is instead an observational study to back up previous claims about formation of mixed FC: HC surfactant micelles. Cyclohexane has been used as the alkane as it is a common fuel proxy used in lab tests for fire-fighting foam formulations. Before investigations into the mixtures, it is important to determine how addition of cyclohexane affects the size of the FC and HC surfactant micelles individually.

7.4.1 Swelling in individual surfactant micelles

SANS is an ideal technique for determining micelle growth on the Ångstrom scale, due to the possibility of simple contrast variation experiments. By selective variation of the SLD of either the surfactant, solvent or alkane within the investigated system, different regions of interest can be highlighted in the SANS measurements. The most common contrasts being drop, core or shell, which are displayed pictorially below in Figure 7.11 using the example of a D$_2$O–SDS–cyclohexane system.

![Image of eluciation of different regions of interest](image)

Figure 7.11: Elucidation of the different regions of interest for a D$_2$O–h/d-SDS–h/d-cyclohexane system.

From the different contrast experiments, it can be seen that elucidation of different regions of interest are possible. Drop contrasts provide determination of the overall size of the droplets, core contrasts highlight the scattering from the core only,
and shell contrasts provide information on the thickness of the surfactant layer. Here, the interest lies in determining the whether addition of cyclohexane has an effect on the overall size of the surfactant micelles and for this reason the investigated contrast is drop. In this case the system contains: h-cyclohexane (SLD = \( \sim -0.25 \times 10^{-6} \, \text{Å}^{-2} \)), h-SDS (SLD = \( \sim -0.40 \times 10^{-6} \, \text{Å}^{-2} \)) and D\(_2\)O (SLD = \( \sim 6.40 \times 10^{-6} \, \text{Å}^{-2} \)). Hence, due the similarities in the h-cyclohexane and h-SDS SLDs, any changes observed in the overall size of the micelles will shown by a characteristic shift to low Q in the SANS profiles. These data for the system containing h-SDS with and without the addition of h-cyclohexane in D\(_2\)O are shown below in Figure 7.12.

Alkanes can be incorporated into the core of HC surfactant micelles and are most commonly exploited as oil-in-water microemulsions.\(^{65, 66}\) Previous studies have shown that swelling in SDS micelles upon addition of an alkane is due to the incorporation of the alkane into the micelle cores, the same behaviour is seen here.\(^{67}\) A clear low Q shift is observed in the SANS profiles (Figure 7.12) upon addition of 5 % v/v of cyclohexane to the SDS micelles. This is further emphasised in the Porod approximations in Figure 7.12b, which showed an increase in the size of the micelles by 6.5 Å upon addition of 5 % vol cyclohexane.

Alkane-induced swelling of FC surfactant micelles on the other hand would not be expected. As previously discussed, in a surfactant solution, the cyclohexane is most likely to migrate to the hydrophobic micelle cores. The antipathy between HC and FC materials will make the incorporation of cyclohexane into FC surfactant micelles unlikely, thus micelle swelling should not be observed. For example, Patel et
al. showed that incorporation of a HC oil into ionic FC surfactant micelle cores to form microemulsions was only possible at high temperatures and in the presence of a co-surfactant. Here, three FC surfactants (structures in Table 7.1) have been mixed with cyclohexane at concentrations above the CMC to determine whether any micelle swelling occurs. Although there is a difference between the SLDs of the FC surfactants and cyclohexane, \( \sim 2.50 \times 10^{-6} \text{ Å}^{-2} \) and \( \sim -0.25 \times 10^{-6} \text{ Å}^{-2} \), respectively, drop scattering (Figure 7.11a) will be observed due to the much larger \( \Delta \rho \) between the solvent (D\(_2\)O) and both the FC surfactants and h-cyclohexane. The SANS profiles and Porod approximations for the D\(_2\)O: anionic FC surfactant: h-cyclohexane systems are shown in Figure 7.13. The SANS profiles/ Porod approximations for the other two D\(_2\)O: FC surfactant: h-cyclohexane systems are presented in the Appendix.

(a) Normalised SANS profiles of Dynax DX1030 with and without cyclohexane at 50 mM.

(b) Porod approximation of the above data. Note, key is the same as above.

Figure 7.13: SANS profiles of Dynax DX1030 with and without addition of h-cyclohexane in D\(_2\)O at a fixed concentration of 50 mM. Porod approximations of the data at high Q show the increase in the size of the micelles. Fitted functions shown as lines. T = 25 °C.

Minor changes are observed when comparing the above SANS profiles of Dynax DX1030 with and without h-cyclohexane in D\(_2\)O. A slight shift in the S(Q) peak to lower Q suggests a slight increase in the overall size of the micelles, and an increase in the scattering intensity suggests a change in either \( \Delta \rho \) or \( \Phi \). Porod approximations (Figure 7.13b) show a very subtle shift in \( Q_{\text{max}} \) \& \( Q_{\text{min}} \) upon addition of the different vol % of cyclohexane, representing an increase of between 0.5 - 1.0 Å in the size of the micelles. This size increase may not be significant and explained due to experimental error in sample preparation, however, the same behaviour is observed for both the 5 and 10 % vol cyclohexane samples and could therefore be a real observation. To keep the modeling of the structural parameters here consistent with previous results
in this Chapter, the samples with and without h-cyclohexane were fit using the same models. The structural parameters associated with all of the individual surfactants are presented below in Table 7.11.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Cyclohexane/ (%) vol</th>
<th>Porod/ Å</th>
<th>$R_{eq}$ / (Å) (±0.1)</th>
<th>$R_{pol}$ / (Å) (±0.1)</th>
<th>Aspect ratio</th>
<th>$\Phi_{Fitted}$</th>
<th>$\Phi_{Calculated}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>0</td>
<td>18.0</td>
<td>22.0</td>
<td>14.5</td>
<td>1.5</td>
<td>0.009</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>24.5</td>
<td>27.7</td>
<td>18.4</td>
<td>1.5</td>
<td>0.012</td>
<td>0.013</td>
</tr>
<tr>
<td>Dynax DX1030</td>
<td>0</td>
<td>23.5</td>
<td>29.0</td>
<td>17.5</td>
<td>1.7</td>
<td>0.022</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>24.5</td>
<td>29.0</td>
<td>19.0</td>
<td>1.5</td>
<td>0.024</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>24.0</td>
<td>29.1</td>
<td>18.7</td>
<td>1.6</td>
<td>0.024</td>
<td>0.025</td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td>0</td>
<td>47.0</td>
<td>64.2</td>
<td>30.5</td>
<td>2.1</td>
<td>0.028</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>47.0</td>
<td>64.0</td>
<td>30.5</td>
<td>2.1</td>
<td>0.026</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>47.0</td>
<td>65.5</td>
<td>29.5</td>
<td>2.2</td>
<td>0.023</td>
<td>0.035</td>
</tr>
</tbody>
</table>

(a) Data for SDS, Dynax DX1030 and Dynax DX2200.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Cyclohexane/ (%) vol</th>
<th>Porod/ Å</th>
<th>$R_{minor}$ / (Å) (±0.1)</th>
<th>Aspect ratio</th>
<th>$\Phi_{Fitted}$</th>
<th>$\Phi_{Calculated}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capstone 1157</td>
<td>0</td>
<td>32.0</td>
<td>20.0</td>
<td>2.5</td>
<td>0.020</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>31.0</td>
<td>20.5</td>
<td>2.5</td>
<td>0.020</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>33.0</td>
<td>21.0</td>
<td>2.2</td>
<td>0.021</td>
<td>0.026</td>
</tr>
</tbody>
</table>

(b) Data for Capstone 1157

Table 7.11: Parameters obtained by fitting SANS data to structural models. $R_{eq}$ is the equatorial radius of an ellipsoid, $R_{pol}$ is the polar radius of the ellipsoid, aspect ratio is defined as $X = R_{eq}/R_{pol}$, $R_{minor}$ is the minor radius, $\Phi_{Fitted}$ is fitted volume fraction and $\Phi_{Calculated}$ is calculated volume fraction based on sample composition. The concentration was fixed at 50 mM for each sample.

The structural parameters associated with modeling SDS shows that addition of h-cyclohexane leads to both an increase in $R_{eq}$ and $R_{pol}$ of 4.7 Å and 3.9 Å, respectively, as well as in $\Phi_{Fitted}$. Dynax DX1030 was the only FC surfactant that showed any increase in micelle size upon addition of h-cyclohexane, represented by an increase in $R_{pol}$ of $\sim$ 1.5 Å but no change in $R_{eq}$. The partially fluorinated nature of Dynax DX1030 may explain why a slight increase in micelle size is observed. As previously discussed, polarity between the CF$_2$CH$_2$ groups in these FC surfactants may allow interactions to occur with HC materials. Non-ionic Dynax DX2200 was shown in Chapter 5 to generate antagonistic affects when mixed with a HC surfactant (SDS) due to both its C8 fluorinated tail and lack of polarity, and therefore interactions with h-cyclohexane are not to be expected. The ideal behaviour shown for Capstone 1157: SDS mixed systems was explained due to favourable interactions of the FC surfactant with the anionic HC surfactant, hence interactions with cyclohexane are not to be expected.

Alkane-induced swelling in both HC and FC surfactant micelles has been investigated through the use of SANS, showing that addition of h-cyclohexane to SDS
causes growth in the micelles by 4.7 Å and 3.9 Å for $R_{eq}$ and $R_{pol}$, respectively. FC surfactant micelles displayed no significant changes in micelle structure upon addition of h-cyclohexane apart from Dynax DX1030: increase in $R_{pol}$ of $\sim 1.5$ Å. Next, h-cyclohexane induced swelling of mixed FC: HC surfactant micelles is investigated.

7.4.2 Swelling in mixed fluorocarbon hydrocarbon surfactant micelles

As previously mentioned, the purpose of this investigation is to determine whether mixed FC: HC surfactant micelle swelling occurs upon addition of h-cyclohexane. In Section 7.3.2, the composition of the FC: HC surfactant mixed micelles were elucidated through the use of contrast variation SANS, with $\chi_{f-surf}$ values being roughly commensurate with the bulk compositions. Although the data were consistent with the formation of mixed FC: HC surfactant micelles, it was argued that formation of a broad range of micelle compositions is a more realistic consideration.\textsuperscript{27, 29} Above, results for the h-cyclohexane induced swelling in the respective FC and HC surfactants showed no significant changes in the FC surfactant micelles, whereas swelling was observed in the HC surfactant. If swelling is reported in the mixed FC: HC surfactant micelles due to the incorporation of h-cyclohexane, it will therefore provide additional evidence for the formation of mixed micelles.

The h-cyclohexane induced swelling of the FC: HC surfactant mixed systems are investigated at fixed concentrations of 50 mM and mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 (FC: HC), i.e. the same as reported above. Note, all of the 0.90: 0.10 mole fraction samples were measured on the LOQ instrument (ISIS, RAL) and others on the D33 instrument (ILL). The SANS profiles for the fluorocarbon surfactant: SDS mixed systems with and without cyclohexane are shown below in Figures 7.14 - 7.16.
Figure 7.14: SANS profiles of Dynax DX1030: SDS mixed systems with and without addition of h-cyclohexane at mole fractions of 0.90: 0.10, 0.50: 0.50, 0.10: 0.90, at fixed concentration of 50 mM. Fitted functions shown as lines. T = 25 °C.
Figure 7.15: SANS profiles of Dynax DX2200: SDS mixed systems with and without addition of h-cyclohexane at mole fractions of 0.90: 0.10, 0.50: 0.50, 0.10: 0.90, at fixed concentration of 50 mM. Fitted functions shown as lines. T= 25 °C.
Figure 7.16: SANS profiles of Capstone 1157: SDS mixed systems with and without addition of h-cyclohexane at mole fractions of 0.90: 0.10, 0.50: 0.50, 0.10: 0.90, at fixed concentration of 50 mM. Fitted functions shown as lines. T= 25 °C.
When the FC surfactant is the majority component within the mixture, i.e. at a mole fraction of 0.90: 0.10, the scattering profiles are essentially all the same with and without h-cyclohexane, apart from very minor shifts to lower Q in the Dynax DX1030: SDS and Dynax DX2200: SDS mixed systems. From the compositional studies in Section 7.3.2, $\chi_{f\text{-surf}}$ values at this mole fraction were $\sim 0.95, 1.00$ and $0.98$ for Dynax DX1030: SDS, Dynax DX2200 and Capstone 1157: SDS, respectively. The $\chi_{f\text{-surf}}$ value for Dynax DX2200 was not possible to calculate due to low concentration samples in Section 7.3.2, so has been assumed from structural data presented in Section 7.3.3. Therefore, at this mole fraction the mixed micelles contain mostly FC surfactants and incorporation of h-cyclohexane produces the same results as observed for the individual FC surfactants.

Changes in the SANS profiles upon addition of h-cyclohexane to the FC: HC surfactants are observed as the mole fraction of SDS is increased. For each FC: HC surfactant mixed system both characteristic shifts to lower Q and intensity increases are displayed in the 0.50: 0.50 and 0.10: 0.90 mole fraction mixtures. As previously shown for the $D_2O$–h-SDS–h-cyclohexane system, these changes are associated with an overall increase in the size of the micelles. The shifts to lower Q are better visualised in Porod approximations which are available in the Appendix.

At mole fractions of 0.50: 0.50 and 0.10: 0.90, $\chi_{f\text{-surf}}$ values were $\sim 0.57$ and 0.00 for the Dynax DX1030: SDS mixed system, $\sim 1.00$ and 0.80 for the Dynax DX2200: SDS mixed system and $\sim 0.60$ and 0.00 for Capstone 1157: SDS mixed system. Note, the $\chi_{f\text{-surf}}$ values for both Dynax DX1030: SDS and Capstone 1157: SDS at a mole fraction of 0.10: 0.90 were assumed due to either lack of scattering or formation of multiple aggregates. None the less, data consistent with the formation of mixed FC: HC surfactant micelles were observed in the compositional studies, and further evidence for this has been shown here by h-cyclohexane induced micelle swelling in the FC: HC surfactant mixtures. The structural parameters associated with the modeling of the data are fully summarised below in Table 7.12.

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>Cyclohexane/</th>
<th>Porod/</th>
<th>$R_{eq}$/</th>
<th>$R_{pol}$/</th>
<th>Aspect</th>
<th>$\Phi$ Fitted</th>
<th>$\Phi$ Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td>Cyclohexane/</td>
<td>(Å)</td>
<td>(Å)</td>
<td>(Å)</td>
<td>ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>23.5</td>
<td>29.0</td>
<td>17.5</td>
<td>1.7</td>
<td>0.021</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>26.0</td>
<td>30.5</td>
<td>19.5</td>
<td>1.6</td>
<td>0.022</td>
<td>0.028</td>
</tr>
<tr>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>21.0</td>
<td>25.0</td>
<td>15.7</td>
<td>1.6</td>
<td>0.013</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>25.0</td>
<td>30.3</td>
<td>19.7</td>
<td>1.5</td>
<td>0.017</td>
<td>0.022</td>
</tr>
<tr>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>19.0</td>
<td>22.0</td>
<td>14.5</td>
<td>1.5</td>
<td>0.011</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>25.0</td>
<td>29.2</td>
<td>19.2</td>
<td>1.5</td>
<td>0.014</td>
<td>0.016</td>
</tr>
</tbody>
</table>

(a) Data for Dynax DX1030: SDS with and without cyclohexane.
CHAPTER 7. COMPOSITION AND STRUCTURE OF MIXED FLUOROCARBON HYDROCARBON SURFACTANT MICELLES

Table 7.12: Parameters obtained by fitting SANS data to structural models. $R_{eq}$ is the equatorial radius of an ellipsoid, $R_{pol}$ is the polar radius of the ellipsoid, aspect ratio is defined as $X = R_{eq}/R_{pol}$, $R_{\text{minor}}$ is the minor radius, $\Phi_{\text{Fitted}}$ is fitted volume fraction and $\Phi_{\text{Calculated}}$ is calculated volume fraction based on sample composition. The concentration was fixed at 50 mM for each sample.

Considering the mixed system Dynax DX1030: SDS first, a slight increase in the size of the micelles is observed in the 0.90: 0.10 mole fraction sample. $R_{eq}$ and $R_{pol}$ increased by 1.5 Å and 2.0 Å respectively. This result is moderately different than the Dynax DX1030 individually, whereby an increase of 1.5 Å was observed in $R_{pol}$ and no change in $R_{eq}$. These differences may not be significant and can possibly be explained due to experimental error. Both the 0.50: 0.50 and 0.10: 0.90 mole fraction samples produced an increase in the micelle size upon addition of h-cyclohexane and for the 0.10: 0.90 mole fraction, it should be noted that the structural parameters are comparable to the data measured for SDS alone (see Table 7.11a). This therefore providing further evidence for the assertion that no significant concentration of FC surfactants are present in the mixed micelles at this mole fraction.

Although the compositional data for the Dynax DX2200: SDS mixed systems were hard to interpret due to the low concentrations of the samples, structural changes showed that the size of the mixed micelles tended towards that of the individual FC surfactant micelles at high FC surfactant bulk compositions and vice versa, with

---

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>Cyclohexane/</th>
<th>Porod/</th>
<th>$R_{eq}/(\text{Å})$</th>
<th>$R_{pol}/(\text{Å})$</th>
<th>Aspect</th>
<th>$\Phi_{\text{Fitted}}$</th>
<th>$\Phi_{\text{Calculated}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX2200</td>
<td>(% vol)</td>
<td>(Å)</td>
<td>($\pm 0.1$)</td>
<td>($\pm 0.1$)</td>
<td>ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>0</td>
<td>40.0</td>
<td>58.0</td>
<td>26.0</td>
<td>2.2</td>
<td>0.045</td>
<td>0.070</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>40.0</td>
<td>57.0</td>
<td>30.2</td>
<td>1.9</td>
<td>0.045</td>
<td>0.070</td>
</tr>
<tr>
<td>0.50</td>
<td>0</td>
<td>30.5</td>
<td>42.5</td>
<td>17.1</td>
<td>2.5</td>
<td>0.023</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>31.5</td>
<td>41.1</td>
<td>21.2</td>
<td>1.9</td>
<td>0.025</td>
<td>0.045</td>
</tr>
<tr>
<td>0.10</td>
<td>0</td>
<td>20.0</td>
<td>24.7</td>
<td>14.9</td>
<td>1.7</td>
<td>0.011</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>27.0</td>
<td>31.8</td>
<td>20.7</td>
<td>1.5</td>
<td>0.014</td>
<td>0.021</td>
</tr>
</tbody>
</table>

(b) Data for Dynax DX2200: SDS with and without cyclohexane

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>Cyclohexane/</th>
<th>Porod/</th>
<th>$R_{\text{minor}}/ (\text{Å})$</th>
<th>Aspect</th>
<th>$\Phi_{\text{Fitted}}$</th>
<th>$\Phi_{\text{Calculated}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capstone 1157</td>
<td>(% vol)</td>
<td>(Å)</td>
<td>($\pm 0.1$)</td>
<td>ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>0</td>
<td>33.0</td>
<td>20.0</td>
<td>2.5</td>
<td>0.018</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>31.5</td>
<td>20.0</td>
<td>2.7</td>
<td>0.020</td>
<td>0.026</td>
</tr>
<tr>
<td>0.50</td>
<td>0</td>
<td>27.0</td>
<td>17.0</td>
<td>2.0</td>
<td>0.008</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>40.0</td>
<td>20.0</td>
<td>4.0</td>
<td>0.012</td>
<td>0.020</td>
</tr>
</tbody>
</table>

(c) Data for Capstone 1157: SDS 0.90: 0.10 and 0.50: 0.50 mixed systems with and without cyclohexane.

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>Cyclohexane/</th>
<th>Porod/</th>
<th>$R_{eq}/(\text{Å})$</th>
<th>$R_{pol}/(\text{Å})$</th>
<th>Aspect</th>
<th>$\Phi_{\text{Fitted}}$</th>
<th>$\Phi_{\text{Calculated}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capstone 1157</td>
<td>(% vol)</td>
<td>(Å)</td>
<td>($\pm 0.1$)</td>
<td>($\pm 0.1$)</td>
<td>ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0</td>
<td>19.0</td>
<td>24.1</td>
<td>14.5</td>
<td>1.7</td>
<td>0.011</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>28.0</td>
<td>32.8</td>
<td>21.5</td>
<td>1.5</td>
<td>0.014</td>
<td>0.015</td>
</tr>
</tbody>
</table>

(d) Data for Capstone 1157: SDS 0.10: 0.90 mixed system with and without cyclohexane.
intermediate sizes at a mole fraction of 0.50: 0.50. Mixed micelle compositions cannot be calculated from these data, but it tentatively suggests the formation of mixed micelles. As with the Dynax DX1030: SDS mixed system, the degree of mixed micelle swelling increases as the mole fraction of SDS is increased within the mixed system. No h-cyclohexane induced swelling was observed for the Dynax DX2200 individually, hence the swelling displayed in these mixed systems therefore suggest the formation of mixed FC: HC surfactant micelles.

No h-cyclohexane induced swelling is observed in the 0.90: 0.10 Capstone 1157: SDS mixture due to the $\chi_{f-surf}$ value at this mole fraction of 1.00. For the 0.50: 0.50 mixture, however, the aspect ratio increases by 2.0 upon addition of h-cyclohexane. The aspect ratio is defined in this case as $X = R_{\text{major}}/R_{\text{minor}}$ and therefore feeds through to an increase of $\sim 40$ Å in $R_{\text{major}}$. The 0.10: 0.90 mixture has a SANS profile similar to that of SDS individually, and an increase of 8.7 Å and 7.0 Å in $R_{\text{eq}}$ and $R_{\text{pol}}$, respectively were recorded.

Results have therefore shown that an example alkane can be successfully incorporated into the cores of mixed FC: HC surfactant micelles. This investigation acts as further evidence for the formation of mixed micelles for the surfactants/ samples studied in this Chapter.
7.5 Conclusions

Small-angle neutron scattering (SANS) is a useful technique for determining the composition of micelles in ideal mixtures of hydrocarbon surfactants,\textsuperscript{1–6} often showing good agreement with regular solution theory (RST).\textsuperscript{7–9} The case for non-ideal mixtures containing fluorocarbon (FC): HC surfactant mixtures, however, is slightly more complicated, with the idea of micelle demixing being a topic of debate.\textsuperscript{23–30, 34} SANS studies on FC: HC surfactant mixtures reported formation of mixed micelles, with no observed demixing, with an inhomogeneous distribution of HC and FC surfactants within the micelles.\textsuperscript{26, 27, 29, 34} The micelle solutions were best described as having a broad distribution of different compositions, not necessarily having just one population of mixed micelles.\textsuperscript{29, 34}

In this Chapter, the composition and structure of mixed micelles containing partially fluorinated surfactants bearing different head groups (anionic, non-ionic and zwitterionic) and an anionic HC surfactant, SDS, have been investigated using SANS. The composition of the mixed micelles were determined using contrast variation experiments with h/ d-SDS substitution and compared with calculations using RST.\textsuperscript{1, 2} In general, all of the FC: HC surfactant mixtures showed data consistent with the formation of mixed FC: HC micelles. The mixed micelle composition ($\chi_{f-surf}$) data showed good agreement between SANS and RST in the Capstone 1157 (zwitterionic): SDS mixed system but less agreement in the Dynax DX1030 (anionic): SDS mixed system. In particular, for the Dynax DX1030: SDS 0.50: 0.50 mole fraction mixture, $\chi_{f-surf}$ values of $\sim$0.57 and 0.85 were calculated from SANS and RST, respectively. Essentially ideal behaviour was shown in Chapter 5 at this mole fraction and it would therefore be reasonable to assume ideal behaviour in terms of micelle composition, which is more consistent with the $\chi_{f-surf}$ value determined from SANS measurements. At a mole fraction of 0.10: 0.90, different behaviour was observed in these two mixed systems and contrast matching experiments elucidated formation of two distinct micelle populations in the Capstone 1157: SDS mixed system, where the Dynax DX1030: SDS mixture emulated scattering of pure SDS. The aggregated structure of the Capstone 1157: SDS mixed micelles were shown to change from lamellar to ellipsoidal as the mole fraction of SDS was increased, which was explained due to a decrease in the packing packing parameter brought on increasing the amount of charged surfactants within the micelles.

Analysis for $\chi_{f-surf}$ values of the non-ionic Dynax DX2200: SDS mixed systems proved difficult at multiples of the CAC, due to the use of the CACs determined from surface tension instead of UV-Vis measurements (see Chapter 5 for more detail). Therefore, the data were not clear enough at these low concentrations to provide clear indications on formation on mixed FC: HC surfactant micelles and further experiments at higher concentrations would be necessary. Structural changes in this
mixed system, however, were considered at high concentrations (100 mM), showing changes in the size of the mixed micelles over the range of studied mole fractions. At high FC surfactant bulk compositions, the size of the mixed micelles tended towards that of the individual FC surfactant micelles and *vice versa*, with intermediate $R_{eq}$ and $R_{polar}$ values of 40.0 Å and 18.5 Å at a mole fraction of 0.50: 0.50.

Alkane-induced micelle swelling was not observed in the FC surfactants individually, but SDS showed an increase in $R_{eq}$ and $R_{polar}$ of 6.5 Å and 5.7 Å upon addition of h-cyclohexane. As expected, no swelling was seen in the 0.90: 0.10 (FC: HC) surfactant mixtures, due to the high composition of FC surfactants present within the mixed micelles. However, h-cyclohexane induced swelling was observed in all of the mixed micelles at mole fractions of 0.50: 0.50 and 0.10: 0.90. Alkane-induced swelling of the investigated mixed micelles should only be observed due to the presence of HC surfactants, thus providing additional evidence for the formation of mixed FC: HC surfactant micelles.
References


REFERENCES


Chapter 8

Conclusions and Further Work

8.1 Conclusions

This thesis has detailed an investigation into the solution, surface and bulk properties of three mixed surfactant systems each containing a partially fluorinated surfactant (commonly used in fire-fighting foam formulations) with a different headgroup (anionic, non-ionic and zwitterionic) and a common anionic hydrocarbon (HC) surfactant (sodium dodecylsulfate). The main focus of the work has been to gain important insight into how the above properties of the fluorocarbon (FC) and HC surfactants are affected upon formation of mixed surfactant systems, with a view to aid in the future design of new low FC surfactant containing fire-fighting foam formulations.

The first Chapter focused on determining the surface and bulk properties of the technical grade FC surfactants. In depth investigations into these properties have yet to be carried out on the FC surfactants and are therefore crucial for further characterisation of more complex mixed systems. Surface tension measurements were used to determine the critical micelle concentrations (CMCs) and surface tensions at the CMC ($\gamma_{\text{CMC}}$) for the three FC surfactants. Fluorescence spectroscopy was also used to determine CMCs, with good agreement between the two methods. Dynamic surface tension (DST) measurements were recorded for all FC surfactants, with fast DST behaviour shown for the two small molecule FC surfactants (anionic, zwitterionic) and slower behaviour for the large molecular weight non-ionic surfactant. Data were compared to predictions using the diffusion-controlled models at short and long times, showing diffusion-controlled behaviour at short times and behaviour consistent with the presence of a weak adsorption barrier at long times for all surfactants. All FC surfactants displayed low $\gamma_{\text{CMC}}$ values at very low CMCs, with the lowest reported $\gamma_{\text{CMC}}$ of 15.6 mN m$^{-1}$ for the zwitterionic FC surfactant. Due the nature of the FC surfactants, accurate determination of surface density parameters, areas per molecule ($A_{\text{CMC}}$) and surface excesses ($\Gamma_{\text{CMC}}$), could not be
calculated using the Gibbs adsorption isotherm. Neutron reflectivity (NR) was used to circumvent this by studying the FC surfactants in null reflecting water (NRW; 8 mol % D$_2$O in H$_2$O with a scattering length density (SLD) of 0) allowing for direct quantification of these parameters. The NR results provided easy to follow expected trends in terms of $\Gamma_{\text{CMC}}$ and $A_{\text{CMC}}$ values for the three FC surfactants, with the largest $A_{\text{CMC}}$ ($\sim 65$ Å$^2$)/smallest $\Gamma_{\text{CMC}}$ ($\sim 2.50 \times 10^{-6}$ mol m$^{-2}$) being recorded for the non-ionic surfactant, and the smallest $A_{\text{CMC}}$ ($\sim 31$ Å$^2$)/largest $\Gamma_{\text{CMC}}$ ($\sim 5.22 \times 10^{-6}$ mol m$^{-2}$) being recorded for the zwitterionic surfactant. This high $\Gamma_{\text{CMC}}$ values suggests very efficient packing of the surfactant molecules at the air/water interface, further explaining the very low $\gamma_{\text{CMC}}$ value for the zwitterionic surfactant. It was also interesting to note changes in surface density parameters upon comparing the anionic and zwitterionic FC surfactants, which have similar overall chemical structures. The charge on the anionic FC surfactant fed through to an increase of $\sim 12$ Å$^2$ in $A_{\text{CMC}}$ and a $\sim 1.2 \times 10^{-6}$ mol m$^{-2}$ decrease in $\Gamma_{\text{CMC}}$ compared to the zwitterionic. Small-angle neutron scattering (SANS) was used to identify the self-assembled structures formed by the three FC surfactants, with the differences being understood through the packing parameter. Both the anionic and non-ionic FC surfactants formed oblate spheroids, with larger aggregates being formed by the non-ionic surfactant. The size of non-ionic oblate spheroid aggregates were commensurate with the acrylamide group on the surfactant coiling in the polar axis.$^2$ The zwitterionic FC surfactant produced low-Q scattering with a clear Q$^{-2}$ dependency, reminesent of large lamellar structures in solution. Viscous behaviour was also observed at the studied concentrations and similar FC zwitterionics have been found to display these same behaviours.$^3$ The results in this first Chapter therefore act as a foundation for further systematic investigations into the solution, surface and bulk properties of mixtures containing the three FC surfactants and SDS.

The solution properties of the FC: HC mixed systems were investigated through the use of surface tension, UV-Vis and DST measurements. Surface tension and UV-Vis measurements were used to determine critical aggregation concentrations (CACs) of the surfactant mixtures at five different mole fractions, which ranged from high compositions of FC: low compositions HC and vice versa. The two methods rely on probing either the surface (surface tension) or bulk (UV-Vis) properties of the surfactants and comparable results were generally achieved for the two methods. Regular solution theory (RST) was used to calculate the ideal CAC values and then compared with the experimental values to determine whether the mixing is synergistic, ideal or antagonistic.$^4$–$^6$ Highly antagonistic behaviour was observed for the non-ionic FC: HC mixed systems as was expected due to the presence of the C8 fluorinated tail group and lack of polarity within the molecule. The zwitterionic FC: HC surfactant mixtures displayed ideal behaviour over the range of mole fractions,
resulting from the compensation of both a favourable interaction between the two oppositely charged surfactant head groups and the antagonism between the FC and HC chains.\textsuperscript{7, 8} The anionic FC: anionic HC surfactants produced unusual behaviour; antagonism at high mole fractions of FC surfactant, ideal behaviour at equal mole fractions and synergism at low mole fractions of FC surfactant. Similar trends have been seen in mixtures containing partially fluorinated cationic surfactants and a cationic HC surfactant, whereby NR showed that in the range of low FC compositions, the FC: HC chain antagonism was compensated by a reduction in the immersion of the FC in the solution, which is lost as the composition of FC increases above 50 %.\textsuperscript{9} DSTs of the FC: HC surfactant mixtures were measured at the same range of mole fractions as for the CAC measurements. Through comparison of normalised data plots and effective diffusion coefficients ($D_{\text{eff}}$), it was shown that the $\gamma(t)$ decay of the mixtures were essentially dominated by the more surface active FC surfactants. In most of the FC: HC surfactant mixtures, the presence of SDS tended to increase the rate of $\gamma(t)$ decay and in the zwitterionic FC: HC surfactant mixture, even when the SDS was the majority component (mole fraction of 0.10: 0.90 FC: HC), very low $\gamma_{eq}$ values were reached (18.7 mN m$^{-1}$). These results therefore show that the desired solution properties of FC surfactants (low CMCs and $\gamma_{\text{CMC}}$) can still be achieved in FC: HC mixed systems even when FC surfactants are present at low compositions.

After establishing the solution properties and apparent domination of the FC surfactants in terms of $\gamma(t)$ decay in the FC: HC surfactant mixtures, NR was used to investigate both the surface compositions (for example surface composition of FC surfactant: $\chi'_{\text{s-surf}}$) and surface density parameters of the mixtures at multiple bulk compositions and concentrations. The $\chi'_{\text{s-surf}}$ were determined experimentally by two different approaches as well as compared to theoretical predictions calculated using RST.\textsuperscript{5, 6} The experimental results showed that the $\chi'_{\text{s-surf}}$ is essentially dominated by the FC surfactants in all FC: HC surfactant mixtures and mole fractions with generally good agreement between the two methods, providing further experimental evidence for the mixed systems DST behaviours. Through the use of $h$/ d-SDS contrast variation in NRW, it was possible to determine surface density parameters of both the mixtures (FC/ d-SDS/ NRW) or the FC only (FC/ h-SDS/ NRW, h-SDS and NRW have similar SLD and are thus matched out) at the air/water interface. The surface excess of the FC ($\Gamma_{\text{FC}}$) surfactants in the mixtures was found to increase as the bulk concentration was decreased from 2.00 x CAC to 0.25 x CAC, which became more pronounced when the SDS was the majority component. Dilution of the anionic FC: SDS mixed system at a mole fraction of 0.10: 0.90 for example increased the $\Gamma_{\text{FC}}$ from 2.1 to 3.3 x 10$^{-6}$ mol m$^{-2}$ and in turn increased the $\chi'_{\text{s-surf}}$ from 0.46 to 0.85. NR experiments on mixed surfactant systems have previously shown a bias in $\chi'$ towards the more surface active component, and with large differences in surface activities between the FC and HC surfactants in this work, it is not surprising
that there is a strong suppression of the less hydrophobic HC surfactant at the air/water interface.\textsuperscript{9–11} However, it is important to recognise that even in FC: HC surfactant mixtures containing high bulk compositions of HC surfactant, the FC surfactants dominate the $\chi'_{\text{surf}}$, which can be further enhanced by reducing the bulk concentration to below the respective CACs.

SANS was used to establish the compositions and aggregated structures of the mixed FC: HC surfactant micelles in aqueous solution. Through the use of h/ d-SDS isotopic substitution, mixed micelles were found to be formed with a slight favour in the composition $\chi$ towards the FC surfactants.\textsuperscript{12, 13} Significant differences between the surface and micelle compositions were explained due to the relatively high concentrations in the bulk compared to the surface, thus the composition bias towards FC surfactants will be magnified at the surface. Compositions were studied at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 (FC: HC) for each mixed surfactant system, showing reasonable agreement with the previously determined solution behaviours at mole fractions of 0.90: 0.10 and 0.50: 0.50. At a mole fraction of 0.10: 0.90, however, further contrast variation experiments revealed possible formation of two distinct populations of micelles in the zwitterionic FC: SDS mixed system and no/ very little incorporation of FC surfactants into the anionic FC: SDS mixed micelles. Changes in the micelle structures were determined at high bulk concentrations of either 50 or 100 mM. The size of the mixed micelles at high FC bulk compositions tended towards the size of the individual FC surfactant micelles and \textit{vice versa}, with intermediate sizes at a mole fraction of 0.50: 0.50 for both the anionic FC: SDS and non-ionic FC: SDS mixtures. Cyclohexane was added to both the individual surfactants and the mixed systems to determine whether any h-cyclohexane induced swelling occured in the mixed micelles. No swelling was seen in the individual FC surfactants, but swelling was observed in all mixed FC: HC surfactant micelles at mole fractions of 0.50: 0.50 and above, thus providing additional evidence for the formation of mixed micelles.

Overall, these results provide important insight into the use of mixed systems containing partially fluorinated and hydrocarbon surfactants. The highly surface active nature of FC surfactants means that the commonly desired properties of these surfactants can still be achieved in FC: HC surfactant mixtures when present at both low compositions and concentrations, and therefore point towards new ways of formulating these mixtures to contain lower levels of environmentally hazardous FC surfactants.
8.2 Recommendations for further work

There are many areas that could be explored to extend the work presented here, which would both provide other insight into the investigated properties as well as provide further industrial relevance.

1. *Further in-depth DST studies*
   Additional experiments are required for the DST measurements of the FC: HC mixed systems so that full analysis can be carried out. Experiments involving measuring both the mixed systems and the constituent components within the mixed systems at each respective concentration will allow for direct comparisons of both the raw/normalised data and also the diffusion coefficients of the mixed and individual components. Theoretical predictions using short and long time diffusion-controlled limits did not describe the mixed system data well at high mole fractions of SDS due to the model not taking into account interactions between the two surfactants. Incorporating the interaction parameters ($\beta$) could perhaps provide more realistic fits. The results in Chapter 6 showed that decreasing the bulk concentration of the mixed systems increased the composition of FC surfactants at the surface, therefore further experiments at lower concentration would be interesting to investigate also.

2. *Further in-depth SANS and NR studies*
   The mixed micelle composition of the non-ionic FC: SDS surfactant mixtures were studied using the incorrect CAC results, and therefore this aspect needs to be revisited to accurately characterise the mixed micelle compositions. The SANS studies would also benefit from experiments being carried out at both higher concentrations and additional mole fractions, so that a full range of micelle compositions can be realised. NR experiments at additional mole fractions are required, and in addition to this, measuring both the mixed systems and the constituent components within the mixed systems at each respective concentration would be beneficial for accurate surface composition analysis.

3. *Effects of temperature*
   All experiments in the work presented here have been carried out at either 21 or 25 °C, which has been necessary for the initial characterisation of the FC surfactants both individually and as FC: HC surfactant mixtures. However, to make these investigations more relevant to the required application, the solution, surface and bulk properties would need to be characterised at higher temperatures. Previous results have shown that higher temperatures lead to increased mixing in FC: HC surfactant mixtures which could conceivably change both the surface and micelle compositions of the FC surfactants.
4. Characterisation of foaming properties

For a fire-fighting foam formulation to be effective, it must form both very wet and stable foams. Therefore, characterising the foaming properties of the FC: HC mixed systems at different mole fractions/ concentrations would be crucial if new formulations containing lower compositions/ concentrations of FC were to be utilised.

5. Three/ four component mixed systems

Typical formulations contain mixtures of more than two surfactants and investigations into either three or four component mixtures containing the three partially fluorinated surfactants used in this work and SDS would provide additional insight into how the respective surfactants behave in these complex mixtures.
References


Appendix A

Supplementary data
SURFACE AND BULK PROPERTIES OF FLUOROCARBON SURFACTANTS IN FIRE-FIGHTING FOAMS
Method for determining the critical micelle concentrations (CMC)

Each of the surface tension curves were subject to the following analysis. Using the program Origin, the surface tension data were put through a double differential to show points of inflection along the curve, see Figure A.1a. A Gaussian function was then applied over the double differential to accurately assign the point at which the surfactants begin to micellise, shown in Figure A.1b. This method is based on the method by Hait.

(a) Double differential of surface tension data shown in Figure S5 showing the greatest points of inflection along the curve.
(b) Gaussian distribution applied over the double differential to accurately highlight the cmc which can be calculated from the exponential of the value $x_c$.

Figure A.1: Method used to determine critical micelle concentration
CMCs by Fluorescence probe measurements

Although it is clear that the studied FC surfactants give very low surface tensions (<20 mN m\(^{-1}\)) and have low CMCs, due to the nature of the surfactants being from an industrial source, the results must be taken with a degree of caution. To gain some more confidence in the CMC values in particular, fluorescence probe experiments were carried out. These experiments represent a convenient method for assessing the CMC of surfactants (FC surfactants included) and polymers. Pyrene is frequently used as a probe because the ratio in the intensity (I) of the first (\(\lambda = 373\) nm) and third (\(\lambda = 383\) nm) vibrational bands in the emission spectra is indicative of the chromophore environment polarity. By keeping the pyrene concentration fixed and varying the surfactant concentration, \(I_{373}/I_{383}\) vs. concentration can be plotted to determine the CMC. Below in Table A.1, a comparison of the CMC data from both tensiometry results and fluorescence techniques are shown. In addition to this, Figure A.2 shows the comparison between the tensiometry and fluorescence data. In all cases, the fluorescence data show a clear break point at which point the dye is beginning to emit from a more hydrophobic environment, hence the CMC has been reached. Comparable CMC values are produced when considering both the tensiometric and fluorescence data, suggesting that reliable CMCs have been determined.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>CMC from Tensiometry (mM)</th>
<th>CMC from Fluorescence (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax(^\text{TM}) DX1030</td>
<td>1.37 ± 0.05</td>
<td>1.40 ± 0.06</td>
</tr>
<tr>
<td>Dynax(^\text{TM}) DX2200</td>
<td>0.02 ± 0.01</td>
<td>0.02 ± 0.04</td>
</tr>
<tr>
<td>Capstone(^\text{TM}) 1157</td>
<td>0.23 ± 0.02</td>
<td>0.15 ± 0.04</td>
</tr>
<tr>
<td>NaPFO</td>
<td>25.00 ± 0.05</td>
<td>26.00 ± 0.05</td>
</tr>
</tbody>
</table>

Table A.1: CMC Data from Tensiometry and Fluorescence. As described in the main text, these measurements were repeated three times for both techniques to ensure stability of measurements. The uncertainties were therefore taken from the max and minimum values obtained.

Overall, it has been shown that determination of the CMC values has been possible using both surface tensiometry and fluorescence for the three partially fluorinated surfactants, and comparable results are observed.
### APPENDIX A. SUPPLEMENTARY DATA

#### (a) Dynax DX1030 surface tension/fluorescence data

<table>
<thead>
<tr>
<th>Ln[Conc/ mM]</th>
<th>/ (mN m(^{-1}))</th>
<th>I(^{373}) / I(^{383})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-6</td>
<td>60</td>
<td>1.20</td>
</tr>
<tr>
<td>-4</td>
<td>40</td>
<td>1.25</td>
</tr>
<tr>
<td>-2</td>
<td>20</td>
<td>1.30</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>1.35</td>
</tr>
</tbody>
</table>

#### (b) Dynax DX2200 surface tension/fluorescence data

<table>
<thead>
<tr>
<th>Ln[Conc/ mM]</th>
<th>/ (mN m(^{-1}))</th>
<th>I(^{373}) / I(^{383})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>70</td>
<td>1.10</td>
</tr>
<tr>
<td>-8</td>
<td>60</td>
<td>1.15</td>
</tr>
<tr>
<td>-6</td>
<td>50</td>
<td>1.20</td>
</tr>
<tr>
<td>-4</td>
<td>40</td>
<td>1.25</td>
</tr>
</tbody>
</table>

![Graph](image)
Figure A.2: Surface tension and fluorescence data for the three partially fluorinated surfactants. Surface tension data recorded at $T = 25 \, ^\circ\text{C}$, fluorescence recorded at $T = 21 \, ^\circ\text{C}$.
Dynamic Surface tension of FC surfactants

Each dynamic surface tension measurement was repeated three times for each investigated surfactant at all concentrations. The data below is representative of how the three repeat runs compared for the three different surfactants.

(a) Dynax DX1030 1.25 x CMC DST Runs

(b) Dynax DX2200 1.25 x CMC DST Runs
Figure A.3: Representative dynamic surface tension runs for the three partially fluorinated surfactants. T = 25 °C.
Neutron reflectivity in NRW of FC surfactants

Below are normalised neutron reflectivity profiles for the three technical fluorocarbon surfactants in null reflecting water (NRW) at concentrations of 2.50 and 0.40 times the respective CMCs. Additional concentration runs were omitted due crowding of the data. Analysis was carried out on these normalised profiles using Motofit as described in Chapter 4 and the structural parameters for these fits can be found in the same place.

(a) Dynax DX1030 Neutron Reflection Profiles (NRW)

(b) Dynax DX2200 Neutron Reflection Profiles
Figure A.4: Neutron Reflection Profiles for Three Technical FC surfactants in NRW. Critical micelle concentrations have been taken as 1.37 mM, 0.02 mM and 0.23 mM for Dynax DX1030, Dynax DX2200 and Capstone 1157, respectively. Fitted functions shown as lines. T = 25 °C.
Neutron reflectivity profiles in D$_2$O for FC surfactants

The normalised neutron reflection profiles in D$_2$O for the three partially fluorinated surfactants are shown below in Figure A.5. Data were modeled using both single and double layer models, in an attempt to explore hydration effects from the solvent. The model parameters can also be found below in Tables A.2 — A.4. On comparison of the calculated values of $\rho$ for both head and tail groups, it can be seen that the fitted parameters are comparable, suggesting further experiments with different contrasts would be required for a full analysis of the hydration effects from the solvent.
Figure A.5: Neutron Reflection Profiles of the three partially fluorinated surfactants in D$_2$O. Critical micelle concentrations have been taken as 1.37 mM, 0.02 mM and 0.23 mM for Dynax DX1030, Dynax DX2200 and Capstone 1157, respectively. Fitted functions shown as lines. T= 25 °C.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Layer</th>
<th>$\rho_\lambda$ (10$^{-6}$ Å$^{-2}$)</th>
<th>$\tau$ (Å)</th>
<th>Solvent Penetration (%)</th>
<th>Roughness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td>Double Layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Head Group</td>
<td></td>
<td>2.0</td>
<td>9</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>D$_2$O Subphase</td>
<td></td>
<td>6.2</td>
<td>n/a</td>
<td>n/a</td>
<td>3</td>
</tr>
<tr>
<td>Single Layer</td>
<td></td>
<td>1.5</td>
<td>20</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>D$_2$O Subphase</td>
<td></td>
<td>6.2</td>
<td>n/a</td>
<td>n/a</td>
<td>3</td>
</tr>
</tbody>
</table>

Table A.2: Parameters obtained by fitting Neutron reflection to both double and single layer models. FC Tail calculated $\rho = 2.9 \times 10^{-6}$ Å$^{-2}$, Head Group calculated $\rho = 2.0 \times 10^{-6}$ Å$^{-2}$. T= 25 °C.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Layer</th>
<th>$\rho_\lambda$ (10$^{-6}$ Å$^{-2}$)</th>
<th>$\tau$ (Å)</th>
<th>Solvent Penetration (%)</th>
<th>Roughness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX2200</td>
<td>Double Layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Head Group</td>
<td></td>
<td>5.6</td>
<td>6</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>D$_2$O Subphase</td>
<td></td>
<td>6.2</td>
<td>n/a</td>
<td>n/a</td>
<td>3</td>
</tr>
<tr>
<td>Single Layer</td>
<td></td>
<td>2.2</td>
<td>20</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>D$_2$O Subphase</td>
<td></td>
<td>6.1</td>
<td>n/a</td>
<td>n/a</td>
<td>3</td>
</tr>
</tbody>
</table>

Table A.3: Parameters obtained by fitting Neutron reflection to both double and single layer models. FC Tail calculated $\rho = 3.6 \times 10^{-6}$ Å$^{-2}$, Head Group calculated $\rho = 5.5 \times 10^{-6}$ Å$^{-2}$. T= 25 °C.
APPENDIX A. SUPPLEMENTARY DATA

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Layer</th>
<th>$\rho$ $(10^{-6}$ Å$^{-2})$</th>
<th>$\tau$ (Å)</th>
<th>Solvent Penetration (%)</th>
<th>Roughness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capstone 1157</td>
<td>FC Tail</td>
<td>3.0</td>
<td>11</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Head Group</td>
<td>0.5</td>
<td>9</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>D$_2$O Subphase</td>
<td>6.2</td>
<td>n/a</td>
<td>n/a</td>
<td>3</td>
</tr>
<tr>
<td>Capstone 1157</td>
<td>FC</td>
<td>2.0</td>
<td>20</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>Single Layer</td>
<td>D$_2$O Subphase</td>
<td>6.2</td>
<td>n/a</td>
<td>n/a</td>
<td>3</td>
</tr>
</tbody>
</table>

Table A.4: Parameters obtained by fitting Neutron reflection to both double and single layer models. FC Tail calculated $\rho = 3.3 \times 10^{-6}$ Å$^{-2}$, Head Group calculated $\rho = 0.6 \times 10^{-6}$ Å$^{-2}$. T= 25 °C.

Small-angle neutron scattering of FC surfactants

Small-angle neutron scattering measurements were carried out on the same samples at both SANS2D, ISIS, UK and D33, ILL, France. Data from both sources were found to provide similar results and could be fit to the same models. Below in Tables A.5 and A.6 are the parameters obtained by fitting the SANS data from D33 to structural models. Data from both sources were subject to the same analyses.
Figure A.6: Small-angle neutron scattering data for the three partially fluorinated surfactants. Data recorded on D33 at the ILL. Critical micelle concentrations have been taken as 1.37 mM, 0.02 mM and 0.23 mM for Dynax DX1030, Dynax DX2200 and Capstone 1157, respectively. Fitted functions shown as lines. T= 25 °C.
### APPENDIX A. SUPPLEMENTARY DATA

#### Table A.5: Parameters obtained by fitting SANS data to structural models. $R_{eq}$ is the equatorial radius of an ellipsoid, $R_{pol}$ is the polar radius of the ellipsoid, aspect ratio is defined as $X = R_{eq}/R_{pol}$, $N_{agg}$ is the aggregation number and $Z$ is effective charge. $T=25 ^\circ C$. Data taken on D33.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Concentration (x CMC)</th>
<th>Model</th>
<th>$R_{eq}$/Å ($\pm 0.1$)</th>
<th>$R_{pol}$/Å ($\pm 0.1$)</th>
<th>Aspect ratio</th>
<th>$N_{agg}$</th>
<th>$Z$ ($\pm 1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynax DX1030</td>
<td>10</td>
<td>Ellipsoid</td>
<td>29.0</td>
<td>17.0</td>
<td>1.7</td>
<td>97</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>Ellipsoid</td>
<td>30.0</td>
<td>17.7</td>
<td>1.7</td>
<td>108</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>Ellipsoid</td>
<td>30.0</td>
<td>17.7</td>
<td>1.7</td>
<td>108</td>
<td>9.5</td>
</tr>
<tr>
<td>Dynax DX2200</td>
<td>40</td>
<td>Ellipsoid</td>
<td>68.0</td>
<td>25.0</td>
<td>2.7</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>Ellipsoid</td>
<td>68.0</td>
<td>27.0</td>
<td>2.5</td>
<td>338</td>
<td></td>
</tr>
</tbody>
</table>

#### Table A.6: Parameters obtained by fitting SANS data to a structural model for infinite lamellae. $T=25 ^\circ C$. Data taken on D33.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Concentration (x CMC)</th>
<th>Background</th>
<th>Model</th>
<th>Thickness (Å) ($\pm 1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capstone$^{\text{TM}}$ 1157</td>
<td>10</td>
<td>0.05</td>
<td>Lamellar</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.05</td>
<td>Lamellar</td>
<td>26</td>
</tr>
</tbody>
</table>
SOLUTION PROPERTIES OF FLUOROCARBON HYDROCARBON SURFACTANT MIXTURES
Mixed critical aggregation concentrations determination

The critical aggregation concentrations of the partially fluorinated: hydrocarbon surfactant mixtures were determined using both surface tension measurements and UV-Vis. These data are presented below.

Surface tension measurements

Surface tension measurements were carried out on all of the FC: HC surfactant mixtures at 25 °C using the Krüss automatic dosing unit on the Krüss K100. The samples at the different mole fractions were made up at concentrations above the respective CMCs of the constituent components and ultra pure water was automatically added to the stock solution until a predefined concentration is reached. Data for the Dynax DX1030: SDS and Dynax DX2200 mixed systems are shown below and the Capstone 1157: SDS mixed system was presented in Chapter 5.
Figure A.7: Surface Tension vs. ln(Concentration) for both the Dynax DX1030: SDS and Dynax DX2200: SDS mixed systems at varying mole fractions. T= 25 °C.
UV-Vis measurements

Dynax DX1030: SDS

Figure A.8: Raw UV-Vis data for the Dynax DX1030: SDS mixed system at multiple concentrations/compositions. The CACs are determined through plots of max A ($\lambda$ = 496 nm) vs. concentration. T = 21 °C.
Dynax DX2200: SDS

(a) Dynax DX2200: SDS 0.90: 0.10 raw UV-Vis data

(b) Dynax DX2200: SDS 0.90: 0.10 CAC

(c) Dynax DX2200: SDS 0.75: 0.25 raw UV-Vis data

(d) Dynax DX2200: SDS 0.75: 0.25 CAC

(e) Dynax DX2200: SDS 0.50: 0.50 raw UV-Vis data

(f) Dynax DX2200: SDS 0.50: 0.50 CAC
Figure A.9: Raw UV-Vis data for the Dynax DX2200: SDS mixed system at multiple concentrations/compositions. The CACs are determined through plots of max A ($\lambda = 496$ nm) vs. concentration. $T = 21 ^\circ C$. 
Capstone 1157: SDS

(a) Capstone 1157: SDS 0.90: 0.10 raw UV-Vis data

(b) Capstone 1157: SDS 0.90: 0.10 CAC

(c) Capstone 1157: SDS 0.50: 0.50 raw UV-Vis data

(d) Capstone 1157: SDS 0.50: 0.50 CAC

(e) Capstone 1157: SDS 0.10: 0.90 raw UV-Vis data

(f) Capstone 1157: SDS 0.10: 0.90 CAC

Figure A.10: Raw UV-Vis data for the Capstone 1157: SDS mixed system at multiple concentrations/ compositions. The CACs are determined through plots of max A ($\lambda = 496$ nm) vs. concentration. T= 21 °C.
Dynamic surface tension of water: ethanol mixtures

Measurements of the dynamic surface tension of water: ethanol mixtures were carried out to determine the accuracy and reproducibility of the Krüss BP100. The raw dynamic surface tension profiles are shown below.

![Dynamic surface tension of water: ethanol mixtures](image)

Figure A.11: Water ethanol mixed systems. T= 25 °C.

Dynamic surface tension of SDS

![Dynamic surface tension of SDS](image)

Figure A.12: Dynamic surface tension profiles of SDS at multiple concentrations above and below the respective CMC. CMC taken as 8.2 mM. T= 25 °C.
Modeling of FC: HC surfactant mixtures dynamic surface tension data using short and long time diffusion coefficients

In Chapter 5, dynamic surface data of mixed FC: HC surfactant systems were modeled using short and long time diffusion coefficients. Only data for the 0.50: 0.50 mole fraction samples were presented in the Chapter, the other models are included below.

Dynax DX1030: SDS

(a) Dynax DX1030: SDS 0.90: 0.10 mole fraction model

(b) Dynax DX1030: SDS 0.75: 0.25 mole fraction model
Figure A.13: DST for the Dynax DX1030: SDS mixed systems at mole fractions of 0.90:0.10, 0.75: 0.25, 0.25: 0.75 and 0.10: 0.90. fractions. All concentrations are at respective CACs. CACs presented in Chapter 5. The red, dark blue and cyan lines are theoretical calculations using Equations 1.8 and 1.11, respectively.
Dynax DX2200: SDS

(a) Dynax DX2200: SDS 0.90: 0.10 mole fraction model

(b) Dynax DX2200: SDS 0.75: 0.25 mole fraction model
Figure A.14: DST for the Dynax DX2200: SDS mixed systems at mole fractions of 0.90:0.10, 0.75: 0.25, 0.25: 0.75 and 0.10: 0.90. All concentrations are at respective CACs. CACs presented in Chapter 5. The red, dark blue and cyan lines are theoretical calculations using Equations 1.8 and 1.11, respectively. Note: the long time model has been used to predict the $\gamma(t)$ of the Dynax DX2200: SDS mixed system at longer times than measured.
Capstone 1157: SDS

(a) Capstone 1157: SDS 0.90: 0.10 mole fraction model

(b) Capstone 1157: SDS 0.75: 0.25 mole fraction model
### APPENDIX A. SUPPLEMENTARY DATA

<table>
<thead>
<tr>
<th>Surface Age (s)</th>
<th>Surface Tension (mN m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>20</td>
</tr>
<tr>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>100</td>
<td>60</td>
</tr>
</tbody>
</table>

---

(c) Capstone 1157: SDS 0.25: 0.75 mole fraction model

(d) Capstone 1157: SDS 0.10: 0.90 mole fraction model

Figure A.15: DST for the Capstone 1157: SDS mixed systems at mole fractions of 0.90:0.10, 0.75: 0.25, 0.25: 0.75 and 0.10: 0.90. All concentrations are at respective CACs. CACs presented in Chapter 5. The red, dark blue and cyan lines are theoretical calculations using Equations 1.8 and 1.11, respectively.
INVESTIGATIONS INTO THE SURFACE COMPOSITIONS OF FLUOROCARBON HYDROCARBON SURFACTANT MIXTURES
Neutron reflectivity data for FC: HC surfactant mixtures

Neutron reflectivity data for the Dynax DX2200: d-SDS and Capstone 1157: d-SDS mixed systems were measured on both the SURF and FIGARO beam lines at ISIS and the ILL, respectively. The SURF data was included in Chapter 6 and the FIGARO data are shown below.

![Graph](image)

(a) Dynax DX2200: d-SDS 2.00 x CAC

![Graph](image)

(b) Capstone 1157: d-SDS 2.00 x CAC

Figure A.16: Neutron reflectivity profiles of Dynax DX2200: d-SDS and Capstone 1157: d-SDS mixed systems at three mole fractions: 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 (FC: d-SDS) in NRW. All data are at 2.00 x CAC to ensure monolayer saturation. Data for the fitted functions can be found in Chapter 6. T= 25 °C
Mixed FC: HC surfactant neutron reflectivity profiles below respective CACs

Neutron reflectivity was used to study the FC: HC surfactant mixtures at concentration both above and below the respective mixed system CACs. The neutron reflectivity profiles for the data at concentrations below the CAC are presented below. The fitted parameters are presented in Chapter 6.

(a) Dynax DX1030: h/d-SDS 0.25 x CAC

(b) Dynax DX2200: d-SDS 0.25 x CAC
Figure A.17: Neutron reflectivity profiles of Dynax DX1030: d/h-SDS, Dynax DX2200: d/h-SDS and Capstone 1157: d/h-SDS mixed systems at three mole fractions: 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90 (FC: d/h-SDS) in NRW. All data are at 0.25 x CAC. T= 25 °C
COMPOSITION AND STRUCTURE OF MIXED FLUOROCARBON HYDROCARBON SURFACTANT MICELLES
Composition of mixed FC: HC surfactant micelles

Small-angle neutron scattering with h/d-SDS contrast variation was used to determine the compositions of mixed FC: HC surfactant micelles. The data for all of the FC: HC mixed systems at different concentrations/ bulk compositions are presented below and the calculated compositions are presented in Chapter 7.
Dynax DX1030: SDS

(a) Dynax DX1030: SDS 0.90: 0.10 5 x CAC

(b) Dynax DX1030: SDS 0.90: 0.10 10 x CAC

(c) Dynax DX1030: SDS 0.90: 0.10 20 x CAC

Figure A.18: SANS profiles of Dynax DX1030: d/h-SDS mixed systems in D₂O at a mole fraction of 0.90: 0.10 and concentrations of 5, 10 and 20 x CAC. Data on the right is the ratio of the scattering intensities from the two isotopic combinations (FC: h-SDS)/ (FC: d-SDS). T = 25 °C
Figure A.19: SANS profiles of Dynax DX1030: d/h-SDS mixed systems in D₂O at a mole fraction of 0.50: 0.50 and concentrations of 5, 10 and 20 x CAC. Data on the right is the ratio of the scattering intensities from the two isotopic combinations (FC: h-SDS)/ (FC: d-SDS). T= 25 °C
Dynax DX2200: SDS

(a) Dynax DX2200: SDS 0.50: 0.50 25 x CAC

(b) Dynax DX2200: SDS 0.50: 0.50 50 x CAC

(c) Dynax DX2200: SDS 0.50: 0.50 100 x CAC

Figure A.20: SANS profiles of Dynax DX2200: d-/h-SDS mixed systems in D$_2$O at a mole fraction of 0.50: 0.50 and concentrations of 25, 50 and 100 x CAC. Data on the right is the ratio of the scattering intensities from the two isotopic combinations (FC: h-SDS) / (FC: d-SDS). T = 25 °C
Figure A.21: SANS profiles of Dynax DX2200: d/h-SDS mixed systems in D$_2$O at a mole fraction of 0.10: 0.90 and concentrations of 100 x CAC. Data on the right is the ratio of the scattering intensities from the two isotopic combinations (FC: h-SDS)/ (FC: d-SDS). T = 25 °C
Capstone 1157: SDS

Figure A.22: SANS profiles of Capstone 1157: d/h-SDS mixed systems in D$_2$O at a mole fraction of 0.90: 0.10 and concentrations of 10 and 20 x CAC. Data on the right is the ratio of the scattering intensities from the two isotopic combinations (FC: h-SDS)/ (FC: d-SDS). T= 25 °C
APPENDIX A. SUPPLEMENTARY DATA

Figure A.23: SANS profiles of Capstone 1157: d/h-SDS mixed systems in D₂O at a mole fraction of 0.50: 0.50 and concentrations of 5, 10 and 20 x CAC. Data on the right is the ratio of the scattering intensities from the two isotopic combinations (FC: h-SDS)/ (FC: d-SDS). T= 25 °C
Structural data for mixed FC: HC surfactant micelles/constituent components

Small-angle neutron scattering measurements of the mixed FC: HC surfactant micelles were measured at high concentrations of either 50 or 100 mM. The individual FC and HC surfactants were also measured at the respective concentrations present with in the mixture. These data, as well as the fitted structural parameters are shown below for all FC: HC surfactant mixtures.
Dynax DX1030: SDS

Figure A.24: SANS profiles of Dynax DX1030: h-SDS mixed systems as well as Dynax DX1030 and h-SDS at the respective concentrations present within the mixed system at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90. Fitted functions shown as lines. T = 25 °C.
Dynax DX2200: SDS

Figure A.25: SANS profiles of Dynax DX2200: h-SDS mixed systems as well as Dynax DX2200 and h-SDS at the respective concentrations present within the mixed system at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90. Fitted functions shown as lines. T = 25 °C.
Figure A.26: SANS profiles of Capstone 1157: h-SDS mixed systems as well as Capstone 1157 and h-SDS at the respective concentrations present within the mixed system at mole fractions of 0.90: 0.10, 0.50: 0.50 and 0.10: 0.90. Fitted functions shown as lines. T = 25 °C.
Guinier and Porod of Capstone 1157: SDS mixed systems at high and low concentrations

High concentrations

(a) Guinier approximations for the 0.90: 0.10 and 0.50: 0.50 Capstone 1157: SDS mixed systems at 50 mM

(b) Porod approximation for the 0.10: 0.90 Capstone 1157: SDS mixed systems at 50 mM

Figure A.27: Guinier and Porod Approximations for the Capstone 1157: SDS mixed systems at 50 mM
Low concentrations

(a) Guinier approximations for the 0.90: 0.10
Capstone 1157: SDS mixed systems at 10 x CAC

(b) Guinier approximations for the 0.50: 0.50
Capstone 1157: SDS mixed systems at 10 x CAC

(c) Porod approximation for the 0.10: 0.90
Capstone 1157: SDS mixed systems at 10 x CAC

Figure A.28: Guinier and Porod Approximations for the Capstone 1157: SDS mixed systems at 10 x CAC
Cyclohexane induced swelling in FC surfactant micelles

(a) Dynax DX2200 with and without h-cyclohexane

(b) Dynax DX2200 with and without h-cyclohexane Porod Approximations

(c) Capstone 1157 with and without h-cyclohexane

(d) Capstone 1157 with and without h-cyclohexane Porod Approximations

Figure A.29: SANS profiles of Dynax DX2200 and Capstone 1157 with and without addition of h-cyclohexane in D$_2$O at a fixed concentration of 50 mM and Porod approximations of the high Q data. Fitted functions shown as lines. T= 25 °C.
Porod approximations for cyclohexane induced swelling in mixed FC: HC surfactant micelles

In Chapter 7 h-cyclohexane induced swelling was observed in mixed FC: HC surfactant micelles. The Porod approximations associated with the SANS data are presented below for all FC: HC mixed systems at multiple compositions.

Dynax DX1030: SDS

Figure A.30: Porod approximations of Dynax DX1030: h-SDS: h-cyclohexane systems.
Dynax DX2200: SDS

Figure A.31: Porod approximations of Dynax DX2200: h-SDS: h-cyclohexane systems.
Capstone 1157: SDS

(a) Capstone 1157: SDS 0.90: 0.10

(b) Capstone 1157: SDS 0.50: 0.50

(c) Capstone 1157: SDS 0.10: 0.90

Figure A.32: Porod approximations of Capstone 1157: h-SDS: h-cyclohexane systems.
MATLAB code for mixed surface and micelle compositions
Mixed surface compositions

\[ \text{\texttt{symsx}} \]

\[ \text{\texttt{vpasolve}}((x^2) \log(\alpha C_m / x C_0^1) == ((1 - x)^2) \log (1 - \alpha C_m / (1 - x) C_2^0), x) \]

where \( C_1^0, C_2^0 \) and \( C_m \) are the molar concentrations in the solution phase of surfactant 1, surfactant 2 and the mixture, respectively, \( \alpha \) is the mole fraction of surfactant 1.
Mixed micelle compositions

>> symsx
>> vpasolve((x^2) * log(xCMCm/xCMC1) == ((1 - x)^2)log * (1 - xCMCm/(1 - x)CMC2), x)

where $CMC_1$, $CMC_2$ and $CMC_m$ are the critical micelle concentrations of surfactant 1, surfactant 2 and the mixture, respectively, $\alpha$ is the mole fraction of surfactant 1.