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

by

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A DISSERTATION

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DISSERTATION APPROVAL PAGE

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

This dissertation has been accepted and approved in partial fulfillment of the requirements for the Doctor of Philosophy degree in the Department of Chemistry and Biochemistry by:

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DISSERTATION ABSTRACT

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Doctor of Philosophy

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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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Robertson, E. J.; Carpenter, A. P.; Olsen, C. M.; Ciszewski, R. K.; Richmond, G. L. Metal Ion Induced Adsorption and Ordering of Charged Macromolecules at the Aqueous/Hydrophobic Liquid Interface. *J. Phys. Chem. C* **2014**, 118, 15260-15273.

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For my family.

TABLE OF CONTENTS

Chapter Page

LIST OF FIGURES

Figure Page

Figure Page

LIST OF TABLES

Table Page