Bubbles, Thin Films and Ion Specificity

by

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B.Sc.(Hons) LL.B. (Hons), ANU

A thesis submitted for the degree of Doctor of Philosophy

of

The Australian National University

THE AUSTRALIAN NATIONAL UNIVERSITY

January 2009

Preface

This thesis is an account of research undertaken within the Department of Applied Mathematics, Research School of Physical Sciences and Engineering, within the Australian National University.

This thesis comprises my original work; however some aspects of the work were undertaken in collaboration with others. In Chapter 2, on bubble coalescence and surface tension in mixed electrolytes, the surface tension measurements were carried out by Lehoa Scruton and some of the bubble coalescence data were obtained by Casuarina Dalton. The work in Chapter 5 on thin films was done in the laboratories of, and in collaboration with, colleagues at the University of Queensland Professor Anh Nguyen, Dr Stoyan Karakashev and Mr Phong Nguyen. Mr Phong Nguyen assisted in experimental set-up and instrument use, and Dr Karakashev carried out the theoretical analysis. The bubble terminal rise measurements in Chapter 6 were carried out at the Ian Wark Research Institute, University of South Australia, in collaboration with Mr Luke Parkinson and Professor John Ralston. Luke Parkinson designed and built the bubble rise instrument, and assisted with its use.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university. To the best of my knowledge, it contains no material previously published or written by another person, except where due reference is made in the text.

Christine Henry

Acknowledgements

First, many thanks to my supervisor, Vince Craig, for all the support, help, ideas and editing. Thanks especially for your drive and belief in the work, which kept it going forwards when I had doubts. You were right!

The Department of Applied Maths has been a great place to work, and I thank everyone who made my time here so enjoyable. Tim Sawkins and Anthony Hyde provided technical assistance and advice, and Margo Davies and Jan James kept everything running smoothly. Tim Senden was a great friend, advisor and editor, always willing to offer suggestions. Chiara Neto was an advisor, and helped me get started in research. Toen Castle, my officemate for most of the PhD, was a steady source of friendship, music, unfamiliar words and fun conversation. Many others gave social support in the tearoom and the beer garden – an incomplete list: Anna Carnerup, Drew Evans, Shaun Howard, Steve Hyde, Stu Ramsden, Vanessa Robins, and Adrian Sheppard.

Every conference I went to provided a fresh charge of scientific inspiration and energy, and some great friendships – thanks to people I talked with (and bodysurfed with) at ACSSSC ’06 and ’08, Cancun ’06, ECIS ’07, and all the Kioloa trips. Thanks also to collaborators and to everyone at the University of Melbourne, the University of Queensland and the Ian Wark Research Institute who helped out when I visited. CRC SmartPrint provided scholarship assistance throughout the PhD.

Canberra is my hometown, and the nature, geography and weather are part of my life. As I move on (literally and figuratively) I acknowledge that these years wouldn’t have been the same anywhere else.

My family offered unwavering support. All the Canberra friends provided a life outside uni, especially with the increasingly luxurious coast trips. Paul Barnsley, among other things, fed me a steady supply of comics. I couldn’t have got through without various other cultural and pop-cultural distractions – Salon, The Daily Show, the Colbert Report and Wired all assisted. A PhD involves much more than just science, and I’ve had the freedom over the past four years to meet a lot of cool people, read a lot, learn a lot, and develop my interests in all directions. Thanks to everyone who helped.

Abstract

Bubbles in water are stabilised against coalescence by the addition of salt. The white froth in seawater but not in freshwater is an example of salt-stabilised bubbles. A range of experiments have been carried out to investigate this simple phenomenon, which is not yet understood.

The process of thin film drainage between two colliding bubbles relates to surface science fields including hydrodynamic flow, surface forces, and interfacial rheology. Bubble coalescence inhibition also stands alongside the better known Hofmeister series as an intriguing example of ion specificity: While some electrolytes inhibit coalescence at around 0.1M, others show no effect. The coalescence inhibition of any single electrolyte depends on the combination of cation and anion present, rather than on any single ion.

The surfactant-free inhibition of bubble coalescence has been studied in several systems for the first time, including aqueous mixed electrolyte solutions; solutions of biologically relevant non-electrolytes urea and sugars; and electrolyte solutions in nonaqueous solvents methanol, formamide, propylene carbonate and dimethylsulfoxide. Complementary experimental approaches include studies of terminal rise velocities of single bubbles showing that the gas-solution interface is mobile; and measurement of thin film drainage in inhibiting and non-inhibiting electrolyte solution, using the microinterferometric thin film balance technique.

The consolidation of these experimental approaches shows that inhibiting electrolytes act on the non-equilibrium dynamic processes of thin film drainage and rupture between bubble surfaces – and not via a change in surface forces, or by ion effects on solvent structure. In addition, inhibition is driven by osmotic effects related to solute concentration gradients, and ion charge is not important.

A new model is presented for electrolyte inhibition of bubble coalescence via changes to surface rheology. It is suggested that thin film stabilisation over a lifetime of seconds,

is caused by damping of transient deformations of film surfaces on a sub-millisecond timescale. This reduction in surface deformability retards film drainage and delays film rupture. It is proposed that inhibiting electrolyte solutions show a dilational surface viscosity, which in turn is driven by interfacial concentration gradients. Inhibiting electrolytes have two ions that accumulate at the surface or two ions that are surface-excluded, while non-inhibiting electrolytes have more evenly distributed interfacial solute. Bubble coalescence is for the first time linked through this ion surface partitioning, to the ion specificity observed at biological interfaces and the wider realm of Hofmeister effects.

Publications

Aspects of the work presented in this thesis have been, or will be, presented in the following journal articles.

1. Henry, C. L.; Dalton, C. N.; Scruton, L.; Craig, V. S. J., Ion-specific coalescence of bubbles in mixed electrolyte solutions. *J. Phys. Chem. C* **2007,** 111, 1015-1023.

2. Henry, C. L.; Craig, V. S. J., Ion-specific influence of electrolytes on bubble coalescence in nonaqueous solvents. *Langmuir* **2008,** 24, 7979-7985.

3. Henry, C. L.; Parkinson, L.; Ralston, J. R.; Craig, V. S. J., A mobile gas-water interface in electrolyte solutions. *J. Phys. Chem. C* **2008,** 112, 15094-15097.

4. Craig, V. S. J.; Henry, C. L., Specific ion effects at the air-water interface - experimental studies. In *Specific Ion Effects*, Kunz, W., Ed. World Scientific Publishing: *Submitted for publication.*

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6. Henry, C. L.; Nguyen, P.; Karakashev, S. I.; Nguyen, A. V.; Craig, V. S. J., Electrolyte effects on lifetime, rupture and drainage kinetics of surfactant-free nonaqueous thin films. *In Preparation*.

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8. Henry, C. L.; Craig, V. S. J., Specific ion effects in bubble coalescence: Quantitative determination of α and β and the link to the Hofmeister series. *In Preparation.*

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