

VIBRATIONAL SUM FREQUENCY SPECTROSCOPY INVESTIGATIONS OF
MIXED SURFACTANT SYSTEMS AT THE OIL – WATER INTERFACE

by

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A DISSERTATION

Presented to the Department of Chemistry and Biochemistry
and the Graduate School of the University of Oregon
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy

September 2019

DISSERTATION APPROVAL PAGE

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Title: Vibrational Sum Frequency Spectroscopic Investigations of Mixed Surfactant Systems at the Oil – Water Interface

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DISSERTATION ABSTRACT

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Doctor of Philosophy

Department of Chemistry and Biochemistry

September 2019

Title: Vibrational Sum Frequency Spectroscopy Investigations of Mixed Surfactant Systems at the Oil – Water Interface

The boundary between two immiscible liquids is known to play host to numerous chemical reactions and interactions despite making up a relatively small fraction of the overall system as a whole. Surfactants, the primary classification of the compounds studied herein, are known to preferentially order at an oil-water interface and lower the surface tension between the two fluids. A thorough understanding of surfactant behavior is necessary in order to make the most efficient use of their properties in applications as wide reaching as enhanced drug delivery, waste water treatment, oil spill recovery and oil remediation to name a few.

In this dissertation, vibrational sum frequency spectroscopy, a surface selective vibrational non-linear optical technique, is used to measure selected surfactant vibrational modes in order to obtain a fundamental understanding of surfactant and co-surfactant behavior and interaction at the often difficult to probe buried oil-water interface. Additional surface tensiometry measurements help to shed light on these complex interfacial behaviors and work to aid in the subsequent VSFS analysis.

Interfacial studies specifically designed to identify and characterize the cationic head group behavior of hexadecyltrimethylammonium bromide (CTAB) are presented first. The identification of the head group modes was aided through the use of selectively deuterated CTAB surfactants. The behavior of the CTAB head group was found to be concentration dependent and can act in future studies as a valuable proxy for determining the relative interfacial environment experienced by the surfactant head group. The knowledge acquired from the head groups of CTAB coupled with the alkyl tail behavior now serve as the baseline system and deviations measured due to the presence of an additional surfactant introduced to the system can be properly evaluated.

CTAB mixed with 1-hexanol serves as our model mixed cationic/nonionic system and displays unusual surface synergy. Hexanol is shown to be surface active but disordered at the interface when alone in solution. When CTAB is introduced to the system a reorientation of both surfactants is observed even as hexanol helps to promote additional co-adsorption of CTAB to the interface.

This dissertation includes both published and unpublished co-authored materials.

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ACKNOWLEDGMENTS

I would like to express a deep and heartfelt thank you to everyone, great and small, that has lent me support and strength during this time of my life. First and foremost I would like to thank my adviser Dr. Geraldine Richmond, who has acted as my guide and has been a constant source of support during my years working in her lab at the University of Oregon. You were an inspiration in the way you helped me to think about my research, the scientific community and the world at large.

I would like to thank my fellow lab members, both those still here today and others who have since graduated and moved on to bigger and brighter things. I could not have asked to join a more friendly and welcoming lab environment. Dr. Ellen Robertson acted as my first mentor within the lab. Her initial support and guidance helped to set me on a path to success, and I am forever grateful. Past lab members Nicholas Valley, Sumi Wren, Laura McWilliams, Jenny Hensel, Clive Kittredge, Jet Meitzner and Brandon Schabes helped me in too many ways to enumerate here. Thank you for your willingness to listen to me ramble about my research and adding your own unique insight and perspective. Thank you to my current lab mates Andrew, Bri, Rebecca, Evan, Emma, Konnor and Marc and I wish you all the best of luck as you continue to pursue your own research within the lab. Also thank you to all of my office mates who baked cupcakes for me on my birthday, they were delicious. This has been an amazing lab and I feel honored to call all of you not just my colleagues but friends too.

Furthermore, I would like to thank Dr. Fred Moore from Whitman College, Dr. Larry Scatena from the SLF, and Linas Saulys from Ekspla who were always willing to help troubleshoot and problem solve when I encountered problems on the laser. Your willingness to lend a hand is much appreciated and your insights into any problems encountered saved me from spinning my wheels on many occasions.

To Priscilla and Shiloh, thank you for keeping me sane and calm while simultaneously keeping the lab running smoothly and efficiently. And also for supplying the lab with all the chocolate and candy we would ever need.

To my committee members, thank you for your time, your continued support, all your helpful comments on my research, and your willingness to listen.

Finally, I want to extend my deepest thanks to my friends and family outside of the university. To my best friend Elizabeth, who would spend hours on the phone talking to me and commiserating about grad school when we finally remembered to call each other. I was trying to remember that phrase of ours: “Your Shih Tzu is llama”. To my parents, Tom and Mary Kay, my brother and sister, Adam and Rebecca, my grandparents, and the furry friends, Frexie and Meemur. None of what I have accomplished here would have been possible without your love and support. Thank you for always reminding me that no matter where I go, I will always have a family to come home too. I love you all!

This research was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Condensed Phase and Interfacial Molecular Science Division under award number DE-SC0014278.

For my family.

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