ACIS 2005

Australian Colloid & Interface Symposium

Crowne Plaza Hotel
Coogee Beach, Sydney

February 13th – 17th 2005

Programme and Abstracts

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Abstracts

Cover: The Australian map & text graphic is based on an AFM scratch lithography image kindly generated from a supplied JPEG file by Asylum Research, Santa Barbara. The‘ rising sun’ representation shows the small angle X-ray scattering pattern recorded from an inverse hexagonal surfactant mesophase. Courtesy Dr. Patrick Hartley (CSIRO Molecular Science) & Prof. Suresh Bhargava, (RMIT).

Welcome and Introduction

As chair of the organizing committee, it is with great pleasure that I welcome you to the Australian Colloid and Interface symposium 2005. This is the second of our regular biennial national conferences, which now alternate each February with our long running and popular Australian Colloid and Surface Science Student Conferences.

Based on the success of ACIS 2003, we have again selected the Crowne Plaza Coogee as the venue for the conference. We hope that you enjoy the facilities of the hotel, as well as it's proximity to Coogee beach, and the city of Sydney.

The ACIS 2005 program has been designed to span both fundamental and technological aspects of colloid and interface science, as well as to highlight some of the exciting new directions in which our discipline is moving. My thanks go to our theme chairs for their assistance in assembling the scientific program of the symposium.

We also gratefully acknowledge the support of all our sponsors in offering both the financial and in-kind support which has been essential in allowing us to assemble the symposium program. Please peruse the back cover of this abstract book for a complete listing of the sponsors of ACIS 2005.

My special thanks also go to all the members of the symposium organizing committee. It has been my privilege to work with an excellent and motivated team in putting together ACIS 2005.

During the conference, should you have any questions, or if there is anything we can do at all to make your stay more comfortable, please don't hesitate to contact Krista Mentjox at the registration desk.

With best wishes for an enjoyable and informative ACIS 2005

Patrick Hartley
Conference Chair, ACIS 2005
Vice–Chair, Colloid and Surface Science Division
Royal Australian Chemical Institute

Conference Organising Committee

Dr Patrick Hartley, CSIRO Molecular Science (Conference Chair)
Dr Michael James, Bragg Institute (Local Organiser)
Prof. Russell Crawford, Swinburne University of Technology (Conference Website/Social Program Coordinator/Treasurer)
Dr Erica Wanless, University of Newcastle (Conference Secretary)
Dr Gayle Morris, Ian Wark Research Institute, University of South Australia (Sponsorship Co-ordinator)
Dr Peter Harbour, CSIRO Molecular Science (Poster Session Coordinator)
Dr David Yates, Yates Technical Services Pty Ltd (Abstract book)
Dr Ian McKinnon, Monash University
Prof. Greg Warr, University of Sydney
Krista Mentjox, Conference Focus

Theme Chairs

Functional Interfaces & Advanced Coatings	Prof. John Ralston (Ian Wark Research Institute) Dr Simon Edwards (bStrategic)
Scattering in Colloidal Systems	Prof. John White (ANU) Dr Michael James (ANSTO)
Solid Liquid Separations	Prof. Peter Scales (University of Melbourne) Dr Phil Fawell (AJ Parker CRC for Hydrometallurgy)
Nanobiotechnology & Biointerfaces	Prof. Frank Caruso (University of Melbourne) Prof. Hans Griesser (Ian Wark Research Institute)
Food Colloids	Dr Maryann Augustin (Food Science Australia) Dr Ian McKinnon (Monash University)
Emerging Science and General Papers	Assoc. Prof. George Franks (University of Newcastle) Dr Patrick Hartley (CSIRO Molecular Science)

PROGRAM

Sunday, 13th	4:00 – 5:00 pm	Registration (Level One, Crowne Plaza)	
	5:00 – 7:00 pm	Pre-conference mixer (Terrace Rooms, Crowne Plaza)	
Monday, 14th	9:00	Welcome (Oceanic Ballroom, Crowne Plaza)	
	9:15 – 10:15	**The Alexander Lecture**	
		Oceanic Ballroom West	Oceanic Ballroom East
	10:40 – 5:45	**Functional Interfaces**	**Solid Liquid Separation**
	6:00 – 8:00 pm	Poster Session & Drinks	
Tuesday, 15th	9:00 – 11:25	**Functional Interfaces**	**Nanobiotechnology & Biointerfaces**
	11:25 – 4:45	**Scattering in Colloidal Systems**	**Nanobiotechnology & Biointerfaces**
Wednesday, 16th	9:00 – 10:15	**RACI Colloid and Surface Science Division Plenary Lecture**	
	10:40 – 1:00	**Emerging Science**	**Scattering in Colloidal Systems (cont'd)**
	2:00 – 5:05	**Emerging Science**	**Food Colloids**
	7:30 pm	Conference Dinner	
Thursday, 17th	9:00 – 12:30	**Emerging Science**	**Food Colloids**
	12: 30	Conference close & lunch	

Monday 14th, **OCEANIC BALLROOM WEST**

9:00		Welcome
9:15	John Ralston Alexander Lecture	Solid-Liquid Interactions and Functional Surface Wettability
10:15 – 10:40		MORNING TEA

Functional Interfaces & Advanced Coatings

10:40	Takehiko Kitamori (Keynote)	Surface and Interface Control and Effects in Micro-Nano Chemical Systems on Chips
11:20	Karin Jacobs	Thin Films of Complex Fluids: Towards a Control of Flow Properties
11:40	Colin Bain	Surfactant Effects on Hydrodynamic Flows
12:00	Joel De Coninck	Dynamics of Imbibition into a Micro-Pore with a Heterogeneous Surfaces
12:20	Mika Kohonen	Engineered Wettability in Tree Capillaries
12:40	Terry Blake	The Influence of Pore Wettability on the Dynamics of Imbibition and Drainage
1:00 – 2:00		LUNCH
2:00	Paul Jenkins	Coatings in Industrial Applications: The Role of Surface and Adhesive Forces
2:20	Hans Riegler	Wetting Properties, Interfacial Mobility and Aggregation Behaviour of Long Chain Alkanes at Solid/Vapour Interfaces
2:40	Ulrich Jonas	Micro- and Nanostructures by Colloid-Assembly onto Patterned Silane Layers
3:00	Brian Vincent	Liquid Core-Polymer Shell Particles
3:20	Clive Prestidge	Nanoparticles at the Droplet-Water Interface
3:40 – 4:05		AFTERNOON TEA
4:05	James McQuillan	Influence of Adsorbed Water on Phonon and UV-induced IR Absorptions of TiO_2 Photocatalyst Films
4:25	Rachel Caruso	Modification of Structured Titanium Dioxide Materials for Dye-Sensitised Solar Cell Application
4:45	Gayle Morris	Hydrophobised Titania Pigment Surfaces
5:05	Simon Biggs	Self-Assembled Stimulus Responsive Monolayers of Block Copolymer Micelles
5:25	Erica Wanless	The Adsorption Behavioiur of pH Responsive Block Copolymers on Silica: The Effect of Aggregation

6:00 - 8:00 pm **Poster Session (Terrace Rooms)**

Monday 14th **OCEANIC BALLROOM EAST**

9:00		Welcome
9:15	John Ralston (Alexander Lecture)	Solid-Liquid Interactions and Functional Surface Wettability
10:15 – 10:40		MORNING TEA

Solid Liquid Separation

10:40	Lee White (Keynote)	The Future of Compressional Rheology
11:20	Shane Usher	Comparison of Thickener Performance with Model Predictions
11:40	Ates Erk	NMR-Investigation and Dynamic Modelling of the Local Solids Volume Fraction During the Compression of Filter Cakes
12:00	Konika Khan	Effect of Fractal Dimension on Compressive Yield Stress of Flocculated Suspension
12:20	Christian Kugge	Pressure Filtration of Cellulose Fibres
12:40	Aaron Olsen	A Geometric Approach to Collision Efficiency Factors and Optimum Flocculant Dosage
1:00 - 2:00		LUNCH
2:00	Peter Yates	Silica Nano-Particles as Flocculants. Effect of Particle Size on Dewatering Colloidal Alumina
2:20	Mogens Hinge	Synthesis of Poly(N-Isopropylacrylamide-co-Acrylic Acid) Model Compounds for Filtration Experiments
2:40	Anthony Stickland	Non-Traditional Constant Filtration Behaviour
3:00	Andrew Owen	The Effect of Solution Age upon the Activity of Polyacrylamide-Based Flocculants
3:20	George Franks	Stimulant Sensitive Flocculation and Consolidation
3:40 – 4:05		AFTERNOON TEA
4:05	Ateş Erk	Determination of the Shear Yield Stress of Fine Particulate Sediments and Filter Cakes During Solid-Liquid Separation
4:25	Boon Hoong Ong	The Behaviour of Magnetite in the Preparation of Lumen-Loaded Magnetic Fibre
4:45	David Beattie	XPS and TOF-SIMS Study of a Chalcopyrite-Pyrite-Sphalerite Mixture Treated with Xanthate and Sodium Bisulphite
5:05	Peter Harbour	Mesoporous Transition Metal Oxides: Characterisation and Application
5:25	Anh Nguyen	The Role of Colloidal Forces in the Capture of Nano and Submicron Particles by Air Bubbles in Flotation
6:00 - 8:00 pm		**Poster Session (Terrace Rooms)**

Tuesday 15th **OCEANIC BALLROOM WEST**

Functional Interfaces & Advanced Coatings

9:00		Announcements
9:10	David Quere (Keynote)	Wetting of Textured Materials
9:50	Greg Hope	Formation Processes of Copper Sulfide Thin Films
10:10	Rossen Sedev	Wettability and Surface Energetics of Rough Fluoropolymer Surfaces
10:30	Dennis Palms	Crystallisation of Zinc Oxide in the Presence of Functionalised Surfaces
10:50 – 11:05		MORNING TEA
11:05	Alidad Amirfazli	Analysis of Contact Angle Hysteresis for Super Hydrophobic Surfaces

Scattering in Colloidal Systems

11:25	Bob Thomas (Keynote)	The Widespread Occurrence of Bilayer Type Structures at Interfaces as Revealed by Neutron Reflectometry
12:05	Shenda Baker	Neutron Scattering Investigations Nanoporous Films and Substrates For Functional Bilayers
12:25	Greg Warr	Structure of Nonionic Micelles in Molten Ethylammonium Nitrate at Room-Temperature.
12:45	Andrew Nelson	The Structure of the Di-Block Copolymer P2VP-PEO as a Function of pH and Temperature
1:05 - 2:00		LUNCH
2:00	Adam Perriman	Unfolding Free Energy of β-Lactoglobulin at the Air-Water Interface: a Neutron and X-Ray Reflectometry Study.
2:20	Ian Gentle	Probing the Action of Lung Surfactant with Neutron and X-Ray Reflectometry
2:40	Theyencheri Narayanan	High Resolution X-Ray Scattering Studies of Self-Assembled Colloidal Systems
3:00	Stuart Prescott	Understanding the UV-Visible Scattering of Non-Spherical Metallic Nanoparticles
3:20 – 3:45		AFTERNOON TEA
3:45	David Cookson	Colloid and Interface Studies Using SAXS and X-Ray Reflectometry at ChemMatCARS
4:05	Keith McLean	X-Ray and Neutron Reflectivity Studies of Plasma Polymer Coatings
4:25	John Bartlett	The Role of Interparticle Potential in the Morphology of Spray-Dried Powders from Nanoparticle Sols

Tuesday 15th **OCEANIC BALLROOM EAST**

Nanobiotechnology & Biointerfaces

9:00		Announcements
9:10	Steve Granick (Keynote)	Watching Molecules Diffuse at Soft and Hard Surfaces
9:50	William Ducker	Unnatural Proteins for the Control of Surface Forces
10:10	Christophe Barbe	Sol-Gel Particles for Controlled Release Applications
10:30	Ian Larson	Does Everything Depend on Interparticle Forces? A Real Pharmaceutics Problem
10:50 – 11:05		MORNING TEA
11:05	Laurence Meagher	Surface Modification of Biodegradable Polymers Using a Layer by Layer Approach
11:25	Hans Joerg Mathieu (Keynote)	RF-Plasma Surface Activation and Analysis of Polymers Leading to Biomedical Materials at the Nanometer Scale
12:05	Bronwyn Battersby	Massive Biocolloid Libraries for Disarming Deadly Viruses
12:25	Sharon Sagnella	Biomimcry of the Extracellular Matrix for Endothelialization
12:45	Justin Gooding	The Self-Assembly of Aligned Carbon Nanotube Arrays for Communicating with Proteins
1:05 – 2:00		LUNCH
2:00	Felix Meiser	Bioconjugation of Fluorescent Rare-Earth-Doped Nanoparticles
2:20	Jeannette McAlpine	Adsorbed Layer Structure and Crystal Growth Modification
2:40	Jerry Heng	The Surface Properties of Crystalline Pharmaceutical Solids
3:00	Yang Jing	Hydroxamate Ligands and Bacterial Adhesion to Metals
3:20 – 3:45		AFTERNOON TEA
3:45	Kristen Bremmell	Protein Interactions with Modified Biointerfaces
4:05	Yulia Efimova	A Multi-Technique Investigation of Protein Adsorption at a Hydrophilic Solid Interface
4:25	Susanne Giasson	On the Correlation Between Molecular Interactions and Behavior of Polymer-Functionalized Surfaces

Wednesday 16th **OCEANIC BALLROOM WEST**

9:00		Announcements / Introduction
9:15	Alice Gast (RACI Plenary)	Protein Ordering on Lipid Membranes - Biomimetic Phase Transitions
10:15 – 10:40		MORNING TEA

Emerging Science & General Papers

10:40	Fred Lange (Keynote)	Controlling Forces between Particles with Bifunctional Monoalkyl Molecules
11:20	Peter Majewski	Silane-Based Self-Assembled Monolayers for Water Treatment
11:40	Vince Craig	Boundary Slip in Newtonian Liquids: An Experimental Approach
12:00	Paul Fitzgerald	Photo-Polymerisation of Surfactant Structures at Solid Interfaces
12:20	Celesta Fong	Submicron Particles Produced from Urea-Based Liquid Crystalline Phases
12:40	Patrick Spicer	Crystal Comets: Dewetting During Emulsion Crystallization
1:00 – 2:00		LUNCH
2:00	Josef Holzwarth	Aggregation of Block-Copolymers in Aqueous Solutions: Thermodynamics, Structure and Dynamics
2:20	Ben Boyd	Viscous Self-Assembly Phases in Oral Drug Delivery
2:40	Durga Acharya	Phase and Rheological Behavior of Wormlike Micellar Solutions in Mixed Surfactant Systems
3:00	Carlos Rodriguez	Rheology and Dynamics of Micellar Cubic Phases and Related Emulsions
3:20	Michelle Gee	The Spectroscopic Observation of Polymer Film Structure and Chain Dynamics
3:40 – 4:05		AFTERNOON TEA
4:05	Thomas Healy	Charge Regulation in Site Ionization Double Layers Involving Specific Adsorption of Ions
4:25	Hsien Chen Ma	Diffusioosmosis of Electrolyte Solutions along a Charged Plane Wall
4:45	Calum Drummond	High Power Carbon-Based Electrical Double Layer (Super) Capacitors

7:30 pm **Conference Dinner**

Wednesday 16th **OCEANIC BALLROOM EAST**

9:00		Announcements / Introduction
9:15	Alice Gast (RACI Plenary)	Protein Ordering on Lipid Membranes - Biomimetic Phase Transitions
10:15 – 10:40		MORNING TEA

Scattering in Colloidal Systems

10:40	Eric Kaler (Keynote)	Polymerization in Complex Fluids
11:20	Andrew Jackson	Nanoscale Structure of Milk: Milk Protein Aggregation
11:40	Stephen Holt	Self Assembly of Membrane Protein Arrays at the Solid/Liquid Interface
12:00	Karen Edler	Formation Mechanisms in Surfactant-Templated Silicates
12:20	Ronny Vavrin	Time Resolved Neutron and Light Scattering on Colloidal Gels
12:40	Mark Henderson	An X-Ray Reflectivity Study of Evaporation Induced Self-Assembled Titania-Based Films
1:00 – 2:00		LUNCH

Food Colloids

2:00	Nissim Garti (Keynote)	Designer Microemulsions for the Food Industry
2:40	Peter Wilde	The Influence of Interfacial Mechanics on the Creaming and Rheology of Oil-in-Water Emulsions
3:00	Timothy Wooster	Interfacial Rheology as a Technique for Probing Food Emulsion Stability
3:20	Jenny Rusli	Use of Protein-Sugar Conjugates for Microencapsulation of Oils
3:40 – 4:05		AFTERNOON TEA
4:05	James Beattie	The Charge on the Pristine Oil/Water Interface
4:25	Nirmesh Jain	Ostwald Ripening of Water-In-Oil Emulsions
4:45	Alex Djerdjev	Self-Induced Depletion Flocculation of a Polydisperse O/W Emulsion

7:30 pm **Conference Dinner**

Thursday 17th **OCEANIC BALLROOM WEST**

Emerging Science & General Papers

9:00		Announcements
9:10	Hans-Jürgen Butt (Keynote)	Atomic Force Microscopy: A Routine Tool or Emerging Technique?
9:50	Raymond Dagastine	AFM Measurements of Hydrodynamic Forces between Deformable Drops: Experiments
10:10	Roger Horn	Observations of Interesting Hydrodynamic Effects on a Fluid Drop Close To a Solid Wall
10:30	Derek Chan	Prediction of Interesting Hydrodynamic Effects on a Fluid Drop Close To a Solid Wall
10:50 – 11:10		MORNING TEA
11:10	Franz Grieser	Cavitation Bubble Temperature in Aqueous Solutions Containing Surface Active Solutes
11:30	Muthupandian Ashokkumar	The Effect of Surface-Active Solutes on Bubble Coalescence in the Presence of Ultrasound
11:50	Shannon Notley	Direct Measurement of Surface Forces between Regenerated Cellulose Surfaces in an Aqueous Environment
12:10	Yang Gan	Surface Hydroxyl Groups on Sapphire (α-$\mathrm{Al_2O_3}$) (0001) in Water: an Atomic Force Microscopy Study
12:30		CLOSE & LUNCH

Thursday 17th **OCEANIC BALLROOM EAST**

Food Colloids

9:00		Announcements
9:10	Peter Wilde (Keynote)	Food Colloids: Bridging the Gap between Fundamental Research and Complex Application
9:50	John Carver	Milk Casein Proteins As Molecular Chaperones and Stabilisers of Protein Food Components
10:10	Ian McKinnon	Solubilised Caseins and their Effect on the Surface Properties, Foamability and Foam Stability of Skim Milk
10:30	Iko Burgar	Advanced NMR Characterisation of Microencapsulated Food Products
10:50 – 11:10		MORNING TEA
11:10	Shantha Kosaraju	Liposomal Delivery Systems for Nutraceutical Applications
11:30	Raymond Mawson	Applications of Ultrasound in the Food Industry
11:50	Cheryl Chung	Physical and Oxidative Stability of Tuna Oil-in-Water Emulsions Stabilised by Whey and Soy Proteins
12:10	Raymond Mawson	Radical Chemistry During the Ultrasonic Treatment of Food Materials
12:30		CLOSE & LUNCH

POSTER PRESENTATIONS (Terrace Rooms)

6:00 – 8:00 pm Monday 14th

SPONSORED BY CSIRO MOLECULAR SCIENCE

Functional Interfaces & Advanced Coating

1	Alidad Amirfazli	Development of a Novel Instrument Combining Fluorescent Microscopy and Surface Tension Measurement Tools for Liquid-Liquid Interfaces
2	Alidad Amirfazli	A Novel Methodology using Laser to Pattern Self-Assembled Monolayer Surfaces
3	Rob Atkin	Core-Shell Particles with pH-responsive Vinylpyridine Shells from Silica-Microgel Heteroaggregates
4	Robert Chan	Structure of Polymerised Surfactant Films at Solid/Solution Interfaces
5	Scott Dickie	Distinguishing between Surface Hydroxyl Groups of Boehmite Using ATR-IR. (presented by A/Prof. Jim McQuillan)
6	Daniel Eldridge	Divalent and Trivalent Metal Ion Adsorption onto Inorganic Substrates
7	Drew Evans	Measurement of Film Stress using a Cantilever Bending Technique
8	Saeed Farrokhpay	Titania Pigment Distribution in Dry Water-Based Paint Films in the Presence of Polymeric Dispersants (presented by Dr Gayle Morris)
9	George Ganakas	Thiol-Based Plasma Polymer Coatings for Bioscience Applications
10	Nicola Lake	A Novel Model of DNA Bases
11	Ben Muir	Novel Surface Coatings for Array Based Applications
12	Chiara Neto	Satellite Holes Formation in Thin Polymer Films
13	Christophe Schatz	An Investigation of pH-Responsive Diblock Copolymer Micelles Adsorbed on Silica Particles by Confocal Microscopy
14	Elvira Tjipto	Effect of pH on the Assembly of Weak Polyelectrolyte Multilayer Films
15	Lucy Wang	Investigation of Self-Assembled Monolayers on Mercury Using a Surface Force Apparatus (SFA)

Nanobiotechnology & Biointerfaces

16	Gordon Bewsell	Understanding Metal Ion Adsorption onto Biological Substrates through Surface Characterisation
17	Till Böcking	Covalent Modification of Flat Single Crystal and Porous Silicon Surfaces for Biosensor Applications
18	Adam Feiler	A Study of the Biolubricating Properties of Mucin
19	Xin Gao	On the Chemical Control of the Poly(dimethylsiloxane) Interface
20	Thomas Kaasgaard	Phase Behavior and Small-Scale Structure of One- and Two-Component Phosphatidylcholine Lipid Bilayers
21	Gwen Lawrie	Self-Assembly and Surface Modification of Multilayer Membranes for Cell Microencapsulation.
22	Minoo Moghaddam	A Novel Class of Synthetic Cationic Lipid Vectors Facilitating the Efficient Delivery of Genes and Proteins
23	Anthony Quinn	Kinetic and Nanostructural Analysis of Protein Adsorption on Tailored Substrates
24	Dallas Warren	Spontaneous Aggregation and Dynamics of Mixed Bile Salt / Phospholipid Micelles and Lipid Formulations Using Molecular Dynamics Simulations

Solid Liquid Separation

25	Linh Tuyet Chiem	Probing Polymer-mineral Interactions with Vibrational Spectroscopy
26	Glenn McCann	AFM Study of Silica-Silica Interaction in Dodecylamine Solutions
27	David Verrelli	The Effect of Coagulant Dose and pH upon Drinking Water Sludge Dewaterability
28	Pirre Yla-Maihaniemi	A Novel Method for Investigating Solid-liquid Interactions: Inverse Liquid Chromatography

Emerging Science & General Papers

29	Miguel Araos	Self-Assembly of Nonionic Surfactants into Lyotropic Liquid Crystals in Ethylammonium Nitrate, a Room-Temperature Ionic Liquid
30	Ainul Aziz	Network Deformation of Coagulated Colloidal Suspensions
31	Annabelle Blom	Growth of Adsorbed Quaternary Ammonium Surfactant Films on Mica Observed Using AFM
32	Annabelle Blom	Temperature-Dependence of Adsorbed Layer Structure of nonionic Surfactants on Silica
33	Tam Chau	Non-DLVO Behaviour at the Oil-Water Interface: a Specific Ion Effect
34	Jarred Clasohm	Investigating Slip Boundary Conditions With Squeeze Film Measurements in the SFA and AFM
35	William Ducker	Evanescent Wave AFM
36	Simon Ferguson	The Influence of Ionic Liquids on Emulsion Systems
37	Tamar Greaves	Mössbauer Spectroscopy Investigation of the Electrochemical Behavior of Nontronite- and Montmorillonite-Modified Carbon Electrodes
38	Jason Kilpatrick	Nanorheology Using a Modified Commercial Atomic Force Microscope
39	Rogerio Manica	AFM Measurements of Hydrodynamic Forces Between Deformable Drops: Theory
40	Anastasios Polyzos	Metallomicelles as Catalysts for Ester Hydrolysis
41	Ignacio Moreno-Villoslada	The Importance of Aromatic Rings on the Formation of Water-Soluble Polymer - Low Molecular-Weight Molecule Complexes
42	Kathryn Topp	Oligomeric Surfactants Through Polymerisation
43	Ivan Vakarelski	Silica Surfaces Nanotribology in Aqueous Solutions

Scattering in Colloidal Systems

44	Krisztian Baranyai	Hydrocarbon Solvency and Reverse Micelle Formation in Microemulsions
45	Liliana de Campo	Reversible Phase Transitions of Nanostructured Lipid Systems in Confined Geometry
46	Elliot Gilbert	QUOKKA: The Small Angle Neutron Scattering Instrument at the Australian Replacement Research Reactor
47	Elliot Gilbert	What Do You Want to Know About Nanostructure ?
48	Tracey Hanley	SANS Study of Novel Dendritic Polymers Prepared Using Raft Polymerization
49	Michael James	When Thin is Sexy – The Future of Neutron Reflectometry in Australia

A.E. Alexander Lecture

SOLID-LIQUID INTERACTIONS AND FUNCTIONAL SURFACE WETTABILITY

John Ralston

Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus,
Mawson Lakes, Adelaide, South Australia, 5095

John.Ralston@unisa.edu.au

The interaction between a liquid and a solid surface is the key to understanding wetting phenomena, irrespective of whether they are static or dynamic. A very large number of natural and industrial processes rely on the delicate manipulation of this interaction. Controlled wetting is of central importance in microfluidics, mineral flotation, high speed coating, electronic display technologies, oil recovery, lubrication and plant protection.

At the molecular level, one can alter the distribution and charge of surface groups on functional surfaces, vary the number of hydrogen bonds, change molecular configuration, perform chemical grafts etc. External stimuli such as light, electric potential, heat and magnetism can lead to subtle control of wettability. Physical and chemical heterogeneity can have a major impact upon wettability, thus the clever design of surface architecture is a key element in controlling both wettability and liquid movement. When a liquid moves over a solid surface, displacing air or another liquid, the primary routes of energy dissipation must be identified if the mechanism is to be understood. Molecular events play a dominant role here, as shown through experiment, theory and simulation.

Keynote Lecture

SPONSORED BY FUTURE MATERIALS

SURFACE AND INTERFACE CONTROL AND EFFECTS IN MICRO-NANO CHEMICAL SYSTEMS ON CHIP

Takehiko Kitamori

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

kitamori@icl.t.u-tokyo.ac.jp

Micro-nano chemical and bio systems on microchips are expected as promising tools for basic sciences and industrial applications. Our research groups have integrated various kinds of micro systems, such as analysis, diagnosis, synthesis, combinatorial, cell biological, bioassay, electrochemical, physico-chemical, and nano-fluidic systems onto microchips. And their superior characteristics and performances have been proved.

All of these systems are based on our original methodologies for micro integration.

1) Micro unit operations and (MUO) and continuous flow chemical processing (CFCP)
2) Thermal lens microscope (TLM)
3) Silane coupled radical polymerization (SCRP) for surface modification

The first ones MUO and CFCP are the generalized methods for design Unit operations such as mixing, reaction, extraction and others in micro space are developed by using micro channels, and they are able to be combined each others freely for constructing total chemical processes. The second item TLM is an ultra sensitive detection method at ymol (10^{-24} mol) level determination of non-fluorescent molecules. TLM is a kind of optical absorption spectrometry in micro space based on the thermal lens effect. The last one is surface modification method.

These methods have enabled integration of any kinds of chemical and bio systems on microchips almost freely, while the conventional electrophoresis chips are limited in application range. We have integrated over one hundred kinds of systems on chips, and their applications ranged from pure sciences to practical applications.

Especially, specific interface area (S/V) is very large in micro channels, hence chemical modification their inner surface is very important for controlling and functionalizing the surface. The surface have been modified by many kind of functional molecules such as catalysts, proteins, affinity modifiers, sleeve controller and so on by our SCRP method. Typical examples of the surface modifications and their application to clinical analysis, cell bioassays, microchip chemical plant, will be introduced in the lecture. And finally, we have observed the change of material properties of water in nano-channels, and the results will be also introduced.

THIN FILMS OF COMPLEX FLUIDS: TOWARDS A CONTROL OF FLOW PROPERTIES

Karin Jacobs

Saarland University, Saarbrücken, Postfach 15 11 50, D-66041 Saarbrücken, Germany

Liquids confined to small scales can exhibit peculiar properties that can be of special interest for technical applications, e.g. for industrial coatings or lab-on-chip devices. For instance, if the layer is only a few nm thick, hydrodynamic instabilities can occur that lead to a bead-off of the coating. We will present experiments on thin (2nm-300nm) macromolecular films dewetting solid substrates, the wettability of which can be varied [1-4]. With the help of the effective interface potential, which we determined for our experimental systems, we discuss the interplay of short- and longrange forces and the possibilities for influencing the stability of the liquid layer. Also dynamic properties can be accessed: The viscosity, for instance, of a polystyrene film of nm thickness is reduced by roughly six orders of magnitude as compared to the bulk liquid value, enabling a higher through-put of liquids at small scales.

[1] K. Jacobs, R. Seemann, G. Schatz, and S. Herminghaus, Langmuir 14 (1998) 4961.
[2] R. Seemann, S. Herminghaus and K. Jacobs, Phys. Rev. Lett. 87 (2001) 196101.
[3] S. Herminghaus, K. Jacobs and R. Seemann, Eur. Phys. J. E 12 (2003) 101.
[4] J. Becker et al., Nature Materials 2 (2003) 59.

SURFACTANT EFFECTS ON HYDRODYNAMIC FLOWS

Colin D. Bain

Department of Chemistry, University of Oxford, U.K.

Rapidly expanding liquid surfaces occur frequently in the deposition of coatings, for example, where a sheet of liquid strikes a moving web in a curtain coater, in the formation of droplets in an inkjet print head, or in the spreading of a liquid drop on a solid substrate. The adsorption of surfactants at the liquid–air interface can affect the hydrodynamics in two ways. First, surfactants reduce the surface tension and increase the Gibbs elasticity of the surface. The dynamic surface tension controls the Laplace pressure in the fluid and is a key parameter in the break-up of jets into drops. Second, non-uniformities in the surfactant distribution lead to surface tension gradients that drive bulk hydrodynamic flows tangential to the surface (Marangoni effects). An understanding of these surfactant effects is beneficial for the control of coating processes and the production of uniform films.

The study of surfactant effects on short timescales (<1 s) is greatly facilitated by steady-state experiments involving the continuous expansion of a liquid surface. Two such platforms have been adopted at Oxford: the overflowing cylinder (OFC) and the liquid jet. The design and hydrodynamics of the OFC [1] and the axisymmetric jet [2] have been well-described in the literature. The main experimental probes used to study the flowing liquid surface – ellipsometry [1(a),2(a)], laser Doppler scattering [1(a),2(a)] neutron reflection [3], and infrared spectroscopy [4] – will be briefly explained. Three applications will then be described:

- Marangoni effects in an OFC
- Effect of micelles on adsorption
- Mixed surfactant systems

[1] (a) Manning-Benson. S.; Bain, C. D.; Darton, R. C. *J. Colloid Interface Sci.* **1997**, *189*, 109;
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DYNAMICS OF IMBIBITION INTO A MICRO-PORE WITH A HETEROGENEOUS SURFACE

G. Martic, T.D. Blake and J. De Coninck

Centre for Research in Molecular Modelling, Materia Nova / University of Mons-Hainaut,
Parc Initialis, 7000 Mons, Belgium

We use large-scale molecular dynamics simulations to study the dynamics of liquid penetration into a cylindrical pore having a randomly heterogeneous surface comprising areas of different wettability. Our results show that the equilibrium contact angle in the heterogeneous pore is well described by Cassie's law. As in the case of the uniform pore studied previously, the dynamics of penetration can be described by the Lucas-Washburn equation corrected to include the effect of a dynamic contact angle. The dissipation at the three-phase line, which gives rise to the dynamic contact angle, may be characterized in terms of a friction coefficient. Interestingly, the wetting-line friction on the heterogeneous surface also turns out to be a linear function of the fractional concentration of the areas of different wettability analogous to Cassie's law.

ENGINEERED WETTABILITY IN TREE CAPILLARIES

Mika M. Kohonen and Vincent S. J. Craig

Department of Applied Mathematics, Research School of Physical Sciences and Engineering,
Australian National University, Canberra ACT 0200, Australia

mika.kohonen@anu.edu.au

Nature has evolved the ultimate microfluidic system to enable trees to transport water to heights of up to 100 metres without using a pump. A complex network of capillaries interconnected by safety valves enables trees to transport water and to survive the onslaught of drought and freezing temperatures. Despite almost a century of research our understanding of this fascinating system remains incomplete. In particular, there is a clear gap in our knowledge concerning the wettability of the conducting pipes and safety valves, with numerous contradictory statements appearing in the literature.

In this presentation I will describe our observations on the wettability of tree capillaries, focussing on what appears to be a beautiful example of natural engineering of surface wettability. Decades of anatomical studies have revealed that trees growing in dry and/or cold climates often have various forms of geometrical sculpturing on the internal surfaces of the conducting pipes. The function of such structuring has long been the subject of speculation, and many of the current ideas are plainly in error. We argue that the function of such structures is to increase the wettability of the capillaries, an effect which can be considered to be the inverse of the well-known Lotus effect.

THE INFLUENCE OF PORE WETTABILITY ON THE DYNAMICS OF IMBIBITION AND DRAINAGE

T.D. Blake and J. De Coninck

Centre for Research in Molecular Modelling, University of Mons-Hainaut, Parc Initialis,
7000 Mons, Belgium

Large-scale molecular dynamics simulations are increasingly being used to study the details of wetting processes. Using such techniques, we have shown that the classical Lucas-Washburn equation commonly employed to describe capillary imbibition and drainage should be modified to include dynamic contact-angle effects. In addition, we have confirmed that these effects can be accounted for using the molecular-kinetic theory of dynamic wetting. In a further publication we presented theoretical arguments and experimental evidence that the velocity of wetting depends on the intrinsic wettability of the solid surface in such a way that there exists an optimum contact angle at which the velocity of wetting is a maximum. Here, we combine these ideas to demonstrate how the maximum speeds of capillary imbibition and drainage are affected both by the pore wettability and the pressures used to drive capillary displacement. In particular, we introduce the concept of dynamic wetting transitions (DWT) and discuss how these limit displacement efficiency and can be manipulated by controlling pore wettability. DWT occur when the dynamic contact angle approaches its limiting values of 180° and zero. Following a transition, the displaced phase is entrained on the wall of the capillary and may reorganise to form a train of liquid indices that resist further liquid displacement. A better understanding of these effects is likely to be beneficial in optimising the performance of many capillary processes such as those involved in oil recovery.

COATINGS IN INDUSTRIAL APPLICATIONS: THE ROLE OF SURFACE AND ADHESION FORCES

Paul Jenkins

Unilever R&D Port Sunlight, Quarry Road East, Bebington, Wirral, CH63 3JW. UK

paul.jenkins@unilever.com

Many commercial applications of colloidal dispersions are encountered in the creation of functional coatings on substrate surfaces. Typical examples include paints, photographic films and cosmetics. In many of these applications, the dispersion is designed to become 'controllably unstable' during use in order that the coating will deposit onto the substrate of relevance. In essence, the surface and adhesional forces in the system must be optimised.

This is also true in other industrial practices such as mineral processing, silicone wafer manufacture and fabric washing. In these applications, surface and adhesional forces must be also be controlled in order to succesfully remove particles from the substrate of interest – the aim is to render the particles colloidally stable with respect to the substrate to which they are adhered. Examples include removing gangue particles from valuable minerals, contamination from wafers and soils from clothes.

In this paper, I will describe fundamental studies that have been performed to understand the mechanisms underlying some of the applications alluded to above. Amongst the techniques that have been applied are Atomic Force Microscopy, Rheology, Infra-red Spectroscopy, ToFSIMS, Electrophoresis and Optical Reflectometry. The fundamental studies will be placed in the context of commercial examples.

WETTING PROPERTIES, INTERFACIAL MOBILITY AND AGGREGATION BEHAVIOUR OF LONG CHAIN ALKANES AT SOLID/VAPOUR INTERFACES

Paul Lazar and Hans Riegler

Max-Planck-Institut for Colloid und Interface Science, D-14476 Potsdam/Golm, Germany

Hans.Riegler@mpikg.mpg.de

Molecularly thin coverages of long chain n-alkanes (e.g. $C_{30}H_{62}$) on solid surfaces undergo a series of wetting and ordering transitions. They are excellent model systems to study the physics of wetting, 2-dimensional ordering and molecular transport under confinement.

For instance, with sufficient surface coverage, at undercooling, partially wetting droplets of alkane melt nurture the radial growth of concentric, solid circular multilayer terraces ("sunny-side-up configuration" with the egg white = terraces and the yolk = centre droplet). The temperature behaviour of this terrace growth is quite unique: its speed decreases with increasing temperature, it stops at the melting point, and above the melting point it is reversed (shrinking terrace radius)! The time evolution of the terrace radii and the droplet volumes shows the exchange of alkane molecules between terrace and droplet in a diffusive-like flow ($\approx t^{0.5}$). We propose a molecularly thin alkane film on top of the terraces. The direction and strength of the flow through this film is given by the chemical potential gradient between droplet perimeter and terrace edge. Thus, the flow is approximately linearly proportional to the sample temperature (no thermal gradient!). Thus, for the first time under isothermal conditions, we present the controlled, even reversible, two-dimensional, diffusive flow through a precursor-like film due to the decoupling of transport and driving potential.

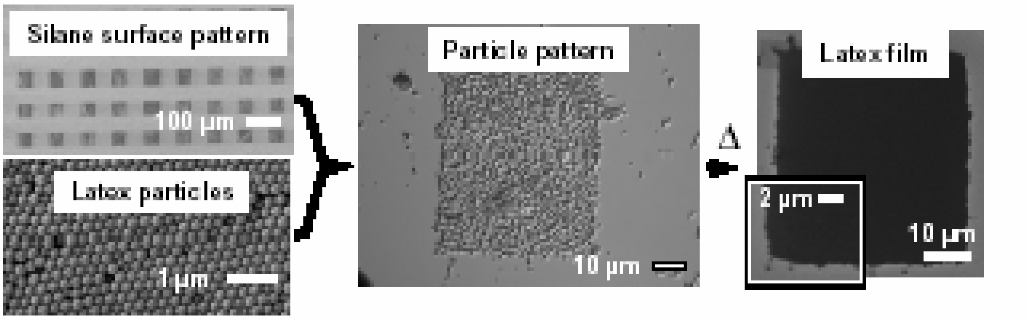
MICRO- AND NANOSTRUCTURES BY COLLOID-ASSEMBLY ONTO PATTERNEDSILANE LAYERS

Christian Krüger, Arancha del Campo, Charles-André Fustin, Diana Boos, Ulrich Jonas

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

jonas@mpip-mainz.mpg.de

Nanostructured surfaces are of high technological interest and are utilized in self-cleaning surfaces, anti-reflecting surfaces, adhesion control (protein resistance and anti-fouling), chemo- and biosensors, optical filters, electromechanical devices, microfluidics and play an important role in separation technology. Colloid particles in the size range from several nm up to micrometers are readily available from a large variety of materials (inorganic, organic, from insulator to metals) and can be adsorbed onto substrates to generate nanostructured surfaces. For many of the described applications lateral patterning of the adsorption sites for the colloid particles is necessary. Our work focuses at the site-specific assembly of colloidal particles onto laterally patterned silane layers on silicon, quartz, and glass substrates, which are generated by a combination of photolithographic patterning with the silanization process. Furthermore, direct surface patterning of photoprotected silane monolayers can be achieved with newly synthesized silanes. Particular emphasis has been placed on studying the effect of different surface functionalities on the colloidal self-assembly process.



The figure above shows an example of negatively charged polybutylmethacrylate particles which are selectively adsorbed onto a positively charged ammoniumsilane pattern surrounded by an inert hydrocarbon monolayer. In suspension the particles form a submonolayer due to a balance of attractive and repulsive Coulomb interaction. Depending on the drying conditions, like solvent evaporation speed and local particle concentration, particle submonolayers or ordered multilayers can be obtained due to capillary forces at the drying front. This method allows the preparation of laterally structured colloid crystals with an optical stop band as a consequence of the lattice periodicity. Thin structured polymer films are obtained from assemblies of fusible latex particles by annealing at elevated temperature. Based on their complex properties such ultrathin film structures might find potential applications as optical elements in photonic devices, as waveguides, as active elements in sensors, or as microstructured adhesives.

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LIQUID CORE - POLYMER SHELL PARTICLES

Rob Atkin, Peter Dowding, Andrew Loxley and Brian Vincent

School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK

brian.vincent@bris.ac.uk

Core-shell particles (microcapsules), dispersed in water, with liquid cores and polymer shells of controlled thickness and morphology, are excellent candidates for the controlled release of "active" molecules, such as pharmaceuticals, agrochemicals, perfumes, flavors, dyes, inks, etc. Various methodologies have been reported for making such capsules. In this paper we will discuss a novel method for the preparation and characterization of a variety of different microcapsules, including ones with oil cores and others with aqueous cores, depending on the nature of the active material to be released. The general method used for their preparation is based on *intern*al phase separation of the polymer wall from the droplets of either an oil/water emulsion or a water/oil emulsion depending on the nature of the internal phase required. For the aqueous core particles, the external oil phase is replaced (after shell formation) by an aqueous phase. Control of the various interfacial tensions is critical in obtaining particles with a shell (rather than an "acorn" structure"). The size of the microcapsules, and the polymer wall thickness and permeability can be readily controlled using this method. Characterization of the microcapsules is mainly based on light scattering, optical microscopy and SEM (of the broken microcapsules).

Some data will be presented for release rates and amounts of model active materials, and how this is affected by changes in the various system parameters, such as the size of the liquid core, the polymer shell thickness, and the nature of the polymer shell.

NANOPARTICLES AT THE DROPLET-WATER INTERFACE

Spomenka Simovic and Clive Prestidge

Ian Wark Research Institute, University of South Australia, Mawson Lakes 5095, Australia

clive.prestidge@unisa.edu.au

The interfacial properties of oil droplets, e.g. structure, stability and molecular transport properties may be controlled by the presence of adsorbed nanoparticle layers. Nanoparticle stabilized fluid structures have many potential applications, e.g. as controlled release delivery systems for pharmaceuticals and neutraceuticals, and in micro- and nano- fluidics. We report on the adsorption behavior of 50nm silica particles at the polydimethylsiloxane droplet-water interface and the influence of particle hydrophobicity, droplet deformability and the surface electrical properties of both particles and droplets. The relationships between the adsorbed nanoparticle layer structure, droplet stability and the oil-to-water transport have also been elucidated.

Fully hydrated silica nanoparticles adsorb with low affinity, reaching a maximum surface coverage that corresponds to a close packed monolayer, based on the effective particle radius and controlled by the salt concentration. Hydrophilic nanoparticle layers introduce a barrier to coalescence of ~1kT, only slightly reduce the coalescence kinetics and form kinetically unstable networks at high salt concentrations. Furthermore, they have a limited influence on the release kinetics of di-butyl phthalate a model lipophilic molecule from with the droplets.

Chemically hydrophobised silica nanoparticles, over a wide range of contact angles (25 to $>90^o$), adsorb at the droplet interface with high affinity and to multilayer coverages. Adsorption isotherms are pH and salt dependent, but weakly contact angle dependent. Adsorption affinity is significantly reduced by droplet cross linking; this relates to differences in the interfacial layer structure and penetrability. The highly structured and rigid adsorbed layers significantly reduce coalescence kinetics. At or above monolayer coverage, stable flocculated networks of droplets form, whereas at sub-monolayer coverages, limited coalescence is observed and interfacial saturation restricts the droplet size increase. For interfacial coverages in the range 0.7 to 1.0, “mesophase-like” microstructures form; the physical form and stability of which depends on the contact angle. Layers of hydrophobic silica nanoparticle are semipermeable to di-butyl phthalate and significant sustained release properties can be engineered. Activation energies for release are ~ 600 $kJmol^{-1}$ and ten times higher than for polymeric barriers.

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INFLUENCE OF ADSORBED WATER ON PHONON AND UV-INDUCED IR ABSORPTIONS OF TIO_2 PHOTOCATALYST FILMS

David S. Warren and A. James McQuillan

Department of Chemistry, University of Otago, P. O Box 56, Dunedin, New Zealand

jmcquillan@alkali.otago.ac.nz

The detailed mechanisms of TiO_2 interfacial photocatalytic processes have still to be established. Adsorbed species such as water, oxygen and peroxide are expected to affect the kinetics but their influences have not yet been clearly determined. During the process of photocatalysis, photogenerated electrons and holes are believed to be trapped at surface Ti^{4+}-OH centres forming Ti^{3+} sites and surface OH radicals respectively.

$$e^- + Ti^{4+}OH \rightarrow Ti^{3+}OH$$

$$h^+ + Ti^{4+}OH \rightarrow Ti^{4+}OH^{\cdot}$$

The role of water associated with these traps sites is the source of considerable interest. Infrared absorption spectroscopy has been widely used for surface studies but there have been few *in situ* IR studies of TiO_2-related surface species during photocatalytic processes.

Ekström and McQuillan[1] used attenuated total reflection infrared (ATR-IR) spectroscopy to monitor the photoconversion of adsorbed glyoxalate to adsorbed oxalate on P25 TiO_2 under aqueous solution. They observed with UV irradiation a broad asymmetric absorption peaking at 878 cm^{-1} and attributed it to TiO_2 surface structures or to surface peroxo species. Nakamura et al [2,3] also used ATR-IR spectroscopy to identify peroxides as intermediate species of both the oxygen reduction reaction and the oxygen photoevolution reaction.on nanocrystalline TiO_2 samples in aqueous solution. They also observed UV-induced asymmetric peaks in the 800-950 cm^{-1} region. Yamakata et al[4] have used time-resolved IR spectroscopy to observe a similar absorption extending from 3000 to 900 cm^{-1}. The attribution of this absorption has been variously to free carriers or to shallow trap electrons.

We have used ATR-IR spectroscopy to study the influence of adsorbed water and 365 nm irradiation on the IR absorptions of Degussa P25 photocatalyst films. Removal of adsorbed water results in the appearance of sharp absorptions at 828, 745, and 685 cm^{-1} attributed to TiO_2 surface phonons. UV irradiation of dry TiO_2 results in a broad IR absorption which increases in absorbance towards lower wavenumbers, peaks at 880 cm^{-1}, and then drops sharply. The broad absorption generated by the UV light has been assigned to excitation of shallow trap electrons to the conduction band with an excitation energy of ~0.1 eV.

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MODIFICATION OF STRUCTURED TITANIUM DIOXIDE MATERIALS FOR DYE-SENSITISED SOLAR CELL APPLICATION

Timothy R. Carter[1], David B. Menzies[2] and Rachel A. Caruso[1]

1 PFPC, School of Chemistry, The University of Melbourne, Melbourne 3010
2 School of Physics and Materials Engineering, Monash University, Melbourne 3800

rcaruso@unimelb.edu.au

Titanium dioxide is a non-toxic semiconductor that is used in a range of areas including photovoltaics and photocatalysis. Research is being conducted to determine methods in which control of morphology and variation in composition can be used to improve the performance of titanium dioxide materials in such applications.

In this study, sol-gel synthesis combined with a templating technique was chosen as the method in which the titania was fabricated. Variations in the synthesis route have been studied to determine the overall effect these alterations have on the morphology and performance of the titanium dioxide. For example, low concentrations of zirconia and silica precursors were mixed with the titanium(IV) isopropoxide, or the amorphous titania and calcined titania were post-treated by immersing the structures in dilute solutions of a range of precursors; including precursors for titanium dioxide, zirconia and silica. The final materials have been examined by using electron microscopy, X-ray diffraction and gas sorption to determine accessible surface area. The materials have also been incorporated and tested as working electrodes in dye-sensitised solar cells. The photovoltaic properties of the materials will be presented along with a summary of the morphology and composition changes.

HYDROPHOBISED TITANIA PIGMENT SURFACES

Eric Capelle, Leanne Britcher and Gayle Morris

Ian Wark Research Institute, ARC Special Research Centre for Particle and Material Interfaces, University of South Australia, Mawson Lakes, SA 5095, Australia.

Gayle.Morris@unisa.edu.au

Pigment surfaces are chemical modified using coupling agents to render the surface hydrophobic for dispersion into plastic matrices. This enables the incorporated titania pigment to provide opacity to plastic materials. Incomplete dispersion of pigments causes uneven colouring and the optimum effects of the pigment are not fully utilised. Organic compounds such as polyols, silicone oils and fatty acids have been used industrially for this purpose. Our previous studies have shown that octadecyl fatty acid derivatives extensively and effectively hydrophobise the pigment particle surface although the strength of the surface interaction is limited. Incorporating the strong interaction phosphates have for metal oxide surfaces, this investigation involves the utilisation of phosphate functionalised octadecyl.

The level of interaction between octadecyl phosphonic acid and the pigment surface is reported as a function of octadecyl phosphonic acid concentration and solvent conditions. The variation in surface interactions correlate with the change in the pigment surface properties, determined from adsorption isotherms and surface tension measurements. Adsorption studies have utilised direct thermal gravimetric analysis (TGA) and FTIR methods. Information concerning the conformation of the phosphonic acid at the pigment surface and the nature of the interaction have also been obtained with TGA and FTIR.

SELF-ASSEMBLED STIMULUS RESPONSIVE MONOLAYERS OF BLOCK COPOLYMER MICELLES

Simon Biggs[1], Grant Webber[1], Steven P. Armes[3] and Erica J. Wanless[2]

1. Institute of Particle Science and Engineering, School of Process, Environmental and Materials Engineering, University of Leeds, Leeds LS2 9JT.
2. Chemistry, School of Environment and Life Science, The University of Newcastle, Callaghan, NSW 2308, Australia.
3. Department of Chemistry, Dainton Building, Brook Hill, Sheffield,S3 7HF, UK

s.r.biggs@leeds.ac.uk

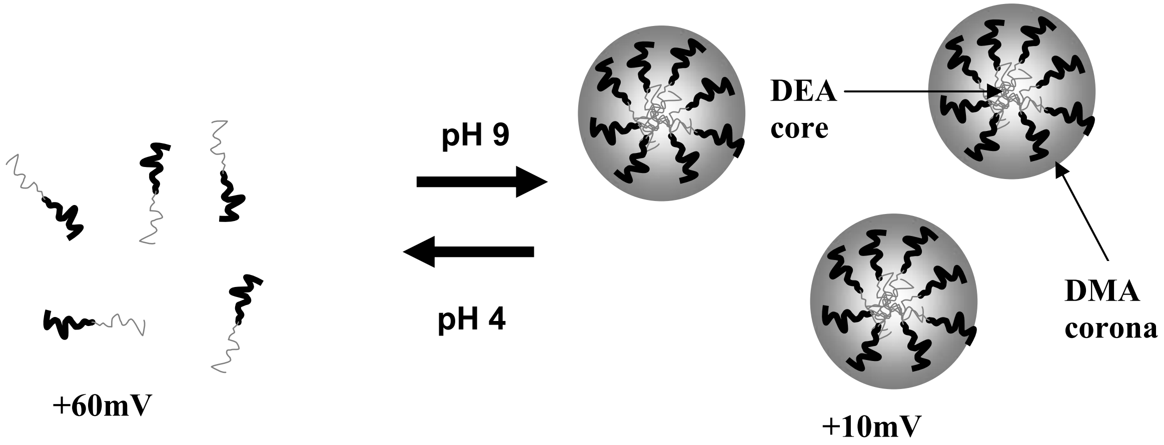
Surface coatings that can act as carriers for active molecules and which respond to an external stimulus for release of those actives have potential uses in a wide range of technology applications including smart packaging and drug release. The formation of functionalised, smart surface coatings with a well-organised nanostructure on a solid substrate is one of the key challenges for the development of 'platform' technologies for the so-called 'nanotechnology revolution'. While considerable progress in the development of 2-D films has been made, little progress has been reported for well-organised 3-D films. Our current research addresses this knowledge gap through a systematic investigation of the conditions necessary to develop 3-D surface coatings using stimulus-responsive block copolymer micelles. Accurate control of the adsorption of these nanoparticles at the solid-aqueous interface will give fine control over molecular location in three dimensions, a pre-requisite for higher order functional nanomaterials. The range of potential applications for such systems is vast and includes smart packaging, drug delivery materials, photonics, and molecular filtration devices. We will present a range of data using in-situ AFM images and ellipsometric measurements to observe and quantify the adsorption. In addition, we will present data that illustrates the reversible opening-closing cycles for layers of these micelles

THE ADSORPTION BEHAVIOUR OF pH RESPONSIVE BLOCK COPOLYMERS ON SILICA: THE EFFECT OF AGGREGATION

Murray Baker, Emelyn Smith and Erica Wanless

School of Environmental and Life Sciences, University of Newcastle, Callaghan, 2308
erica.wanless@newcastle.edu.au

An investigation into the adsorption behaviour of the diblock copolymer poly(2-(dimethylamino)ethyl methacrylate)-*block*-poly(2-(diethylamino)ethyl methacrylate) (DMA_{93}-DEA_{24} $M_n \sim 20\,000$ $g.mol^{-1}$) at the silica/aqueous solution interface was carried out combining contact angle measurement and optical reflectometry. Both blocks of the copolymer are weakly basic and charge/discharge as a function of pH, where the DEA block is slightly more hydrophobic in the uncharged state resulting in the formation of micelles (Bütün, V.; Armes, S.P.; Billingham, N.C., *Polymer* 2001, 42, 5993). This transition between unimers and micelles is reversible and occurs over a narrow pH range. Our interest is in the interaction of these species with silica surfaces and the changes that occur in adsorbed mass and hydrophobicity as the pH is changed. We have also investigated the effect of selective quaternisation of the DMA block to impart a permanent charge.



Optical reflectometry was used to monitor the changes in adsorbed mass as a function of pH where it was observed that for unquaternised and lightly quaternised samples considerable desorption occurs with an initial wash at pH 9 that we attribute to the loss of loosely associated micelles. Then a wash with pH 4 shows further loss due to the opening of the micelles and a loss of copolymer chains that may not be physically in contact with the surface. Adsorption isotherms for all copolymers investigated show a rapid increase to a plateau region at very low concentrations

The captive bubble technique was used for contact angle measurements onto identical silica wafers. Adsorption was investigated by adsorbing initially in both unimer (pH 4) and micelle (pH 9) forms followed by a stepwise change the pH of the supernatant. It was found that the changes in hydrophobicity observed compared well with the change in adsorbed mass measured and this leads to a greater understanding of this system.

Keynote Lecture

SPONSORED BY FUTURE MATERIALS

WETTING OF TEXTURED MATERIALS

David Quéré

Physique de la Matière Condensée, Collège de France, Paris, France.

dpsquere@yahoo.fr

We analyze the specific wetting properties which can be induced by texturing a substrate, and making it either pre-suffused with an oil (which yields a hemi-solid, hemi-liquid surface), or hydrophobic. In both cases, the materials can become slippery, and we discuss the conditions for inducing such non-stick behaviour. Then, we show some of the unusual drop dynamics generated by these surface treatments.

FORMATION PROCESSES OF COPPER SULFIDE THIN FILMS

Carolyn Munce[1], Gretel Parker[1], Stephen Holt[2] and Greg Hope[1]

[1] Griffith University and CRC for MicroTechnology School of Science, Nathan, Qld, 4111, Australia
[2] ISIS, Rutherford Appleton Laboratory Chilton, Didcot, OXON, OX11 0QX, UK

g.hope@Griffith.edu.au

The preparation of chalcogenide thin films by chemical bath deposition (CBD) has attracted much attention because of its simplicity, low cost, low deposition temperatures and availability of starting materials. Starting materials are generally metal salts used in the presence of a complexing agent, and a chalcogenide source, for sulfur typically thiourea or thioacetamide. Copper sulfide is of specific interest because of its relevance to mineral processing and the many established and prospective applications in photovoltaics, solar control coatings and in other electronic devices. Also the bonding and scattering properties of the various copper sulfide phases are well matched for neutron reflectivity and vibrational spectroscopic investigation.

The deposition of thin copper sulfide films by CBD on to glass microscope slides, single crystal silicon or polycrystalline platinum surfaces, was undertaken from an aqueous thiourea based bath. The as-deposited and annealed films have been characterised using Raman spectroscopy, infrared spectroscopy, electron microscopy, and neutron reflectance. Film deposition takes place following an induction period that is temperature dependent. Deposition times of 35 or 40 minutes at 40 °C, showed a 20 nm increase in thickness from 76 to 96 nm in a 5 minute period when measured using neutron reflectivity at ISIS. Typically the deposited films could be modelled with two layers and solid solid and solution solid interface roughness near 3 nm and 9 nm respectively. TEM images indicate that the as prepared films are composed of spherical agglomerates, and FTIR found H_2O within the coating which was lost during heat treatment. Raman spectra of the as prepared films are characterised by a broad band at 420 cm^{-1}, that shifted to a covellite–like value of 474 cm^{-1}, either on heating in air at 150 °C or under the 442 nm laser excitation.

WETTABILITY AND SURFACE ENERGETICS OF ROUGH FLUOROPOLYMER SURFACES

Rossen Sedev, Manrico Fabretto and John Ralston

Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus,
Adelaide, SA 5095, Australia

rossen.sedev@unisa.edu.au

Surface roughness affects the wettability of materials. Wenzel's equation relates the equilibrium contact angles on rough and smooth surfaces. In addition to that change, however, roughness induces a considerable contact angle hysteresis, i.e. many metastable positions of the contact line become possible and therefore the contact angle measured depend on whether the contact line has advanced or receded beforehand. In order to use Wenzel equation one must calculate an average contact angle or, alternatively, eliminate the hysteresis.

Hydrophobic solid surfaces with controlled roughness were prepared by coating glass slides with an amorphous fluoropolymer containing varying amounts of silica spheres. Advancing and receding contact angles were measured with the Wilhelmy plate technique. The hysteresis was significant but could be reduced by subjecting the system to acoustic vibrations. Surface roughness affects all contact angles but only the vibrated ones follow Wenzel equation. The average contact angle is a good approximation for the vibrated one provided that roughness is not too large or the angles too small.

Zisman's approach was employed to obtain the critical surface tension of wetting for the rough surfaces. It increases with roughness in accordance with Wenzel equation. Advancing, receding and vibrated angles yield different results. Advancing angles are characteristic of the main hydrophobic component, while vibrated ones represent better the average wettability of the whole surface.

CRYSTALLISATION OF ZINC OXIDE IN THE PRESENCE OF FUNCTIONALISED SURFACES

Dennis Palms[1,2], Craig Ian Priest[2], Rossen Sedev[2], John Ralston[2], Gerhard Wegner[1]

1. Max-Planck-Institute for Polymer Research, Mainz, Germany
2. Ian Wark Research Institute, Adelaide, Australia

dennis.palms@unisa.edu.au

Zinc Oxide is a widespread material, both in industry and research. It is a semiconducting binary oxide with excellent properties such as gas sensitivity, piezoelectricity, and photoconductivity. Having just one crystalline phase, it serves as a suitable model system for controlled crystallization without phase transitions complicating the study. Recently, much experimental and theoretical research has been conducted to study the morphological control of ZnO powders and thin films to meet the requirement of applications in different fields. Thin films of ZnO on solid substrates are lately being used for electronic applications. Polyelectrolytes, e.g. block or graft copolymers bearing sulfonic or carboxylic acid groups or surface functionalized latices, have shown a marked influence on the crystallisation of ZnO in solution; to combine these two concepts, patterned self-assembled monolayers of functionalised alkane thiols and alkane silanes were prepared on gold and silica substrates, respectively, using UV- photolithography. These composite surfaces served as templates for zinc oxide (ZnO) crystallisation. When patterns containing hydrophilic and hydrophobic regions were exposed to a 0.01 M zinc nitrate crystallising solution, nucleation occurred selectively on the hydrophobic regions. After 90 minutes, hexagonal prisms of about 2 µm length and 50-100 nm in diameter had grown on the thiol surfaces; on the silanised surfaces the prisms were about 4 µm long with a diameter of around 500 nm. In both cases the crystal growth is uniform with the c-axis perpendicular to the surface.

ANALYSIS OF CONTACT ANGLE HYSTERESIS FOR SUPERHYDROPHOBIC SURFACES

Wen Li and Alidad Amirfazli

Department of Mechanical Engineering, University of Alberta, Edmonton, AB, T6G 2G8
Canada

a.amirfazli@ualberta.ca

Contact angle (CA) phenomenon is important from both academic and practical perspectives. It has been widely studied for at least 200 years and well understood in many aspects. However, interesting wetting behavior can occur when micro- or nano-metric spatial dimensions come into play (e.g., superhydrophobicity), which requires further study. New experimental strategies have been used (e.g., lithography or nanofabrication) to create superhydrophobic surfaces with CA larger than 150°. Large CA or limited contact area reduces the adhesion or friction between liquids and solid surfaces. Such surfaces would have ideal liquid-shedding properties and could be useful in many industrial applications such as glass coatings, microfluidics and pesticide. Successful applications in many cases do not depend only on a large CA but also on low contact angle hysteresis (CAH).

In this presentation a free energy thermodynamic analysis will be discussed for typical superhydrophobic surfaces fabricated today that significantly simplifies calculations of free energy barrier associated with CAH phenomena. A microtextured surface with pillar structure, typical of one used in experimental studies, is used as an example. We demonstrate that the predicted CAH and equilibrium contact angles are consistent with experimental observations and predictions of Wenzel's and Cassie's equations, respectively. We also establish a criterion for transition between noncomposite and composite wetting states. The results and methodology presented can potentially be used for designing superhydrophobic surfaces.

Keynote Lecture

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THE FUTURE OF COMPRESSIONAL RHEOLOGY

Lee White

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh,
PA 15213-3890, United States

white@andrew.cmu.edu

Compressional rheology, as applied to solid/liquid separation unit operations, has been advanced considerably in the last decade. The addition of the concept of compressive yield stress to the mechanical equations of two-phase flow has enable us to model such one-dimensional processes as batch settling, continuous thickening, pressure and vacuum filtration, centrifugal settling and filtration and even the top-drying of suspensions. Such modeling has led to the development of experimental methods for the rapid determination of the rheological parameters and the beginning of an understanding of how the short range inter-surface forces determine the magnitude of the yield stress and how it can be chemically manipulated to achieve given separation goals. Recently, as we have attempted to model two-dimensional separation processes, it has become apparent that the model is incomplete. For centrifugal decantation and edge-drying of coatings, the assumptions of compressional rheology are not sufficient to determine the solution of the two-phase flow equations. A possible additional constraint is postulated that, hopefully will allow the extension of the model to these higher dimensional situations without the introduction of other parameters.

COMPARISON OF THICKENER PERFORMANCE WITH MODEL PREDICTIONS

Shane P. Usher

Particulate Fluids Processing Centre, Department of Chemical and Biomolecular
Engineering, The University of Melbourne, Victoria, 3010, Australia

spusher@unimelb.edu.au

An algorithm has been developed to predict steady state thickener operation from fundamental material properties, properly accounting for compression of the suspension network structure within the sediment bed with a pseudo-2D consolidation model based on the theoretical framework developed by Buscall and White in 1987. Comparison of process performance with model predictions has been performed for a large number of industrial thickening operations. Comparisons suggest that there are extra contributions to the rate and extent of dewatering that the model does not predict. Many of these discrepancies, which manifest as enhanced extents and rates of dewatering, are attributable to a number effects involving shear and channelling. Shear effects that cause floc densification can involve rakes, sloped walls and general buffeting in effectively fluidised sections of the equipment with long solids residence times. Channelling phenomena which involve improved rates of liquid transport through non-homogeneities in the solids concentration distribution can be mechanically created through rakes and rods and can also evolve naturally in the sedimentation of flocculated and coagulated materials. The differential between predicted and actual performance is material property, flocculant type and thickener configuration and operation dependant.

NMR-INVESTIGATION AND DYNAMIC MODELLING OF THE LOCAL SOLIDS VOLUME FRACTION DURING THE COMPRESSION OF FILTER CAKES

Ates Erk, Harald Anlauf, Werner Stahl and Hermann Nirschl

Institute for Mechanical Process Engineering and Mechanics, University of Karlsruhe (TH),
Straße am Forum 8, D-76131 Karlsruhe, Germany

ates.erk@mvm.uka.de

Solid-liquid separation of fine particulate suspensions is of widespread importance in many fields of process technology. Examples include the industrial production of pigments and ceramics as well as food processing and wastewater treatment.

The principle mechanisms of solid-liquid separation processes are sedimentation and filtration. Both cases include the formation and compression of a liquid saturated bulk (sediment or filter cake). The compressive properties of the bulk determine the operating parameters of solid-liquid separation devices and the achievable separation results.

The solids volume fraction of the bulk strongly depends on the local stress. In the transient state a liquid transport within the porous system takes place. As a result, a time-dependent gradient of the solids volume fraction develops. Spatially resolved information about the solids volume fraction as a function of time under different conditions (e.g. pressure, pH) allows better understanding of the physical mechanisms and thus more precise modelling. The required data can be gained by NMR-methods in a non-destructive and highly resolved way.

Within this paper experimental and calculated results concerning solids volume fraction profiles during the formation and compression of fine particulate kaolin and titania filter cakes are presented. The experimental measurements were carried out with an in-situ-filtration-cell which was integrated into a NMR-tomograph (Bruker Avance 200 SWB) for spin density measurement (^{1}H-NMR).

A numerical model for the calculation of the local solids volume fraction during formation and compression of filter cakes and sediments was developed. The calculated results were compared with the experimental NMR-data.

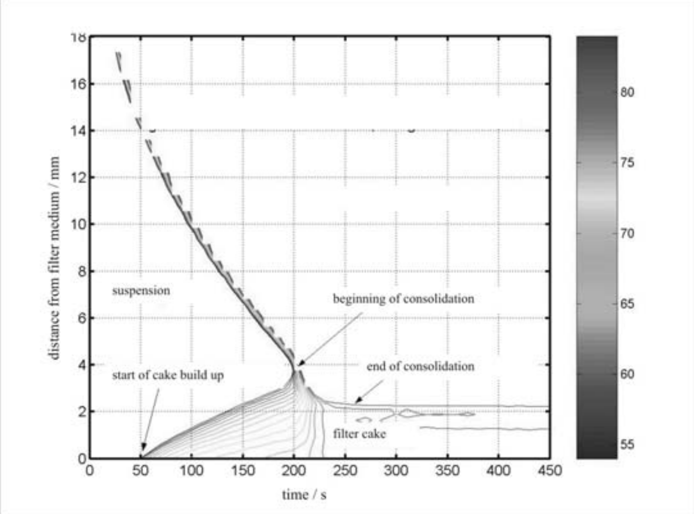

Fig. 1: NMR-measurement during formation and consolidation of a kaolin filter cake (coloured lines represent lines of identical solids volume fraction)

EFFECT OF FRACTAL DIMENSION ON COMPRESSIVE YIELD STRESS OF FLOCCULATED SUSPENSION

Konika Moushumi Khan and Graeme Bushell

Particle and Catalyst Technologies Research Group, School of Chemical Engineering and Industrial Chemistry, University of New South Wales, NSW, 2052, Australia.

Konika.khan@students.unsw.edu.au

The aggregation of particles forming larger structures plays very important role in many industrial processes. Floc microstructure affects the formation of sediments, filter cakes and other particulate collectives and has a large impact on the design and operation of solid – liquid separation equipments. However it is not well understood how floc structure can have an effect on sediment property.

In flocculated suspensions, above sufficiently high concentration, particles form an interconnected network which possesses a network strength defined as compressive yield stress. In some models [1,2] compressive yield stress is described to follow power-law function of solid concentration where power-law exponent is associated with fractal dimension of floc. However, these models are not in good agreement with experimental results. This study examined the effect of floc microstructure on compressive yield stress of sediment bed.

The project is approached with computer simulations with flocs of different structure under compression to examine the influence of structure of flocs on network strength with detailed information that are not accessible in real physical systems.

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PRESSURE FILTRATION OF CELLULOSE FIBRES

Christian Kugge[1,2], Hanna Bellander[1,3] and John Daicic[1]

1. Institute for Surface Chemistry, Royal Institute of Technology, Box 5607, SE-114 86, Stockholm, Sweden
2. Department of Applied Mathematics, Research School of Physical Sciences and Engineering, ANU, Building 60, 0200, Canberra, Australia
3. Billerud Karlsborg AB, SE-952 83, Karlsborg, Sweden

Christian.Kugge@anu.edu.au

The compressional rheology of cellulose fibre suspensions has been studied using a pressure filtration technique. The dewatering of these systems is described by a range of key properties of the suspension, such as the compressive yield stress, permeability and solids diffusivity. This enables the consolidation process to be characterised. We have investigated the effect of a commercial debonding agent additive on the compressional properties of a fibre suspension. Such agents are commonly used in the production of hygiene products where they are added to decrease the strength of fibre-fibre bonds. Here we investigate their effect on the compressive response of fibre suspensions as an illustration of how these measurements can be used to characterise the influence of additives on bulk properties. The results indicate that addition of debonder causes cracks in the fibre bed and a somewhat higher dewatering rate, as the solids level is increased.

A GEOMETRIC APPROACH TO COLLISION EFFICIENCY FACTORS AND OPTIMUM FLOCCULANT DOSAGE

Aaron Olsen[1], George Franks[1], Simon Biggs[2] and Graeme J. Jameson[1]

1. Centre for Multiphase Processes, the University of Newcastle, Callaghan, NSW, 2308, Australia.
2. Department of Process, Environmental & Materials Engineering, University of Leeds, Leeds, LS2 9JT, UK

aaron_h_olsen@yahoo.com.au

A geometric model is presented for quantitatively describing the collision efficiency factor (the probability of a binary particle or aggregate collision resulting in adhesion) of flocculating particles. The model is developed specifically for flocculation of oppositely charged solid spherical particles (hetero-aggregation), but also addresses the limitations of earlier models developed specifically for polymeric flocculation. Whilst these earlier models are based on the relative fractions of bare particle surface and that covered by flocculant, the model presented is based on the relative surface area of oppositely charged particles exposed to collisions. Optimum relative particle concentration is used as a measurable parameter in support of our model; the data obtained showing a much closer correlation with our predictions than those of previous models.

SILICA NANO-PARTICLES AS FLOCCULANTS: EFFECT OF PARTICLE SIZE ON DEWATERING COLLOIDAL ALUMINA

Peter D. Yates, George V. Franks, Graeme J. Jameson

Centre for Multiphase Processes, University of Newcastle, Callaghan NSW, 2308, Australia

peter.yates@studentmail.newcastle.edu.au

The recycling of water used in today’s industries is becoming more important as access to water for processing purposes is becoming scarce. Currently, water soluble polymers are the most commonly used aggregation aid in dewatering processes, however the extent of dewatering is limited due to the polymers affinity to water. In some cases not one but two additions of polymer are required because polymer aggregates cannot re-form once broken down in shear. It is therefore desirable to keep polymer dose low because, high doses of polymer flocculant result in high residual cake moisture. One possible solution to this problem is to use particles as the flocculant instead of long chain polymers. We use small silica nano-particles with opposite charge to the 300 nm alumina particles in order to flocculate the alumina suspension. We have investigated the effect of the size of the silica particles on the flocculation of the alumina suspension for particle size ratios (small silica particle radius divided by larger alumina radius, r/R) from 0.03 to 1.0. We will present the effect that different sized silica has on the aggregate structure, size and strength, as well as the resulting filtration behaviour. The size and fractal dimension of the hetero-aggregates produced was determined by low angle light scattering. The size of the aggregates was measured after being sheared at a given rate for a period of time. The aggregates with largest size at any particular time were deemed to have the strongest inter-particle bonds. It was found that smaller silica particles had the weakest interaction with the larger alumina particles, but produced the most efficient flocculation in terms of weight of silica added. As the size ratio increased the number of silica particles needed for optimum flocculation decreased (but the weight percent increased). Also the attractive force between the two species increased. Aggregates formed at size ratios close to 1.00 gave larger and stronger floccs. These results are consistent with calculations of the forces between silica and alumina particles using Hogg, Healy and Fuerstenau heterocoagulation theory. The compressive yield stress P(y) and hindered settling data R(ϕ) from filtration experiments will also be presented.

SYNTHESIS OF POLY(N-ISOPROPYLACRYLAMIDE-CO-ACRYLIC ACID) MODEL COMPOUNDS FOR FILTRATION EXPERIMENTS

Mogens Hinge[1], Morten L. Christensen[1], Peter J. Scales[2] and Kristian Keiding[1]

1. Section of Chemistry, Department of Life Sciences, Aalborg University, Denmark.
2. Particle Fluid Processing Center, University of Melbourne, Parkville, Australia.

kk@bio.auc.dk

Theoretical development within solid/liquid separation in colloidal systems is largely based on inorganic, low charged and incompressible particles. These do not reflect the properties in biosolid/organic systems. There is therefore a need for a development of colloidal and particles which mimic these biosolid/organic systems and thereby make a basis for further theoretical development with respect to filtration.

Poly(N-isopropylacrylamide-*co*-acrylic acid) microgels are synthesized by free-radical surfactant free emulsion polymerization as an organic model system for biosolids. The model system is investigated by titration, differential scanning calorimetry (DSC) and capillary rheometry. The titration experiments indicates that the polymerization is a block copolymerization and the DSC result show that the blocks of poly(N-isopropylacrylamide) are not randomly distributed in the microgels. Capillary rheometry indicates that the blocks of poly(acrylic acid) are placed on the surface of the microgels. The combination of these three results reveal that the microgels have a core mainly consisting of poly(N-isopropylacrylamide) and a diffuse/cloudy surface consisting mainly of poly(acrylic acid).

The core/shell structure of the microgels is a good model for Danish sewage sludge which consists of a core of microcolonies and a shell of extracellular polymer substance (EPS). EPS combined with microcolonies is a highly charged (0.5-2 mmol/g) material. This property is modeled by the microgels by using varying concentrations of acrylic acid as co-monomer. The microgels have a charge density between 0.2 and 0.9 mmol/g.

Preliminary filtration experiments show that filtration properties of the microgel model system significantly differs from the properties for inorganic colloidals such as titaniumdioxid.

NON-TRADITIONAL CONSTANT FILTRATION BEHAVIOUR

Anthony D. Stickland, Ross G. de Kretser, Peter J. Scales

Particulate Fluids Processing Centre, Department of Chemical and Biomolecular
Engineering, The University of Melbourne, Parkville 3010, Australia

a.stickland@pgrad.unimelb.edu.au

Pressure filtration is a common industrial process used for solid/liquid separation and laboratory technique used to measure the compressional rheological properties of suspensions. Traditional approaches to the modelling of constant pressure filtration behaviour of particulate systems stipulate quadratic behaviour of time with filtrate volume. However, this is not necessarily a fundamental attribute of pressure filtration, but rather a result of the assumptions made of the compressibility and permeability of the material. This work solves diffusion-type constant pressure filtration governing equations using a finite element technique to demonstrate that filtration, under certain circumstances, is expected to show negligible quadratic behaviour. Materials that exhibit such behaviour have often been classified as non-traditional and methodologies have been developed to interpret such trends. This work illustrates that such behaviour is in fact covered by extant filtration models and does not require any extra interpretation of the forces involved. Furthermore, it is shown that traditional or non-traditional behaviour is dependent upon the initial solids concentration and the applied pressure, such that the filtration of a suspension may show relatively long cake formation times at low initial concentrations or pressures, and relatively short times at high initial concentrations or pressures.

THE EFFECT OF SOLUTION AGE UPON THE ACTIVITY OF POLYACRYLAMIDE BASED FLOCCULANTS

Andrew T. Owen, Phillip D. Fawell and Christine Rae

A.J. Parker CRC for Hydrometallurgy, P.O. Box 6982, Waterford 6152, Australia

andrew.owen@csiro.au

In hydrometallurgical processes requiring solid-liquid separation from fine particle slurries, polymeric flocculants are often added to induce aggregation and enhance sedimentation. Aqueous solutions of high molecular weight polyacrylamides are known to undergo time-based changes in their properties. Most previous studies into the impact of ageing on flocculation have focused on long time-scales, having little relevance to an industry where ageing times prior to use can be as short as 20 minutes.

In this study polyacrylamide and polyacrylamide/acrylate co-polymers of varying molecular weight, were examined at ageing times from one hour to six days for different make-up conditions. Their relative flocculation performance was assessed continuously in a Couette mixing device (stationary outer cylinder, rotating inner cylinder) on the basis of settling rates and *in situ* size characterisation with a focused beam reflectance measurement (FBRM) probe.

For very high molecular weight polymers (both powder and emulsion form), regardless of anionic character, the dosages required to achieve measurable flocculation decreased as the flocculant solution age increased, with optimal performance attained at times of between 48 and 72 hours. For lower molecular weights, optimal activity was reached in as little as a few hours with activity steadily decreasing upon extended ageing to 144 hours. There was no discernable difference in aggregate size distribution when settling rates were matched, suggesting that the effective flocculant concentrations were influenced by the solution age. A mechanism for the early stages of flocculant dissolution is proposed that involves the release of discrete polymer chains from highly agglomerated species, the former dominating flocculation activity.

The emulsion-based flocculants exhibited a higher proportion of their maximum activity immediately after make-up, however there was still considerable benefit obtained from further ageing. The impact of increasing the duration of applied shear during emulsion make-up was also examined, with relative activity decreasing for longer make-up times.

STIMULANT SENSITIVE FLOCCULATION AND CONSOLIDATION

George V. Franks, Carola Sepulveda, and Graeme J. Jameson

Chemical Engineering and the Centre for Multiphase Processes, University of Newcastle,
Callaghan NSW 2308, Australia,

george.franks@newcastle.edu.au

A novel method of flocculation resulting in both rapid sedimentation and low sediment moisture is described. It relies on changing the inter-particle forces from repulsive to attractive (aggregation and fast settling results) and then back to repulsive (densification of sediment then occurs). The majority of the clarified liquid can be removed immediately following the sedimentation stage as is common practice. Following change of inter-particle potential back to repulsive, additional water is expressed from the sediment bed. The sediment bed volumes can be reduced by between 10 to 45 percent depending upon the conditions. The change in inter-particle force is controlled by a stimulus such as pH or temperature. The technique is demonstrated without polymer using the isoelectric point for a pH sensitive flocculation. Addition of the polyelectrolyte chitosan produce improved pH sensitive flocculation and consolidation. It is also demonstrated that methylcellulose is an effective temperature sensitive flocculant. Sediment height as a function of time and final sediment bed densities are used to demonstrate that both rapid sedimentation and low sediment moisture are not mutually exclusive.

DETERMINATION OF THE SHEAR YIELD STRESS OF FINE PARTICULATE SEDIMENTS AND FILTER CAKES DURING SOLID-LIQUID SEPARATION

Ates Erk, Harald Anlauf, Werner Stahl and Hermann Nirschl

Institute for Mechanical Process Engineering and Mechanics, University of Karlsruhe (TH),
Straße am Forum 8, D-76131 Karlsruhe, Germany

ates.erk@mvm.uka.de

Rheological properties of fine particulate suspensions are of importance in many different solid-liquid separation processes such as filtration and gravity or centrifugal sedimentation. Often rheological properties determine the processability of suspensions in a certain solid-liquid separation device. The shear rheology has a significant effect on conveyability and/or flow of suspensions within centrifuges and filters and on solids discharge (e.g. sediment transport in decanter centrifuges and solids discharge from disc stack separators).

The compressive rheology determines the compactibilty of a certain sludge under pressure and thus the residual moisture. For optimum solid-liquid separation equipment selection, design and scale-up it is important to know the compressive and rheological material functions of the system which is to be processed (e.g. solids volume fraction, permeability and yield stress as a function of the solids compressive pressure). Both shear and compressive rheology of fine particulate suspensions strongly depend on interparticle forces and on the resulting microstructure.

Since in filters and centrifuges the sediment or filter cake is always subjected to a significant normal stress, the normal stress dependency of the shear yield stress has to be taken into account.

This study especially examined the influence of a superposed normal stress on the shear yield stress. The investigations were carried out with a modified Jenike shear cell. The influence of solids volume fraction and variable inter-particle forces (controlled by pH) were investigated. A simulation program to calculate the shear yield stress in a sediment or a filter cake during its formation and compression was developed.

The possibility to improve separation results and processability by controlling the rheological properties of a suspension, for example by adjusting the surface chemistry, and the application to industrial solid-liquid separation processes will be discussed.

THE BEHAVIOUR OF MAGNETITE IN THE PREPARATION OF LUMEN-LOADED MAGNETIC FIBRE

B. H. Ong[1], S. Zakaria[2] and T. G. M. van de Ven[3]

1. Faculty of Engineering, Multimedia University, Jalan Multimedia, 63100 Cyberjaya, Selangor, Malaysia
2. Materials Science Program, School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
3. Pulp and Paper Research Centre, McGill University, 3420 University Street, Montreal, Quebec, H3A 2A7 Canada

bhong@mmu.edu.my

Magnetic cellulose fibres have been successfully produced by the lumen-loading process. Lumen loading allows filler particles to be introduced exclusively into the lumens of wood fibres while leaving the external surfaces free of filler. The filler is protected by the cell wall from dislodgement during papermaking and the particles do not interfere with inter-fiber bonding. This leads to a lumen loaded fibre with high resistance to unloading during papermaking and result in papers with a higher strength than those conventionally loaded to the same level. To improve the lumen loading degree, polymeric retention aids have been introduced. Polyethylenimine (PEI) as retention aid in the preparation of lumen loaded fibre has been found beneficial in the preparation of magnetic cellulose fibres. In this paper, the characteristics of the magnetite surface and its behaviour in water solution in the presence of PEI and aluminum sulfate, the mechanism of adsorption and the kinetics of lumen loading are fully elucidated.

Electrophoretic mobility of magnetite is positive in acidic solution and becomes more negative with increasing pH. pH_{pzc} is about 5.5. The magnetite particles are negatively charged without any addition of PEI. The particles reach the point of zero charge when ~0.15 mg/g pigment of PEI is added and become positively charged with further addition of PEI. Ratio output by magnetite from PDA 2000 shows that magnetite colloids exist in multiparticles aggregate form in water, caused by the magneto-dipole interactions. During lumen loading, magnetite particles enter the lumen as smaller aggregates. It is found that high shear is essential in breaking up magnetite filler aggregates, which otherwise are too large to enter the lumen. Their spontaneous reflocculation within the lumen enhances the lumen loading process. Scanning electron microscopy was used to investigate the morphological structure of the lumen-loaded fibres.

XPS AND TOF-SIMS STUDY OF A CHALCOPYRITE-PYRITE-SPHALERITE MIXTURE TREATED WITH XANTHATE AND SODIUM BISULPHITE

Tatiana N. Khmeleva, Tsvetomir V. Geogiev, Marek Jasieniak, William Skinner
and David A. Beattie

Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes Boulevard, Mawson Lakes 5095, Australia,

David.Beattie@unisa.edu.au

Unintentional activation of pyrite and sphalerite, through the dissolution of copper from chalcopyrite, adversely affects the selectivity of flotation separation in complex sulphide ores containing these minerals. Inorganic depressants, such as cyanide and sulphite, are often used to alter the surface properties of the activated minerals in an attempt to prevent their collection. Most detailed surface studies on activation, and subsequent deactivation, have involved single mineral investigations and intentional activation (with $CuSO_4$). We present flotation data, X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements of a mineral mixture of chalcopyrite, pyrite, and sphalerite exposed to collector (IBX), in the absence and presence of sodium bisulphite ($NaHSO_3$).

XPS results indicate that the galvanic interactions during grinding caused significant oxidation of the minerals when compared to single mineral experiments. Flotation testing revealed that unintentional activation does occur, indicated by the increase in sphalerite recovery in the presence of the xanthate collector. The addition of sodium bisulphite was shown to depress the two activated minerals (pyrite and sphalerite) without significantly affecting the recovery of chalcopyrite. ToF-SIMS analysis of flotation concentrate and tail samples indicated that copper activation is responsible for the flotation of pyrite and sphalerite and that sodium bisulphite depresses these minerals by removing hydrophobic sulphur species from the mineral surface. In addition, the ToF-SIMS analysis of this three mineral system gives the first direct evidence that the increased surface exposure of $Zn(OH)_2$, formed in solution due to the copper activation of sphalerite, is responsible for depressing pyrite in the presence of copper ions and sphalerite.

MESOPOROUS TRANSITION METAL OXIDES: CHARACTERISATION AND APPLICATION

Peter J Harbour[1], Jamie Booth[2] and Patrick G Hartley[1]

1. CSIRO Molecular Science, Bag 10 Clayton South Mdc Victoria Australia 3169
2. RMIT Department of Applied Chemistry, GPO Box 2476V, Melbourne 3001

peter.harbour@csiro.au

Transition metal mesoporous materials are of considerable interest for catalysis, energy storage and separation technologies due to their inherently high surface area. Arsenic contamination of drinking water supplies is one application where the advantages of high surface area, and thus high adsorption capacity, but rapid settling materials can be exploited. In this presentation, we show the characterization of a number of high surface area materials including iron oxide, titanium dioxide made by a simple and inexpensive hydrolysis technique developed at CSIRO Molecular Science. A number of techniques were used to analyze the material including: powder x-ray diffraction, small angle x-ray scattering, field emission scanning electron microscopy, and pore volume and surface area analysis via standard BET gas adsorption. Some applications of these materials are also demonstrated.

THE ROLE OF COLLOIDAL FORCES IN THE CAPTURE OF NANO AND SUBMICRON PARTICLES BY AIR BUBBLES IN FLOTATION

Anh V. Nguyen, Peter F. George, and Graeme J. Jameson

Discipline of Chemical Engineering and Special Research Centre for Multiphase Processes,
The University of Newcastle, Callaghan NSW 2309, Australia

Anh.Nguyen@newcastle.edu.au

The capture of fine particles by air bubbles is central to froth flotation, which is widely used in the recovery of minerals and coal from the rock. The capture efficiency is known to decrease with decreasing particle size. The opposite trend has also been observed for the flotation of colloidal particles, which is governed by Brownian diffusion.

This study examined the role of colloidal forces in the capture of nano and submicron particles. A theoretical framework is presented to determine the collection efficiency of nano- and sub-micron particles. The theory incorporates Brownian diffusion, colloidal and microhydrodynamic interactions that come into effect at small separation distances. The governing equations were solved numerically using the Crank-Nicholson method with variable step size. The simulation shows the significant role of the attractive colloidal forces between hydrophobic surfaces: No capture is possible in the absence of hydrophobic forces. Predictions from the model are compared with experimental results obtained in a small laboratory column cell, in which silica particles with 40 nm, 100 nm and 1 μm diameters were floated using fine bubbles (~150 μm diameter), and cetyltrimethyl ammonium bromide and Dowfroth (polyglycols) 250 surfactants. The zeta potentials of the particles and bubbles in the surfactant solutions were measured with the Brookhaven ZetaPlus apparatus and Rank Brothers Zeta Meter, respectively. No homocoagulation of the silica particles was confirmed with jar tests, with no evidence of settling over a 24 hour period, and the flotation separation was principally due to heterocoagulation between particles and bubbles. The particle size distribution of the flotation feed and products was analysed with TEM.

Both the theoretical and experimental results show a minimum of the collection efficiency at a particle size in the order of 100nm. With larger particles, the interception and inertial collision predominate the particle capture, while the diffusion and colloidal forces control the collection of particles with a size smaller than the transition size.

Keynote Lecture

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THE WIDESPREAD OCCURRENCE OF BILAYER TYPE STRUCTURES AT INTERFACES AS REVEALED BY NEUTRON REFLECTOMETRY

Robert K. Thomas

Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, OX1 3QZ

robert.thomas@chem.ox.ac.uk

It is now well established that surfactants and amphiphiles adsorb at the hydrophilic/aqueous surface in the form of “bilayer” type aggregates (bilayers is used here to distinguish such structures from monolayers), e.g. micelles, rods, and full bilayers. Recent neutron reflectometry results will be used to explore the effects of surfactant shape and composition on the nature and extent of adsorption of aggregates formed at hydrophilic/aqueous interfaces. The less well characterized phenomenon of “bilayer” formation in contact with polyelectrolytes at interfaces will also be explored and connections made between the two types of system.

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NEUTRON SCATTERING INVESTIGATIONS NANOPOROUS FILMS AND SUBSTRATES FOR FUNCTIONAL BILAYERS

Travis McQueen[1], Greg S. Smith[2], Johannes B. Tan[1] and Shenda M. Baker[1]

1. Department of Chemistry, 301 East 12th Street, Harvey Mudd College, Claremont, CA 91711-7577 USA
2. HFIR Center for Neutron Scattering, Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6393 USA

shenda_baker@hmc.edu

Synthetic lipid bilayers are excellent mimics of cell membranes. In order to experimentally access these thin layers and oriented proteins in membranes, suitable supports which allow for membrane fluidity while assuring membrane stability need to be developed. Nanoporous polymer templates created from the natural phase segregation of immiscible diblock copolymers are uniform arrays with pore sizes naturally on the scale of macromolecules, tens of nanometers, and grain sizes currently on the order of microns. We study the suitability of such templates, appropriately treated to present a hydrophilic surface, as substrates for lipid bilayers with scanning force microscopy and neutron reflectometry. In the process, we use tip deflection curves to establish simple criteria for determining the presence of a lipid layer on the substrates.

Reflectivity measurements on these very thin films can be difficult to analyze in order to produce a unique scattering length density profile. We have combined the direct inversion technique of Blaisie[3] with our more traditional profile dependent fitting routine. Using selcetive deutration of the aqueous phase, we can effectively contrast match the substrate and water revealing only the lipid bilayer. We find that gold coated porous polymers and silicon oxide templates in silicon both appear to be suitable support materials. Monolayer depositions on these surfaces assure uniform coverage, but vesicle fusion often results in multilayers.

3. J. K. Blasie, S. Zheng and J. Strzalka *Phys. Rev. B* **67**, 224201 (2003)

STRUCTURE OF NONIONIC MICELLES IN MOLTEN ETHYLAMMONIUM NITRATE: A ROOM TEMPERATURE IONIC LIQUID

Greg G. Warr[1], and Miguel U. Araos[1]

[1] School of Chemistry, The University of Sydney, NSW 2006, Australia

g.warr@chem.usyd.edu.au

We have shown using small angle neutron scattering (SANS) that poly(oxyethylene) alkyl ether nonionic surfactants self-assemble into micelles and lyotropic liquid crystals in the room-temperature ionic liquid, ethylammonium nitrate. Conventional spherical and cylindrical micelles with a solvophobic core and solvated corona of poly(ethylene oxide) groups are both observe above a well-defined critical micelle concentration, and at high concentrations these exhibit repulsive interactions that cannot be explained simply by a hard-wall repulsion. The micelle shape and size varies systematically with alkyl and ethoxy chain length in a manner that closely parallels micelle structures in water.

THE STRUCTURE OF THE DI-BLOCK COPOLYMER P2VP-PEO AS A FUNCTION OF pH AND TEMPERATURE

Andrew Nelson[1], Michelle Gee[2], Jamie Schulz[1] and Scott McLean[2]

1. Bragg Institute, Building 58, ANSTO, PMB 1, Menai, NSW 2234.
2. School of Chemistry, University of Melbourne, Victoria 3010.

anz@ansto.gov.au

Polymeric micelles are potential systems for controlled drug delivery. This is because poorly soluble drugs can be solubilised within the hydrophobic micelle core, while the outer hydrophilic “shell” protects the drug recognition from the bodies clearance systems.

A potential polymer is poly(2-vinylpyridine)-poly(ethylene oxide) (P2VP-PEO). At low pH, this copolymer remains as unimers since the P2VP and PEO blocks are hydrophilic. However, at high pH the P2VP blocks de-protonate and become hydrophobic, only the PEO block is water-soluble, resulting in micelle formation. In this situation the hydrophobic P2VP forms the micelle core and the hydrophilic PEO a hydrated shell. It is envisaged that in drug delivery systems the polymeric micelle will adsorb to cell membranes in tumours. The pH sensitivity of these micelles would allow them to release their drug load close to the cell membrane, increasing its effectiveness.

Through contrast variation SANS experiments we have determined the internal structure of the micelles (aspect ratio, size, shell hydration and aggregation number, etc) and their interactions with other micelles, as temperature and pH were varied.

UNFOLDING FREE ENERGY CHANGES OF β-LACTOGLOBULIN AT THE AIR-WATER INTERFACE: A NEUTRON AND X-RAY REFLECTOMETRY STUDY.

A. Perriman[1], M J Henderson[1], S A Holt[2], and JW White[1]

1. Research School of Chemistry, Australian National University, Canberra ACT, Australia
2. ISIS, Rutherford Appleton Laboratory, Chilton OX11 0QX, OXON, United Kingdom

jww@rsc.anu.edu.au

The effect of interfaces on the thermodynamics and kinetics of protein unfolding may be accessible by reflectometry of x-rays and neutrons at interfaces. To date, the majority of work on denaturation thermodynamics has related to proteins in solution. Here we present is a study following the changes in surface excess of a globular protein adsorbed at the air-water interface in the presence of a chemical denaturant.

The experiments probe the equilibrium surface structure of *bovine* β-lactoglobulin solutions containing increasing concentrations of guanidinium hydrochloride (G.HCl) at constant temperature. A measure has been made of the contribution of the air-water interface to the chemical denaturation enthalpy of β-lactoglobulin. The approach considered the energetics associated with a hydrophobic amino acid residues in the core of the denatured protein adjacent to the air. The methodology then involved the calculation of the Gibbs free energy of a protein at zero denaturant concentration (ΔG^0) by using the change in the adsorbed layer thickness as the order parameter thereby defining the populations of β-lactoglobulin using either a two or three-state model to describe the denaturation process.

PROBING THE ACTION OF LUNG SURFACTANT WITH NEUTRON AND X-RAY REFLECTOMETRY

Ian Gentle

School of Molecular and Microbial Sciences, The University of Queensland

Natural lung surfactant (NLS) is a substance found at the alveolar air/water interface of animals. Its function is to lower the surface tension and therefore make the action of breathing possible. The lack of NLS is a major cause of respiratory distress syndrome (RDS) in premature infants, which in turn is a major cause of mortality. While the composition of NLS (which contains 4 proteins and more than 10 lipid components) is quite well understood, the functions of the major components and their interactions are not. In particular, attention has focused on one protein, known as SP-B, which is a 79 residue hydrophobic protein that is known to be crucial for the action of NLS in maintaining a condensed lipid monolayer at the interface.

We have used neutron and X-ray reflectometry to study the action of purified components of NLS at the air/water interface. Reflectometry experiments on monolayers of SP-B alone have revealed that the protein undergoes a conformational change upon compression. At large molecular areas the protein unfolds, allowing it to expose the hydrophilic residues to water. When compressed to small areas, it folds into a globular shape[1].

Experiments on mixed films have revealed that the SP-B is preferentially excluded from a layer of the protein with DPPC (the major lipid component of NLS). These observations could have implications for the formulation of improved therapies for RDS.

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HIGH RESOLUTION X-RAY SCATTERING STUDIES OF SELF-ASSEMBLED COLLOIDAL SYSTEMS

T. Narayanan

European Synchrotron Radiation Facility, F-38043, Grenoble, France

narayan@esrf.fr

This talk will give an overview of the new possibilities offered by modern synchrotron sources for probing the microstructure and dynamics of colloidal systems. The high brightness of these X-ray sources permits quantitative X-ray scattering measurements which can be exploited to address some of the long standing issues in colloid science.

This will be demonstrated with two representative examples; (i) the micellar self-assembly in millisecond time scale, and (ii) the counterion distribution in polyelectrolyte brushes. In the former case, time-resolved small-angle X-ray scattering combined with stopped-flow technique was used to probe the dynamics of self-assembly of unilamellar vesicles from a mixture of cationic and anionic micelles in the millisecond range. The transformation involves intermediate disk-like mixed micelles which become unstable beyond a critical size and close to form unilamellar vesicles.

In the second example, anomalous small-angle X-ray scattering was used to elucidate the spatial distribution of counterions in a spherical polyelectrolyte brush. The contrast of counterions can be varied by tuning the incident energy in the close vicinity of their atomic absorption edge. High resolution small-angle X-ray scattering allows to separate the scattered intensity of the counterions (resonant part) from that of the macroion. From the resonant part of the scattering amplitude, the spatial correlation of counterions can be deduced.

UNDERSTANDING THE UV-VISIBLE SCATTERING OF NON-SPHERICAL METALLIC NANOPARTICLES

Stuart W. Prescott and Paul Mulvaney

Particulate Fluids Processing Centre, School of Chemistry, University of Melbourne,
VIC 3010 Australia

s.prescott@unimelb.edu.au

Recent experiments have demonstrated the synthesis of non-spherical gold and silver nanoparticles. Particle morphologies that have been synthesised include hemispherically capped cylinders (nanorods), cubes, triangular prisms and hexagonal prisms.[1-4] The techniques utilised for these syntheses include various electrochemical reactions, the use of particular surfactant systems, and the addition of trace amounts of other metals.

These novel structures have interesting optical properties, with the scattering behaviour in the UV-visible region depending on the orientation of the nanoparticle with respect to the incident light, as well as the polarisation of the incident light; for example, aligned gold nanorods illuminated with polarised white light appear either red or blue depending on the direction of polarisation.

While understanding the scattering spectra of these nanoparticles is non-trivial, it is an essential step in the development of optical applications for these materials. The application of numerical approaches such as the Discrete Dipole Approximation[5] will be described as a method by which experimental spectra may be understood. It will be seen that the Discrete Dipole Approximation approach readily reproduces the major features of the scattering spectra for a range of particle morphologies at least qualitatively. Approaches for improving the quantitative agreement between experimentally determined and simulated spectra will also be discussed.

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COLLOID AND INTERFACE STUDIES USING SAXS AND X-RAY REFLECTOMETRY AT CHEMMATCARS

Cookson, D.J.[1], Viccaro, P.J.[2]

1. Australian Synchrotron Research Program (Bragg Institute) Bldg 434, Advanced Photon Source, Argonne IL 60439, USA
2. CARS - University of Chicago, Bldg 434, Advanced Photon Source, Argonne IL 60439, USA

ChemMatCARS is a synchrotron-based scattering facility that includes the Australian Synchrotron Research Program as one of its financial members. It gives Australian scientists access to world-class facilities on a third generation synchrotron undulator beam.

Included in the instrumentation available to Australians is a SAXS/WAXS camera and liquid surface Reflectometer, capable of operating at x-ray energies between 6 to 30 keV (wavelength range of 0.4 to 2Å).

The high collimation and intensity of a third generation undulator beam has allowed us to study liquid and solid interfaces in both bulk phases (using SAXS) and in dimensionally constrained geometries using liquid surface reflectometry. These techniques allow our users to study self-assembled interfaces in a native state over lengths scales ranging from 1 to 1000 Å. As these interfaces are *in-situ*, their response to different environmental factors such as temperature, shear and surface pressure can be monitored - in some cases as a function of time.

The ability to select the x-ray energy with a band pass ($\Delta E/E$) of better than 10^{-4} allows us the opportunity to use techniques such as anomalous SAXS (ASAXS), which can significantly enhance the contrast of selected atomic species.

A description of these instruments at the ChemMatCARS facility will be presented, along with some examples of data obtained from the instruments over the last few years.

X-RAY AND NEUTRON REFLECTIVITY STUDIES OF PLASMA POLYMER COATINGS

M.James[1], A.Nelson[1], Oiseth, S.K[2]., P.G. Hartley[2] and K.M.McLean[2]

1. Bragg Institute, ANSTO, PMB1, Menai, New South Wales, Australia 2234
2. CSIRO Molecular Science, Bag 10, Clayton South, Victoria 3169, Australia

Keith.McLean@csiro.au

Plasma polymer coatings adhere to and contour the surfaces of most organic and inorganic materials, and are attractive as surface chemical modification systems, since they offer both robustness and inherent surface chemical functionality for further surface chemical derivatisation. A variety of techniques have been used to characterise the physico-chemical properties of surfaces of plasma polymer films. In many cases, however, it is also desirable to probe the internal structure of both modified and unmodified plasma polymer coatings in order to optimise their properties for a given application. Reflectometry techniques are now becoming increasingly important in the characterization of nano-scale structured interfaces. X-ray reflectivity in particular is ideally suited to the study of the internal properties of layered film structures on surfaces, yielding data concerning sub surface structure and material properties. Neutron reflectivity meanwhile offers the ability to characterise surface layers in aqueous environments.

In this study heptylamine and allylamine plasma polymer coatings were prepared on silicon wafers, and analysed using X-ray reflectometry before and after further surface modification procedures (e.g. adsorption of protein species from solution). Surface chemistry of the coatings was characterised using X-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) was also used to characterise both roughness and local film thickness at step-edges on the films. The excellent reflectivity data obtained demonstrate the suitability of plasma polymers for reflectivity studies (primarily due to their low surface roughness). Experiments on plasma polymer layers using neutron reflectivity are also described, which highlight the effect of surface hydration on layer properties.

THE ROLE OF INTERPARTICLE POTENTIAL IN CONTROLLING THE MORPHOLOGY OF SPRAY-DRIED POWDERS FROM AQUEOUS NANOPARTICLE SOLS

J.R. Bartlett[1*], S. Lyonnard[2], E. Sizgek[1], K.S. Finnie[1], Th. Zemb[2] and J.L. Woolfrey[1]

[1] Materials Division, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW, 2234. AUSTRALIA
[2] Service de Chimie Moléculaire, C.E.A. / Saclay, Bât. 125, F-91191, Gif-sur-Yvette cedex , FRANCE

Precursor nanopowders for producing advanced ceramics are often prepared by spray-drying concentrated sols, to produce aggregated particles for ease of handling during subsequent processing. In this study, the effect of ionic strength and solids content on the nanostructure and morphology of mesoporous titania gel microspheres obtained by spray-drying concentrated nanoparticle sols has been investigated using combined small angle and ultra-small angle X-ray scattering (SAXS/USAXS), small angle neutron scattering, electron microscopy and N_2 adsorption. The USAXS and conventional SAXS of the as-prepared powders were measured over three decades in q, enabling their structure to be probed on length scales from 0.5 to > 1000 nm. Absolute scaled measurements in this range show two exponential regimes and a transition region, which were modelled to obtain:

- the surface area of the nanosized pores (Porod region);
- the total porosity of the microspheres (transition region);
- the average size of the microspheres (low-q region).

The relationship between the interaction potential (ionic strength) in the sol and the porosity (micro-structure) of the resulting spray-dried powders will be discussed.

The macroscopic structure (morphology) of the microspheres was also found to be strongly influenced by the ionic strength. In the absence of added salt, fragmentation of the atomised droplets occurs during drying, leading to the formation of fine powder, in addition to gel particles with distorted shapes (*e.g.* donuts). In contrast, addition of appropriate salts results in the formation of well-defined spherical particles. It is shown that these effects can be attributed to the relative magnitudes of the Laplace and osmotic pressures immediately before the sol-to-gel transition. If the Laplace pressure exceeds the osmotic pressure, then well defined spherical particles are obtained. Conversely, distorted particles are formed when the osmotic pressure exceeds the Laplace pressure. For a given droplet with rapidly increasing osmotic pressure during the fast process of drying, the relative magnitudes of the Laplace and osmotic pressures before the sol-to-gel transition thus determine whether compression or fragmentation is favoured.

Keynote Lecture

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POLYMERIZATION IN COMPLEX FLUIDS

Eric W. Kaler[1] and Carlos Co[2]

1. Center for Molecular and Engineering Thermodynamics, Department of Chemical Engineering, University of Delaware, Newark, DE 19716
2. Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH, 45221

kaler@che.udel.edu

Polymerization reactions can be carried out in microstructured fluids, namely microemulsions and vesicular solutions, to yield novel polymer molecules and nanostructures. Microemulsions are equilibrium phases that contain immiscible liquids such as oil and water stabilized by a surfactant film. They are of both scientific and great practical interest. We have carried out polymerization of several monomers in oil-in-water microemulsions and have produced very stable monodisperse latices with particle sizes as small as 10 nm. Fast polymerization rates, high conversions and ultra-high molecular weight polymers are achieved with both oil-soluble and water-soluble initiators. A theory of the process will be described along with confirmatory novel small angle neutron scattering experiments. Further analysis isolates the effects of monomer water solubility, glass transition temperatures, and termination processes on the polymerization pathways. A fairly complete description of the process is in hand.

Closed spherical polymer shells can be synthesized via polymerization of monomers taken up in closed surfactant bilayers called vesicles. Typical vesicle dispersions are fomed by mechanically disrupting a lamellar phase, but vesicles form spontaneously in mixtures of cationic and anionic surfactant. Proper use of surfactant mixtures avoids syntheses of specialized surfactant molecules , and indeed the electrostatic interactions of anionic and cationic surfactants makes available a rich variety of microstructures. The unilamellar vesicles that form spontaneously can be used as templates or molds for polymerization reactions, and the resulting products are characterized by Cryo-TEM and scattering experiments.

NANOSCALE STRUCTURE OF MILK : MILK PROTEIN AGGREGATION

Andrew J. Jackson, John W White

Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

ajj@rsc.anu.edu.au

The nanoscale struture of milk has long been of interest. Much work has focussed on the structure and function of the casein micelle and related calcium salts. This work's aim was to examine the milk fat globule – serum interface. Model milks consisting of hexadecane or toluene as the "fat" component, beta casein or sodium casienate as the protein content, and phosphatidyl choline to form the milk fat globule membrane were studied using neutron and x-ray small angle scattering.

The scattering results from the emulsion experiments revealed significant structure which, through the use of contrast variation, was attributed to aggregation of the protein in solution. Hence the behaviour of solutions of beta casein and sodium caseinate was examined at a range of concentrations and temperatures in order to elucidate the structure of the aggregates. Guinier analysis of the scattering from sodium caseinate solutions gave a consistent radius of gyration of 58±10Å in agreement with the accepted R_g for monomeric beta casein. Evidence of aggregation disappeared from the scattering when the solution concentration was below 3mg/ml.

SELF ASSEMBLY OF MEMBRANE PROTEIN ARRAYS AT THE SOLID/LIQUID INTERFACE

Stephen A. Holt[1], Jeremy H. Lakey[2], Neil Keegan[2] and Sofian M. Daud[1]

1. ISIS, Rutherford Appleton Laboratory, CCLRC, Didcot, OX11 8HA OXON, United Kingdom.
2. School of Cell and Molecular Biosciences, The Medical School, The University of Newcastle-upon-Tyne, NE2 4HH, United Kingdom.

s.a.holt@rl.ac.uk

High density protein arrays on solid surfaces are an increasingly important component of post-genomic technologies where there is a need for protein recognition interfaces in physical devices. Projected applications for these layers include protein array technology for proteome screening; diagnostic "point of care" devices aimed at specific protein or metabolite targets; and biocompatible surfaces for nanoscale design of implant surfaces. Protein-protein recognition usually relies upon the three-dimensional fold of both components. The retention of tertiary structure with the correct orientation relative to the substrate is therefore essential for a well defined functional protein array.

The outer membrane pore forming protein OmpF from *Escherichia coli* has been used to produce protein arrays on gold coated silicon substrates. The protein has been mutated with the addition of a single cysteine residue enabling chemisorption to the gold substrate with the required orientation. A thiolipid is then added to the sample cell to complete the self assembling membrane mimetic at the interface. This approach offers opportunities for electronic detection of events at the interface. Surface plasmon resonance, fluorescence, mass detection and impedance spectroscopy have been used to study these assemblies. Our model depends upon assumption as to the relative distributions of the lipids, proteins and water and the overall thickness of the layers of lipid and protein. Not only is neutron reflectometry the only method which can probe these features, but also we have a clearly defined model which can be compared with the experimental results.

Modelling of the data thus far indicates that we have assembled a protein layer, with the correct orientation, at the interface and that subsequent assembly steps do incorporate lipid into the spaces between the membrane protein structures. Further analysis is underway to determine surface coverage and the ratios of protein to lipid in the layers.

FORMATION MECHANISMS IN SURFACTANT-TEMPLATED SILICATES

Karen J. Edler, Stephen J. Roser, Cristina Fernandez- Martin

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

k.edler@bath.ac.uk

Surfactant-templating is one method of creating nanostructured arrays in inorganic materials. Interactions between surfactant micelles in solution and inorganic precursor molecules as the inorganic polymerises, result in a variety of surfactant liquid crystalline phases trapped within an inorganic matrix. While this method is now routinely used to create nanoporous materials the processes by which the ordered nanoscale structure develops from dilute solutions is still a matter of debate.

We have investigated the development of nanoscale structure in surfactant templated silicates which grow under acidic conditions. In these syntheses, as well as ordered nanoscale structures, the macroscopic form of the material can be controlled. Under different conditions the composites form as uniform spheres, “single crystals”, gyroid shapes or thin films at solid-solution or air-solution interfaces. We have carried out experiments on both surfactant-templated mesoporous films at the air/solution interface and structure development in non-film forming solutions using a range of complementary *in situ* techniques including specular and off-specular x-ray reflectivity, grazing incidence diffraction, small angle X-ray and neutron scattering and Brewster angle microscopy.

From this data a general formation mechanism for the interaction between silica and surfactant micelles in this system is proposed. The polymerising silica can be considered as a polyelectrolyte that interacts with the surfactant micelles. This polyelectrolyte-surfactant system can, under some conditions, undergo a liquid-liquid phase separation (coacervation) at a critical point dependant on the charge and molecular weight of the polymer and the charge on the surfactant micelle. Under other conditions the silica-surfactant aggregate remains as a soluble complex in solution. Growth of ordered nanoscale films occurs via both mechanisms, and the pathway followed determines the rate of nanoscale and macroscale ordering, and affects the structures formed. Understanding of this mechanism has allowed extension of the surfactant templating methodology to materials other than silica.

TIME RESOLVED NEUTRON AND LIGHT SCATTERING ON COLLOIDAL GELS

Ronny Vavrin, Veronique Trappe, Anna Stradner, Joachim Kohlbrecher, Frank Scheffold and Peter Schurtenberger

Department of Physics, University of Fribourg, Chemin du Musée 3, 1700 Fribourg, SWITZERLAND

ronny.vavrin@unifr.ch

We have studied the dynamical and structural properties of destabilized nanoparticle suspensions and gels by a combination of small-angle neutron scattering (SANS), dynamic light scattering (DLS) and diffusing wave spectroscopy (DWS). At the SANS instrument of the Swiss neutron source SINQ we have designed a sample environment where we simultaneously perform SANS, DWS and DLS experiments. In addition we have constructed a multi-angle 3D cross correlation experiment that provides an efficient suppression of multiple scattered light and allows for time resolved measurements of the static and dynamic structure factor for transparent and moderatly turbid suspensions. With the combination of these two setups we acces a broad range of length and time scales perfectly suited for the (non-invasisve) investigation of dense nano- and mesostructured complex fluids and solids.

Here we describe the temporal evolution of the structure and dynamic properties of destabilized particle suspensions over a large range of length and time scales. We monitor the initial cluster growth, the crossover from diffusive motion to network fluctuations at the gel point and the subsequent evolution of the network properties with time.

AN X-RAY REFLECTIVITY STUDY OF EVAPORATION INDUCED SELF-ASSEMBLED TITANIA-BASED FILMS

M.J. Henderson [1], A. Gibaud [2], J-F. Bardeau [2], A.R. Rennie [3] and J.W. White[1]

1. Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia
2. Laboratoire de Physique de l'Etat Condensé, Université du Maine, 72085 Le Mans cedex 9, France
3. Uppsala University, The Studsvik Neutron Research Laboratory, S-611 82 Nyköping, Sweden

mjh@rsc.anu.edu.au

Evaporation induced self assembly (EISA) has been used previously to prepare thin mesostructured silica-based and transition metal oxide based films including titania and zirconia. Using the micellar template concept followed by calcination, optically uniform mesoporous thin metal oxide films can be realized. Mesoporosity is a desirable property of materials based on titania, for example in photovoltaic devices where mesopores would facilitate charge diffusion. However, a large fraction of organised hybrid materials are nanolaminates. This may be so in nature, for example in biomineralisation or by design, where periodic arrangement of film components can be useful for multilayer dielectric coatings, or electron transport for use in optical information storage. For any application a fundamental understanding of the structure of the interfaces by measurement and analysis is a pre-requisite for controlling device performance.

Our primary aim was to use x-ray reflectometry to monitor the time-dependent changes of Bragg diffraction obtained from a titania based film prepared by an EISA method from a $TiCl_4$ -based solution containing a poly(ethylene oxide) surfactant as the template. In addition to following the change in the structure as a function of time, we studied the film thickness and refractive index responses to relative humidity of mesostructured TiO_2 films. These variables included the deposition technique (whether by droplet evaporation or by dip coating), the surfactant:TiO_2 ratio, and the effect of diluting the deposition solution. In order to prepare homogenous highly structured films we explored film deposition at low relative humidity and post-treatment at high relative humidity.

Keynote Lecture

SPONSORED BY THE COLLOID & SURFACE SCIENCE DIVISION OF THE RACI

WATCHING MOLECULES DIFFUSE AT SOFT AND HARD SURFACES

Steve Granick

Departments of Materials Science and Engineering, of Chemistry, and of Physics, University of Illinois, Urbana, IL 61801, USA

Rich new chemistry and physics emerge when one considers surface dynamics, where the environment is distinctly different than in bulk. The intuition of what to expect based on bulk properties is found to break down. Using single-molecule imaging (SMI) and fluorescence correlation spectroscopy (FCS) after two-photon excitation, this laboratory has quantified surface diffusion of various macromolecules adsorbed onto hard surfaces (glass and mica), soft surfaces (supported phospholipid bilayers), and between surfaces (molecularly-thin films in a modified surface forces apparatus). A new picture emerges of what determines surface diffusion.

UNNATURAL PROTEINS FOR THE CONTROL OF SURFACE FORCES

Aysen Tulpar[1], Doug Henderson[2], Richey Davis[2], Kevin van Cott[2] and William Ducker[1,3]*

1. Department of Chemistry, Virginia Tech, VA, USA.
2. Department of Chemical Engineering, Virginia Tech, VA, USA.
3. Department of Chemical Engineering, University of Melbourne, Melbourne, Australia

*wducker@vt.edu

We introduce a method for the stabilization of colloidal particles via the synthesis and adsorption of unnatural proteins. Biosynthesis of protein-based polymers offers the advantages of preparation of complex sequences through control of the primary sequence, monodisperse polymers, ease of combinatorial search for anchor blocks, environmentally-friendly synthesis, use of water as the solvent, and incorporation of a palette of known natural proteins. We have synthesized an unnatural protein with the sequence: thioredoxin-$Pro_{39}Glu_{10}$ for modification of the forces between alumina particles. The polyglutamate sequence, Glu_{10}, is anionic (pH > 3) and is designed to anchor the protein to positively charged solids, e.g. alumina in water (pH <9). The polyproline sequence, Pro_{39}, is neutral. The thioredoxin is a recombinant from of the natural globular protein with a histidine patch (HisPatch-Thioredoxin), and is zwitterionic. The combined thioredoxin-Pro_{39} sequence is hydrophilic with pI ~ 6.3. This block is designed to remain in solution, thereby providing a steric barrier to the approach of two particles in a range of salt and pH conditions. Ellipsometry experiments show that thioredoxin-$Pro_{39}Glu_{10}$ does adsorb to alumina. Force measurements with the Atomic Force Microscopy (AFM) colloid probe technique show that adsorption of the fusion protein leads to repulsive forces that decay exponentially with the separation between the surfaces, and are independent of salt concentration in the range 0.001–0.1 M KNO_3. This demonstrates that the repulsive forces are not electrostatic. We hypothesize that the repulsion is due to confinement and loss of solvent for the adsorbed polymer. The loss of a salt-dependent force shows that adsorption of the fusion protein has effectively neutralized the charge on the alumina.

SOL-GEL PARTICLES FOR CONTROLLED RELEASE APPLICATIONS

Linggen Kong, Scott McNiven, Kim Finnie, Hui-Qiang Lin, Vu Nguyen
and Christophe Barbé

ANSTO, Materials and Engineering Science, Menai NSW 2234

We present a generic approach to the synthesis of sol-gel silica matrices for encapsulating bioactive species, and controlling their subsequent release over periods ranging from hours to months. The bioactive species are incorporated into the matrix during gelation at, or near, ambient temperature, and remain entrapped until the gels are immersed in solution. The release profile can be tailored by controlling the internal structure of the gels (pore volume, size and tortuosity, and surface chemistry). In turn, the gel structure can be precisely tailored by varying such sol-gel processing parameters as the water-to-alkoxide ratio, pH, alkoxide concentration, ageing, drying time and temperature. Hence, the release rate of the encapsulated species is controlled by adapting the structure of the internal pore network to the physico-chemical properties of the drug molecule.

Combining emulsion synthesis with sol-gel technology enables the carrier to be produced in the form of mono-dispersed spherical particles, with an average size that can be varied from 50 nm to 50 µm. The particle diameter is determined by the size of the reverse micelles, which is controlled by the hydrophile-lipophile balance between the surfactant, aqueous phase and non-polar solvent. The release rate of the encapsulated species is controlled by the internal nanostructure of the spheres, which can be tailored (as in bulk gels) by varying the sol-gel chemical parameters.

The ability to independently control the release rate and particle size renders this technology particularly attractive for passive, *in-vivo* targeting of different organs and tumours. Preliminary *in-vivo* bio-distribution results, as well as comparisons with alternative controlled-release carriers based on polymers and liposomes, will also be presented.

DOES EVERYTING DEPEND ON INTERPATICLE FORCES? A REAL PHARMACEUTICS PROBLEM

Nazrul Islam[1], Ian Larson[1], Patrick Hartley[2] and Peter Stewart[1]

1. Department of Pharmaceutics, Faculty of Pharmacy, Monash University, 381 Royal Parade, Parkville 3052, Australia
2. Division of Molecular Science, CSIRO, Clayton 3168, Australia,

ian.larson@vcp.monash.edu.au

Inhalation aerosol therapy provides a useful route of administration of active molecules for both local and systemic action. One of the main devices used to generate aerosols for inhalation therapy is the dry powder inhaler, DPI. DPI's deliver drug in the powder form, generally using the patient's inspiratory airflow for powder deagglomeration and aerosilisation. Effective drug delivery requires deposition of the drug into the pulmonary regions of the lungs. To reach the alveoli (large surface area, high blood flow), particles need to have an aerodynamic diameter of less than ~6 μm. DPI's utilise perhaps the most simple pharmaceutical formulation, a physical mixture of micronised drug particles and large inert carrier particles. The performance of these devices is governed by the degree of disperion and aerosolisation of the formulation which are controlled by the interparticulate forces. But while these delivery systems have been around for decades, little is known about the mechanisms of dispersion or means by which their efficiency can be increased. Commerical DPI's are surprisingly inefficient with only ~15-20% of their drug load delivered to the alveoli.

This study examined the relationship between adhesion forces present in DPI formulations and the efficiency of these formulations. AFM colloid probe force measurements were used to quantify adhesive forces between drug particles (real and model) and various grades of large carrier particles. The efficiency of the DPI formulations was determined by measuring the percentage of aerosolised drug with an aerodynamic diameter of less than ~6 μm. The surface roughness of the carrier particles was measured using laser scanning confocal microscopy. There appeared to be no simple relationships between any of the parameters investigated in this study. Possible reasons for this will be given as will an outline of ongoing investigations.

SURFACE MODIFICATION OF BIODEGRADABLE POLYMERS USING A LAYER-BY-LAYER APPROACH

Laurence Meagher[1] Wei-Bor Tsai[2], and Helmut Thissen[1]

1. CSIRO Molecular Science, Bag 10, Clayton South, VIC 3169
2. Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan

Laurence.Meagher@csiro.au

A growing number of biomaterials and tissue engineering applications rely on the availability of appropriate biodegradable polymers, however, the choice of synthetic biodegradable polymers available is extremely limited. Surface modification of these polymers provides a solution since the surface properties can be tailored to specific applications. However many surface modification methods are not suited for biodegradable polymers. The ideal method would be a simple and versatile procedure which can be applied to complicated geometries such as porous scaffolds and provide a completely biodegradable coating. In this study, we present application of the layer-by-layer (LBL) assembly of poly(amino acid)s to biodegradable substrate materials for use in biomaterials and tissue engineering.

Poly(D,L-lactide) [PDLLA] (Boehringer Ingelheim) was used as a substrate material. Incubations with poly(L-lysine) [PL] and poly(L-glutamic acid) [PG] (Fluka) were carried out in phosphate buffered solutions (2.5 mg/ml, 15 min). Surface hydrolysis was carried out in a 0.01 M sodium hydroxide solution for 15 min. Surface characterisation techniques used were X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscope (AFM) interaction force measurements. Cell attachment and proliferation assays were carried out using porcine chondrocytes isolated from fresh porcine articular cartilage.

Successful surface modification was verified by higher nitrogen concentrations in the surfaces with up to five layers of oppositely charged poly(amino acid)s compared to virgin and hydrolysed PDDLA samples. Surface force measurements indicated that adsorption of poly(L-lysine) resulted in reduced negative surface potentials until after the third PL layer where the surface potential was positive. When PL was the outer layer, the adsorbed poly(amino acid) coating was essentially non-compressible and good agreement with DLVO theory was obtained. For both PG layers, an electrosteric force was measured.

Cell culture experiments showed that for LBL coatings presenting PL, significantly enhanced initial chondrocyte attachment was observed. However longer term cell culture experiments show a different picture. Parallel experiments using serum versus serum free culture conditions demonstrated that adsorbed serum proteins were responsible for this effect.

Keynote Lecture

SPONSORED BY IWRI CENTRE FOR NANO- AND BIO-MATERIALS

RF-PLASMA SURFACE ACTIVATION AND ANALYSIS OF POLYMERS FOR BIOMEDICAL MATERIALS AT THE NANOMETER SCALE

Hans Jörg Mathieu

Swiss Federal Institute of Technology Lausanne, EPFL – Materials Science and Technology
IMX, Station 12, 1015 Lausanne, Switzerland

Hansjoerg.Mathieu@EPFL.ch

Biomaterials in contact with biological systems are prepared by functionalization of soft polymer surfaces to prevent or reduce non-specific protein adsorption. A radio-frequency (RF) plasma is used for surface activation which changes the chemical surface composition within the first 10 nm region [1,2]. Two examples are presented:

(1) NH_3-H_2 plasma treated Polystyrene (PS) chips used for enhanced biological-immobilization for sensors. Such biosensors use fluorescence immunoassays in medical diagnostics. The development of such sensors needs chemical control of the surface composition X-ray Photoelectron Spectroscopy (XPS) and Contact Angle Measurements (CAM) were applied to probe chemical composition with the first 10 nm [3].

(2) *Pseudomonas aeruginosa* is one of the most prevalent bacterial strains in a clinical environment, responsible for 30% of pneumonia cases occurring in intubated patients. [4] A systematic study of plasma deposition to create a plasma fluoropolymer film on native Polyvinylchloride (PVC) is presented. This coating serves as a platform for the preparation of non-fouling surfaces through the physisorption of Polyethylene oxide-like (PEO) polymers. XPS and CAM measurements will be presented to highlight the modifications induced.

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MASSIVE BIOCOLLOID LIBRARIES FOR DISARMING DEADLY VIRUSES

Bronwyn Battersby[1,2], Andreas Ruhmann[2] and Matt Trau[1]

[1] Centre for Nanotechnology and Biomaterials, The University of Queensland, St Lucia 4072, Australia
[2] Nanomics BioSystems Pty Ltd., Level 4, Building 68 Chemistry, The University of Queensland, St Lucia 4072, Australia

bbattersby@uq.edu.au

Deadly outbreaks of viral diseases affect many hundred million people annually worldwide with tens of thousands of fatalities. The case fatality in patients can be as high as 50% and there are currently very few effective vaccine or antiviral drugs available.

Viral proteases are enzymes that help liberate the individual viral proteins from the precursor by catalyzing the hydrolysis of proteins at specific positions. Inhibition of these proteases, which are essential for viral replication, represents a valid mechanism for intervention and potential treatment of viral and/or parasitic diseases. Many pharmaceutical companies are attempting to develop new protease inhibitor drugs that control viral diseases by interfering with this process of viral propagation. Peptide-based protease inhibitors are designed to block the protease enzyme, thereby preventing the enzyme from carrying out its biological function and ultimately inhibiting viral replication. To help combat new outbreaks of infectious viral disease (*ie.*, West Nile and Severe Acute Respiratory Syndrome), the rapid identification of the function of any associated viral protease will aid in the development of substrate-based inhibitor drugs. Thus, the ability to screen existing and newly discovered proteases against a massive library of peptides will not only provide important insights into the mechanism of activity of the protease but will also provide leads for better peptide-based protease inhibitor drugs.

To this end, we have synthesized large polypeptide libraries on functionalized silica beads (~30 μm) using the combinatorial split-and-mix technique. This results in a different peptide being synthesized on each bead. In order to distinguish the particles and identify the bioactive peptides, the beads are optically barcoded with multiple fluorescent colloidal particles, < 1 μm in diameter. Detecting and decoding the barcode through high performance microscopy instrumentation permits identification of bioactive peptides which may be suitable for further validation as protease inhibitors.

BIOMIMCRY OF THE EXTRACELLULAR MATRIX FOR ENDOTHELIALIZATION

Sharon Sagnella[1], Eric Anderson[2], Naomi Sanabria[1], Roger E. Marchant[1,2],
and Kandice Kottke-Marchant[1,3]

1. Department of Biomedical Engineering, Case Western Reserve University, Cleveland, OH 44106, USA
2. Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA
3. Department of Clinical Pathology, Cleveland Clinic Foundation, 9500 Euclid Ave., Cleveland, OH 44195, USA

sms34@cwru.edu

Biomimetic materials that mimic the extracellular matrix (ECM) provide a means of controlling cellular functions such as adhesion and growth, which are vital to successful engineering of tissue-incorporated biomaterials. In order to address this issue, novel "extracellular matrix (ECM)-like" biomimetic surfactant polymers consisting of a poly(vinyl amine) (PVAm) backbone with pendant cell adhesive peptides derived from the heparin and the central cell binding domains of fibronectin were developed to improve endothelial cell adhesion and growth on vascular biomaterials.

Surfaces containing heparin-binding peptide (HBP) sequences were examined for their ability to promote human pulmonary artery endothelial cell (HPAEC) adhesion and growth (HBP1: WQPPRARI, HBP2: SPPRRARVT, HBP1:RGD, and HBP2:RGD) and compared with cell adhesion and growth on fibronectin (FN). Polymer surfaces in which the positively charged arginine (R) residues were changed to alanine (A) residues in the two peptides were utilized as negative controls.

HPAEC adhered fairly equally showing similar stress fiber and focal adhesion formation on all HBP containing materials and the positive FN control. However, the HBP alone was unable to support long-term HPAEC growth and survival showing a loss of focal adhesions and cytoskeletal disorganization by 24 hrs after seeding. With the addition of RGD, the surfaces behaved similarly or better than FN. The negative control polymers showed little to no initial cell attachment, and the addition of soluble heparin into the media reduced initial cell adhesion on both the HBP2 and the HBP2:RGD surfaces. These results indicate that the HBP may be important in promoting initial HPAEC adhesion and spreading, but is not sufficient for long-term endothelialization.

THE SELF-ASSEMBLY OF ALIGNED CARBON NANOTUBE ARRAYS FOR COMMUNICATING WITH PROTEINS

J. Justin Gooding[1], Alison Chou[1], Jingquan, Liu[1], Till Böcking[1,2], Nagindar Singh[1],
D. Brynn Hibbert[1], Dusan Losic[3], Joe G. Shapter[3]

1. School of Chemistry, The University of New South Wales, Sydney, NSW, 2002, Australia.
2. School of Physics, The University of New South Wales, Sydney, NSW, 2002, Australia.
3. School of Chemistry, Physics and Earth Sciences, Flinders University, SA 5001, Australia

justin.gooding@unsw.edu.au

Bioelectronics involves the integration of biological molecules with electronic elements and is of intense interest for biosensing, creating electronic readouts of biomolecular function, the assembly of nanocircuit elements and the conversion of biocatalytic processes into electrical power [1]. A crucial step in all these applications is the transfer of electrons to and from the biological molecule. In many instances however the redox centre of protein of interest is embedded deep within the tertiary structure of the polypeptides. Effective communication to such proteins could be achieved by building conduits for electron movement from the electrode up into the protein. Carbon nanotubes are ideal for this purpose as they have good electron transport properties to redox enzymes and because of their small size, carbon nanotubes could potentially be brought up inside proteins, close to the active site.

Progress towards interfacing carbon nanotubes with redox enzymes is outlined using self-assembly of single-walled carbon nanotubes (SWNT). The oxidative cut SWNTs have carboxylic acid groups on the ends of the tubes which are convenient for coupling with amine groups such as those found on proteins. The tubes are aligned by self-assembly onto a gold electrode modified with an amine terminated self-assembled monolayer. Tapping mode atomic force microscopy measurements confirm the tubes are standing normal to the electrode surface and XPS and FTIR are used to characterize the chemical species on the ends of the tubes. Subsequently, a small redox protein, microperoxidase MP-11, is attached to the other end and interrogated electrochemically. The rate of electron transfer to the enzyme is calculated and found to be independent of the length distribution of the nanotubes [2]. The next step in using SWNTs to communicate with enzymes is to interface nanotubes with proteins where the redox protein has an active site embedded deep within the glycoprotein. e.

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BIOCONJUGATION OF FLUORESCENT RARE-EARTH-DOPED NANOPARTICLES

Felix Meiser, Frank Caruso

Department of Chemical and Biomolecular Engineering, Centre for Nanoscience and Nanotechnology, The University of Melbourne, VIC 3010, Australia,

fmeiser@unimelb.edu.au

Biolabeled nanoparticles have drawn enormous interest in recent years. Fluorescent rare-earth-doped lanthanum phosphate nanoparticles with a narrow size distribution of 5-6 nm have been synthesized by Riwotzki *et al.* 2001.[1] The fluorescence is due to transitions between the well-shielded f-electron and the d-electron states, as well as their local symmetry in their guest crystal. The emission can be tuned by varying the dopant ions (Ce, Tb, Eu etc.). These properties along with their high quantum yield (up to 61%) and high chemical and photobleaching stability make rare-earth-doped nanoparticles potentially attractive biolabels.

The nanoparticles were first modified using the biofunctional molecule 6-aminohexanoic acid. This significantly enhances the colloidal stability of the nanoparticles in water and also provides a carboxylic acid functionality for subsequent protein conjugation. To demonstrate bioconjugation, the tetrameric protein avidin was used. Using the crosslinker ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC), avidin was covalently coupled to the surface of the nanoparticles. The nanoparticle-avidin bioconjugates were characterised by various methods, including absorbance and fluorescence spectrophotometry, microelectrophoresis, analytical ultracentrifugation, and transmission electron microscopy.[2] The bioaffinity of the bioconjugates was verified in binding assays with the dye biotin-fluorescein and in a microarray with biotinylated anti-mouse IgG.

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ADSORBED LAYER STRUCTURE AND CRYSTAL GROWTH MODIFICATION

Jeannette R. McAlpine and Gregory G. Warr

School of Chemistry, The University of Sydney, NSW 2006, Australia

j.mcalpine@chem.usyd.edu.au

Over the past few years atomic force microscopy (AFM) studies have demonstrated that adsorbed surfactant layers at the solid-solution interface frequently have a periodic lateral structure. Spherical and cylindrical aggregates have been imaged patterning hydrophilic substrates including mica, quartz, kaolinite, rutile, and silica; the formation of mesh structures on mica has also been reported recently. In this study, AFM was used to examine the morphology of adsorbed surfactant layers on calcite, an ionic crystal, and to investigate *in situ* whether permanent nanoscale patterning of the crystal surface could be induced using surfactant aggregates as templates.

Straight cylindrical aggregates with a nearest neighbour-spacing of 5.8 nm were imaged when the $10\underline{1}4$ cleavage plane of calcite was contacted with 7 mM tetradecyltrimethylammonium bromide (TTAB) in a saturated solution of $CaCO_3$ at pH 10. Continued exposure to the solution resulted in the growth of multiple layers of TTAB-templated $CaCO_3$ structures, with a cross-section through the sample revealing underlying layers of cylindrical structures parallel to those at the solid-solution interface. The thickness of the TTAB-templated growth layer was at least 109 nm.

Under the same experimental conditions, a single layer of curving cylindrical aggregates with a nearest neighbour-spacing of 5.5 nm was found to form on mica. Exposure to 7 mM TTAB in a five-fold supersaturated $CaCO_3$ solution at pH 10 resulted in the growth of multiple layers of cylindrical $CaCO_3$ structures to a height of 19 nm above the mica surface. These structures retained the curving morphology previously seen, however nearest neighbour-spacing was found to have increased to 6.3 nm. Replacement of TTAB by tetradecyltrimethylammonium carbonate resulted in the growth of straight cylindrical $CaCO_3$ structures similar to those observed on calcite, with multiple layers of these structures forming to a height of 60 nm above the mica surface.

THE SURFACE PROPERTIES OF CRYSTALLINE PHARMACEUTICAL SOLIDS

Jerry Y. Y. Heng, Alexander Bismarck and Daryl R. Williams

Department of Chemical Engineering and Chemical Technology, Imperial College London,
South Kensington Campus, London SW7 2AZ, United Kingdom

d.r.williams@imperial.ac.uk

The surface properties of crystalline materials may influence its wettability, bioavailability, dispersivity, flowability and compactibility. Thus, a comprehensive understanding of pharmaceutical solids surface properties is of both fundamental and practical importance in pharmaceutical product and process engineering.

In this study, paracetamol, aspirin and ibuprofen macroscopic single crystals (>2cm) were crystallised via slow solvent evaporation. The advancing contact angles of the various facets of these crystals were determimed using a liquid sessile drop, and their surface energy were determined using Young's equation as well as various semi-emperical equations. It was observed that contact angles of probe liquids are significantly different on various facets for the same crystalline material. The dispersive surface energy, γ_s^d were fairly constant whilst significant variations in the polar surface energy, γ_s^p were observed. The magnitude of γ_s^p was found to be dependent on the functional groups present, their density and molecular orientation for the different facets. These observations were consistent with results obtained using X-ray photo electron spectroscopy.

Particulate samples (diameters 30µm to 500µm) were prepared by milling of macroscopic crystals, as well as by rapid temperature drop of supersaturated solutions of various actives. These particulate materials were then characterised using inverse gas chromatography. Upon milling induced surface fracture, paracetamol revealed an internal surface differing extensively from the original external surface. The γ_s^d increased by >20% while γ_s^p was significantly lower. Milling of crystals resulted in either crystal fracture exposing the weakest attachment energy facet or amorphisation. Rapid solution recrystallisation resulted in particulate samples with surfaces similar to those observed external properties of macroscopic crystals.

The crystalline solids examined here revealed anisotropic surface properties representative of their local surface chemistry and structural morphology. Milling was shown to result in creation of particles with new surfaces whose properties could vary significantly from crystal surfaces formed via solution crystallisation.

HYDROXAMATE LIGANDS AND BACTERIAL ADHESION TO METALS

Yang Jing and A. J. McQuillan

Department of Chemistry, University of Otago, P.O. Box 56 Dunedin New Zealand

jing@alkali.otago.ac.nz

Siderophores are iron uptake agents produced by numerous bacteria in iron deficient situations, normally containing bidentate hydroxamate, catecholate or carboxylate groups with high affinity for iron ions. A recent in-situ ATR-IR spectroscopy study on titanium dioxide and iron oxide thin films showed that pyoverdin PaA, a siderophore secreted by *Pseudomonas aeruginosa*, forms covalent bonds with metal ions on a metal (oxide) surface. This indicates that pyoverdin and other siderophores may also play a significant role in bacterial adhesion to metal surfaces. However, the interaction between the catecholate group in the siderophore with the surface can be clearly identified from the IR spectra data while that of the two hydroxamate ligands was not distinctive which needs further investigation. A better understanding of the chemical nature of siderophores adsorbed on metal surfaces may help to establish new strategies for biofilm control that are now urgently required in many industries and for medical safety.

In the present study, four hydroxamic acids were selected to model hydroxmate groups in most naturally occurring siderophores: acetohydroxmic acid, N-methylformohydroxamic acid, N-methyl-acetohydroxmic acid and 1-hydroxy, 2-piperidone. The adsorption behavior of these ligands on titanium dioxide thin films was investigated by in-situ ATR-IR spectroscopy with respect to concentration and pH. The binding strength between the ligands and titanium dioxide surface was measured and evaluated with the Langmuir adsorption model. It was found that all the ligands adsorb strongly and can form surface complex on titanium dioxide surface. Characteristic vibration modes were assigned by comparing observed and calculated IR spectra of their solutions at pH=6 and 12. All the geometry optimization and harmonic vibrational calculations of the cis-formed neutral molecules or anions of these ligands was performed with the Spartan program using DFT theory with B3LYP fuctional and 6-31+G(d) basis set.

PROTEIN INTERACTION WITH MODIFIED BIOINTERFACES

Kristen Bremmell[1], Zahida Ademovic[2], Peter Kingshott[2], Hans Griesser[1]

1. Ian Wark Research Institute, University of South Australia, Mawson Lakes SA 5095.
2. Danish Polymer Centre, Risø National Laboratory, Roskilde Denmark

kristen.Bremmell@unisa.edu.au

The development of bio-materials resistant to protein and cell adsorption for use in vivo and in diagnostic techniques has been an important area of study and remains a challenge to biomaterials research. Understanding the mechanism of protein interaction with these surfaces may provide further impetus for development of non-fouling surfaces.

In this study we have investigated fibrinogen adsorption using ^{125}I-radiolablelled fibrinogen adsorption experiments and atomic force microscopy (AFM) as complementary techniques to understand the process of protein interaction with the non-fouling surfaces. The substrates were prepared through plasma polymerization of PEO-like surfaces. A series of surfaces were prepared using different plasma conditions, which produced surfaces displaying various degrees of protein adsorption. Interaction of fibrinogen with the surfaces was then investigated by measuring the interaction forces between a protein-coated sphere in the AFM. On approach, a repulsive force is present and is independent of solution ionic strength. Adhesion between the protein and surface is observed on separation after contact. The characteristic adhesive events decrease in extent and magnitude as the surface demonstrates greater protein adsorption. Changing the applied load resulted in altered protein interaction with each of the surfaces. The interaction force results will be discussed with reference to protein-surface interaction.

A MULTI-TECHNIQUE INVESTIGATION OF PROTEIN ADSORPTION AT A HYDROPHILIC SOLID INTERFACE

Y.M. Efimova, S. Haemers and A.A. van Well

Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, 2629 JB, Delft, the Netherlands

vanwell@iri.tudelft.nl

We study protein adsorption at solid, hydrophilic interfaces with a multi-technique approach. Neutron reflectometry is used to determine the final volume fraction profile. FTIR-ATR is used to measure the adsorption kinetics and possible changes in the secondary structure during adsorption. With radio-labelled proteins and the so-called thin-gap method we determine the exchange between the proteins adsorbed and those in solution. For all techniques a parallel-plate flow cell is used, enabling us to control the supply rate of proteins to the surface. Among others, we used a TiO_2 surface. By changing the pH, the surface charge can be varied (negative, 0, positive). Three different types of proteins were investigated.

ON THE CORRELATION BETWEEN MOLECULAR INTERACTIONS AND BEHAVIOR OF POLYMER-FUNCTIONALIZED SURFACES

Suzanne Giasson

Department of Chemistry and Faculty of Pharmacy University of Montreal, J.A. Bombardier,
C.P. 6128 Succ. Centre-Ville, Montreal, Quebec, Canada, H3C 3J7

suzanne.giasson@umontreal.ca

Polymers at surfaces play a crucial role in surface modification and functionalization. Their role is usually fulfilled by a combination of different types of interaction (electrostatic, steric, hydrophobic, etc). Several experimental and theoretical studies have explored the intrinsic structure and properties of polymer-coated surfaces as a function of grafting density, solvent condition, charge density, ionic strength, pH. The normal and lateral forces between two opposing and moving surfaces bearing different polymers have also been largely investigated. However, the correlation between molecular interactions of polymer-bearing surfaces and their structure, properties and functions, which is not yet fully understood, is essential to better control the behavior of polymer-functionalized surfaces. In this context, we have investigated the molecular interactions and behavior of different water soluble polymers (charged and non-charged) at solid-liquid and liquid-liquid interfaces using Surface Forces Apparatus and Langmuir-Blodgett techniques. We will present results which will help explaining, for instance, how the hydration effects associated with electrostatic interactions of charged polymers can govern the lubricating properties of surfaces (Nature, 2003). We will also explore the combined effect of hydrophobic and electrostatic interactions of copolymers on the stability of lipid membranes (Langmuir, 2004). Moreover, we will discuss the effect of normal load on the lateral molecular dynamic behavior (nanorheology and nanotribology) of water-soluble polymer coated surfaces.

RACI
Divisional
Plenary
Lecture

PROTEIN ORDERING ON LIPID MEMBRANES - BIOMIMETIC PHASE TRANSITIONS

Alice P. Gast

Department of Chemical Engineering, Massachusetts Institute of Technology

gast@MIT.EDU

Giant unilamellar vesicles (GUVs) provide ideal model lipid bilayer membranes for the study of membrane protein structures and cytomimetic processes. An understanding of the intermolecular forces governing protein assembly on and within model cellular membranes helps to elucidate the physical processes governing cell membrane phase separations. We will discuss two such membrane phase transitions. In the first type of transition, the protein streptavidin, bound to the exterior of GUVs alters the membrane mechanical properties when it crystallizes and this ordering can result in changes in the vesicle shape. These surface-bound crystallization transitions can be manipulated by altering the pH or ionic strength of the surrounding medium. We are investigating the way these bound protein layers affect membrane mechanical properties and the retention of solutes inside the vesicle. We study their behavior during mechanical and osmotic stress experiments. There are other situations where surface-associated proteins interact with the local membrane lipid composition. The second system we describe involves membrane microdomains undergoing lipid phase separation and binding proteins to the surface. Caveolae are an example of phase separated membrane microdomains that influence membrane curvature and involve distinct surface protein structures. GUVs offer a model environment for the biophysical study of these complex phase separations.

Keynote Lecture

SPONSORED BY SRC FOR MULTIPHASE PROCESSES

CONTROLLING FORCES BETWEEN PARTICLES WITH BIFUNCTIONAL MONOALKYL MOLECULES

F.F. Lange

Materials Department, University of California, Santa Barbara

Without repulsive shrouds, particles attract one another to form touching, cohesive networks because of their attractive van der Waals forces. Either the electrostatic double layer method, which shrouds the particles with ions (counterion clouds), or the steric method (molecular brushes), can be used to produce repulsive forces. Repulsive forces arise when the shroud of one particle penetrates that of an approaching particle. The separation distance needed to produce repulsion can be controlled by the 'thickness' of the shroud. The van der Waals force can be completely shielded for thick shrouds and the particles are strongly repulsive. When the interaction occurs at very short separation distances, the van der Waals force first causes the particle to be attractive, but repulsive before they touch. For this case, the particles sit in a potential well and form a weakly attractive, but non-touching network. Forces are required to pull attractive particles apart; these networks have a yield stress that is required for shape forming ceramic powders.

The use of akylated powder (OH-M- surface sites reacted with alcohol) and bifunctional molecules that strongly adhere to the surface (C_{12}MonoAlkyl Phosphate) are used to form strongly hydrophobic powders. Different surfactants (e.g., CTAB) adsorbs to produce highly repulsive, hydrophilic particles. The adsorption of these molecules and their effect on rheology, and shape forming will be the major topic of this presentation.

SILANE-BASED SELF-ASSEMBLED MONOLAYERS FOR WATER TREATMENT

Peter Majewski

Ian Wark Research Institute, University of South Australia

"Water" is one of the most abundant substances in the world. However, the conversion of water from various sources to potable and good quality drinking water can be a very demanding task for drinking water suppliers. Shrinking fresh water resources, increasing salinity of bore water, especially in arid areas of the world, and increasing demand in potable, drinking, and irrigation water requires the utilisation even less quality water. Over the past years, the use of organic Self-Assembled-Monolayers (SAMs) for controlling the hydrophobicity of surfaces, modifying the surface chemistry, and synthesis of ceramic thin films has attracted considerable interest worldwide, because of its easy handling and considerably low technical expenditure. However, the use of functionalised SAMs for the removal and immobilisation of inorganic, such as noxious metal cations, has not been studied thoroughly.

The potential of silane-based SAMs with different functionalisation to remove metal cations of various elements from water and the associated chemical reactions at the surface of the SAM as well as those in the water has been studied. The results indicate that functionalised SAMs have a high potential for removing metal cations even at very low concentrations of the cations and over a large pH range of the treated solutions.

BOUNDARY SLIP IN NEWTONIAN LIQUIDS: AN EXPERIMENTAL APPROACH

Vincent Craig

Department of Applied Mathematics, Australian National University, Canberra, ACT 0200
Australia

vince.craig@anu.edu.au

In recent years there has been an explosion of interest in slippage of Newtonian liquids at solid interfaces, especially due to the exciting developments in the fields of microfluidic and microelectromechanical devices. Here we provide an overview of the research conducted at the Australian National University, on the direct measurement of hydrodynamic forces in Newtonian liquids. We use colloid probe atomic force microscopy and a novel nanorheological custom-built apparatus to measure slip at the interface with functionalized and surfactant-coated surfaces. We also try to reconcile or explain the discrepancies between some of the published results, in order to gain a better understanding of the parameters which determine liquid slip.

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PHOTO-POLYMERISATION OF SURFACTANT STRUCTURES AT SOLID INTERFACES

Paul Fitzgerald and Kazue Kurihara

Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2–1–1 Katahira, Aoba-ku, Sendai 980–8577, Japan

paul@tagen.tohoku.ac.jp

We have investigated the polymerisation of surfactant self-assembly structures at solid surfaces, which can form spheres, rods, bilayers (and combinations of these) on length scales of the order of one to 10 nm. Polymerising these structures should ultimately render them permanent to rinsing, which is necessary for any future applications.

We have investigated the polymerisation of a cationic surfactant with a polymerisable counterion, tetradecyltrimethylammonium styrene sulphonate (TTASS). In situ polymerisations were conducted on both mica and silica by photo-irradiation. Polymerisation was followed by absorbance spectroscopy in the region 190 ~ 300 nm and morphological changes were studied with Atomic Force Microscopy (AFM).

Absorbance spectroscopy revealed that polymerisation went to completion after 1.5 ~ 2 hours. The presence of polymer at the surface of silica was spectroscopically confirmed by measuring the spectra after rinsing. The surface excess was estimated to be approximately 2 ~ 5 μmole m^{-2}. Monitoring the peak at 225 nm as a function of rinsing, we observed that the polymerised films were significantly more stable than the unpolymerised films, which were not stable at all to rinsing.

The morphology, prior to polymerisation, on both mica and silica is spheres (or possibly a mesh phase) with a centre to centre spacing of about 8 nm on mica and about 10 nm on silica. The morphology changed little over the course of polymerisation.

Under the right conditions we observed multiple repulsions in the force curve. This corresponds to multiple layers, with spheres as the underlying structure and polymerised rod-like micelles adsorbed over these. After rinsing the surface with pure water the morphology at the surface takes on a rougher appearance with a larger centre to centre spacing but is, for the most part preserved.

SUBMICRON PARTICLES PRODUCED FROM UREA-BASED LIQUID CRYSTALLINE PHASES

Celesta Fong[1], Suresh Bhargava[2], Jamie Booth[2], Calum J. Drummond[1], Irena Krodkiewska[1],
Darrell Wells[1] and Patrick G. Hartley[1]

1. CSIRO Molecular Science, PMB 10, Clayton South, 3169, Australia
2. RMIT, School of Applied Sciences, GPO 2476v, Melbourne, 3001, Australia

celesta.fong@csiro.au

Alkyl ureas are a class of surfactants which have previously received scant attention despite their known anaesthetic activity and effectiveness as alcohol dehydrogenase inhibitors. Much of this oversight stems from the long established belief that the urea head group was not capable of forming liquid crystalline phases. Intermolecular hydrogen bonding within the urea head group is responsible for much of this misconception as this interaction dominates the binary behaviour in water particularly for the short chain alkyl ureas. This work provides evidence for high order liquid crystalline phases in urea based surfactants which are further stable to dispersion into nanoparticles that preserve the integrity of the bulk phase.

For the linear C6-C18 alkyl ureas, the head group interaction remained the dominant factor in determining the melting point behaviour and crystal solubility boundary. Three phases were observed in these systems namely, crystalline solid, a dilute aqueous solution of the alkyl urea plus isotropic liquid and an isotropic liquid. However, the introduction of long chain unsaturation and terpenoid hydrophobes promoted the formation of a (inverse) hexagonal phase. Significantly this phase was stable against dilution and appeared at temperatures close to ambient or the physiological. A further tactic for reducing the influence of hydrogen bonding of the urea head group was modification by the introduction of a hydroxyalkyl moiety.

Colloidal dispersions of the inverse hexagonal phase have been demonstrated in the literature by adulteration of monoolein. These nanoparticles have much reduced viscosities over the bulk phase, high surface area and inherent tortuosity. This provides opportunities for encapsulation of both hydrophilic and hydrophobic small molecules with the added potential for control over release characteristics. In the current study hexosome formation has been verified for a terpenoid urea providing the first example of colloidosome formation not involving monoacylglycerides.

CRYSTAL COMETS: DEWETTING DURING EMULSION CRYSTALLIZATION

Patrick T. Spicer[1] and Richard W. Hartel[2]

1. Complex Fluids Research, Procter & Gamble Corporate Engineering, 8256 Union Centre Blvd., West Chester, OH 45069, USA
2. Department of Food Science, University of Wisconsin-Madison, Madison, WI 53706, USA

spicer.pt@pg.com

Crystallization of oil-in-water emulsions is commonly used to create microstructure in consumer products and to purify small molecules. Natural oils often contain broad chain length distributions so that solid crystals and liquid oil coexist at room temperature. Crystals partitioned at the oil-water interface can bridge oil droplets, a phenomenon known as partial coalescence that can destabilize emulsions. Emulsions containing solid particles are generally stable if the continuous phase preferentially wets the particles, while instabilities result when the dispersed phase does. Interfacial adsorption of particles depends on the oil-water interfacial tension, and the oil-particle contact angle, both of which can be tuned by surfactant adsorption.

Liquid oil emulsion droplets can de-wet their own solid crystals when the surfactant packing parameter is optimized immediately following crystallization. The de-wetting is rapid when cooling rates are high, propelling the droplet around the continuous phase and leaving behind a crystalline "comet tail". At lower cooling rates discrete crystals form and emerge from within the emulsion droplet. The controlled de-wetting of crystals by their own liquid phase offers a means to study emulsion destabilization by solids as well as a new route to self-assembly of colloidal particles.

AGGREGATION OF BLOCK-COPOLYMERS IN AQUEOUS SOLUTIONS: THERMODYNAMICS, STRUCTURE AND DYNAMICS.

Josef F. Holzwarth and Sabine Couderc-Azouani

Fritz-Haber Institute, MPG, Faradayweg 4-6, D-14195 Berlin, Germany.

HOLZWARTH@fhi-berlin.mpg.de

We investigated the thermodynamic and dynamic behaviour of triblock copolymers of the general structure poly-ethylene oxide - poly-propylene oxide - poly-ethylene oxide (PEO-PPO-PEO) in water. Two representative examples were chosen, L64, $(EO)_{13}$-$(PO)_{30}$-$(EO)_{13}$ and F127, $(EO)_{97}$-$(PO)_{69}$-$(EO)_{97}$. The critical micellization temperature (CMT), the enthalpy of micellization ΔH_{mic} and aggregation numbers of 35 to 60 could be determined. The kinetics were characterized by three well defined relaxation processes via iodine-laser temperature-jump and stopped flow. Monomer insertion in the microsecond time range is followed by a size readjustment and finally micellar growth was observed when macroscopic phase separation was approached. Small angle neutron scattering showed aggregates with wet cores of PPO and coronas of fully hydrated PEO. The influence of added surfactants could also be monitored and interactions below and above the CMT of the triblock copolymers were observed, showing synergistic effects. An outlook into future experiments closes the contribution.

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VISCOUS SELF-ASSEMBLY PHASES IN ORAL DRUG DELIVERY

Gregory A Kossena, Tri-Hung Nguyen, Ben J. Boyd, Christopher. J. H. Porter, Ian Larson and W. N. Charman

Department of Pharmaceutics, Victorian College of Pharmacy, Monash University,
381 Royal Pde, Parkville, 3052, Australia

ben.boyd@vcp.monash.edu.au

The oral delivery of lipophilic drugs is complex, involving digestion, dispersion, solubilization and absorption processes. It is well known that the process of digestion of dietary and formulation lipids results in the transient formation of self-assembled liquid crystalline phases such as cubic and hexagonal phase. However the role that these phases play in the solubilization and absorption of lipophilic drugs is not clear.

This study focuses on the impact of viscous self-assembly phases on the oral delivery of a model lipophilic drug, cinnarizine, from two perspectives. Firstly, a bicontinuous cubic phase that may form transiently during the digestion of common formulation lipids based on trilaurin has been identified. Characterization of a bicontinuous cubic phase present in the pseudo-ternary phase diagram of compositions of lauric acid, monolaurin and simulated endogenous intestinal fluid has been conducted. The impact of the presence of this viscous drug-containing mesophase on the absorption of co-administered cinnarizine has been investigated in vivo. Second, in an attempt to reduce the influence of digestion on absorption from a bicontinuous cubic phase, the administration of drug in phytantriol, a non-digestible lipid which also forms a bicontinuous cubic phase, has also been investigated. The presence of cubic phase was found to significantly slow drug release and absorption in vivo. These studies highlight some limitations and opportunities that lipid-based self-assembly phases may offer in oral drug delivery.

PHASE AND RHEOLOGICAL BEHAVIOR OF WORMLIKE MICELLAR SOLUTIONS IN MIXED SURFACTANT SYSTEMS

Durga P. Acharya, Koheita Hattori and Hironobu Kunieda

Graduate School of Environment and Information Sciences, Yokohama National University,
79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan.

acharya@ynu.ac.jp

At certain conditions, small micellar aggregates of some surfactants undergo one-dimensional growth and form very long and flexible worm-like micelles. Above a system-dependent concentration, these giant micelles are entangled to form a transient network and exhibit viscoelastic property. Formation and rheological behavior of worm-like micelles formed by long-chain cationic surfactants in presence of salt has been extensively studied. There are reports of the formation of worm-like micelles in some other surfactant-specific systems. Recently, we found that viscoelastic solutions of wormlike micelles are formed upon addition of lipophilic nonionic surfactants to dilute surfactant solutions.

Upon successive addition of short-chain polyoxyethylene dodecyl ether ($C_{12}EO_n$, $n = 3, 4$) to dilute micellar solution of sodium dodecyl sulphate (SDS), the viscosity increases rapidly above a certain $C_{12}EO_n$ concentration. Dynamic and steady state rheological measurements show that at fixed SDS concentration, increasing the concentration of $C_{12}EO_n$ in the nonionic system sharply increases its viscoelastic properties, and the system approaches the behavior of Maxwellian fluid with long relaxation time. With further increase in $C_{12}EO_n$ concentration, the viscosity decreases and ultimately a phase separation occurs. It is found that $C_{12}EO_3$ increases the viscosity more rapidly than $C_{12}EO_4$ does. With shorter EO-chain, however, a phase separation occurs before a viscoelastic solution is formed. The variation of rheological parameters with surfactant concentrations at fixed SDS/$C_{12}EO_3$ ratio follows a power law with exponents much larger than those predicted by living polymer model. The rheological study was extended to the mixed systems consisting of the mixture of $C_{12}EO_n$ with average n of 3 to study the effect of the dispersion of EO chain on the flow properties and micellar growth.

RHEOLOGY AND DYNAMICS OF MICELLAR CUBIC PHASES AND RELATED EMULSIONS

Carlos Rodriguez and Hironobu Kunieda

Graduate School of Environment and Information Sciences, Yokohama National University,
Tokiwadai 79-7, Hodogaya-ku, Yokohama 240-8501, JAPAN

carlosetsuko@yahoo.com, caferoab@ynu.ac.jp

The rheological behavior of normal micellar cubic phases in $C_{12}EO_{25}$ systems and related emulsions has been investigated. In the aqueous $C_{12}EO_{25}$ binary system, the transition from the cubic phase to the micellar solution is associated with a sudden drop in viscosity and with a small enthalpy of transition.

The elastic modulus and viscosity of cubic phases show a maximum with concentration but remain very high within the range of existence of the cubic phase. Several relaxation processes seem to be present in binary cubic phases, and some of them occur in a time scale that can be followed both by rheology and dynamic light scattering measurements.

Upon addition of small amount of oil (decane), the rheological behavior changes remarkably. As the oil fraction increases, the relaxation times also increase and finally, highly-concentrated, gel-like emulsions are obtained. Contrary to conventional concentrated emulsions, the viscosity of cubic-phase-based emulsions is decreased by increasing the fraction of dispersed phase. The non-maxwellian rheological behavior at low oil fractions is described according to the model of slipping crystalline planes, modified by using a distribution of bulk relaxation times, and good fitting to the experimental data is obtained.

The rheological behavior of reverse micellar cubic phases in block-copolymer systems will also be discussed briefly.

THE SPECTROSCOPIC OBSERVATION OF POLYMER FILM STRUCTURE AND CHAIN DYNAMICS.

Michelle L. Gee, Trevor Smith, Colin Scholes.

School of Chemistry, University of Melbourne, Parkville, VIC 3010. Australia

We have recently developed novel spectroscopic methodologies in which variable angle of incidence time-resolved evanescent wave induced fluorescence (EWIFS) is coupled with time resolved fluorescence anisotropy measurements (TRAMS). By depth profiling we can measure time-resolved fluorescence decay and fluorescence depolarisation and how this varies with distance normal to a surface onto which a species is adsorbed. In this talk we will show how these spectroscopic methods can be used to determine polymer chain dynamics and polymer conformation in cast polymer films. Polymer fluidity and conformation are key characteristics in the application of cast polymer films as self-annealing coatings.

CHARGE REGULATION IN SITE IONIZATION DOUBLE LAYERS INVOLVING SPECIFIC ADSORPTION OF IONS

Derek Y. C. Chan and Thomas W. Healy

Particulate Fluids Processing Centre, The University of Melbourne, Vic 3010, AUSTRALIA.

The Gouy-Chapman-Stern-Grahame (GCSG) model of the electrical doubles layer at site ionization surfaces has provided a comprehensive model for understanding general double layer properties and the effects of charge regulation during interaction of double layers as a function of separation. Surprisingly, no generally useful formulation exists to handle systems where specific adsorption of ions occurs.

We generalize a earlier formulation of charge regulation [J. Chem. Soc. Faraday I **76**, 2844-2865 (1977)] to give a complete analysis of charge regulation under the GCSG model in interacting double layers. The advantage of this analysis it allows us to make semi-quantitative predictions double layer properties at any separation.

We demonstrate the utility of this analysis by considering a system where protons are potential determining ions and where specific anion adsorption results in a shift of the isoelectric point of the interface to lower pH values. The theory is then used to investigate specific adsorption in colloidal alumina dispersions in the presence of specifically adsorbing anions such as citrate and oxalate.

DIFFUSIOOSMOSIS OF ELECTROLYTE SOLUTIONS ALONG A CHARGED PLANE WALL

Hsien Chen Ma, Huan J. Keh

Department of Chemical Engineering, National Taiwan University, Taipei 106-17,
Taiwan, ROC

d92524001@ntu.edu.tw

An analytical study is presented for the steady diffusioosmotic flow of an electrolyte solution along a dielectric plane wall caused by a tangential concentration gradient. The electric double layer adjacent to the charged wall may have an arbitrary thickness and its electrostatic potential distribution is obtained by solving the Poisson-Boltzmann equation. The macroscopic electric field along the tangential direction induced by the imposed electrolyte concentration gradient is determined as a function of the lateral position. A closed-form formula for the fluid velocity profile is derived as the solution of a modified Navier-Stokes equation. The direction of the diffusioosmotic flow relative to the concentration gradient is determined by the combination of the zeta potential of the wall and the properties of the electrolyte solution. For a given concentration gradient of an electrolyte along a plane wall, the magnitude of fluid velocity at a position increases monotonically with an increase in its electrokinetic distance from the wall. The diffusioosmotic velocity can have more than one reversal in direction over a small range of the zeta potential. The effect of the lateral distribution of the induced tangential electric field in the double layer on the diffusioosmotic flow is found to be very significant.

HIGH POWER CARBON-BASED ELECTRICAL DOUBLE LAYER (SUPER) CAPACITORS

Tim Wade,[1] Calum J. Drummond,[2] Franz Grieser [3] and Derek Y.C. Chan [4]

1. CAP-XX Pty Ltd, Units 9 & 10, 12 Mars Road, Lane Cove, New South Wales, 2066.
2. CSIRO Molecular Science, PO Box 184, North Ryde, NSW, 1670.
3. School of Chemistry, The University of Melbourne, Parkville, 3010.
4. Department of Mathematics and Statistics, The University of Melbourne, Parkville

The CAP-XX range of supercapacitors is an excellent current example of the commercialization of Australian colloid and interface science. CAP-XX manufactures, markets and sells supercapacitors, alternatively known as ultracapacitors, electrical double layer capacitors and electrochemical capacitors, to original equipment manufacturers (OEMs) in the wireless communication market space. In this presentation, a brief update on the CAP-XX story will be provided. The high performance of CAP-XX supercapacitors is enabled by nano-structured carbon electrode materials with an extremely large surface area (greater than 1000 m^2 per gram) and pores that are on average less than two nanometres in diameter. Applying a potential allows controlled, rapid and reversible adsorption and desorption of charge carrying ions (sub-nanometre in size) within the carbon nano-pores that gives the high power and energy capability of CAP-XX supercapacitors. These nano-scale properties allow high power devices, the size of a postage stamp, to be used in miniaturised electronic devices, such as portable wireless communication devices. Factors that govern the power density in CAP-XX supercapacitors will be discussed. In particular, the focus will be placed on the role of the separator in the energy storage device.

Keynote Lecture

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ATOMIC FORCE MICROSCOPY: A ROUTINE TOOL OR EMERGING TECHNIQUE?

Hans-Jürgen Butt

Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany,

butt@mpip-mainz.mpg.de

With the invention of the atomic force microscope (AFM) imaging surface structures at high resolution in air or liquid became possible. The introduction of Tapping mode opened the routine imaging of polymers. Processes can be analysed and macromolecules can be manipulated. Beside imaging, new unexpected methods have emerged, which are based on atomic force microscopy. One of these methods is the analysis of surface forces. Using the AFM surface forces, which determine the dispersion of solid particles in a liquid, can be measured routinely. In addition, by coating one face of AFM microcantilevers with receptors for a certain ligand, they can be used as chemical or biochemical sensors. AFM-based techniques are presented and discussed, highlighting applications from our own research.

AFM MEASUREMENTS OF HYDRODYNAMIC FORCES BETWEEN DEFORMABLE DROPS: EXPERIMENTS

Raymond R. Dagastine[1], Derek Y.C. Chan[3], Geoff W. Stevens[1] and Franz Grieser[2]

Particulate Fluids Processing Centre
1. Department of Chemical and Biomolecular Engineering
2. School of Chemistry
3. Department of Mathematics and Statistics
The University of Melbourne, Parkville VIC 3010 Australia

rrd@unimelb.edu.au

The control of emulsion or “soft colloid” dispersion properties including shelf life and stability, coalesce time in processing and overall rheological behaviour is a complex problem dependent many factors including the amount and type of surface-active agents present. There are a large number of experimental methods ranging from straightforward interfacial tension measurements to more complex spectroscopic and scattering techniques all aimed at characterizing the nature of surface-active agents at gas-liquid or liquid-liquid interfaces. The above methods provide a great deal of useful information related to emulsion behaviour, but they are limited to indirect descriptions of the interaction forces between droplets where interaction forces control or mediate most emulsion properties. The sparsity of this type of information for a large number of experimental systems is mainly due to the experimental challenges involved in measuring forces in deformable systems. We employ a novel experimental method (Dagastine, Stevens, Chan, and Grieser. (*JCIS* **273,** 339-342 (2004)) to study the interaction forces between oil droplets using atomic force microscopy (AFM) in the presence of a variety of stabilizers.

The radii of the droplets were well below the capillary length for the system. Therefore gravity effects are negligible, and interfacial tension and interaction forces govern the system behaviour. The approach rate between the droplets was varied to probe both the pseudo-static forces relevant to shelf stability and the hydrodynamic interactions relevant to emulsion processing. We present examples for an anionic surfactant system and a tri-block copolymer system. The issues in analysis and interpretation of these measurements are discussed in conjunction with the talk by Manica *et al.*.

OBSERVATIONS OF INTERESTING HYDRODYNAMIC EFFECTS ON A FLUID DROP CLOSE TO A SOLID WALL

Jason Connor*, Lucy Wang and Roger Horn

Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes SA 5095, Australia
(*present address: PELM Building, Central Queensland University,
Gladstone Campus, PO Box 1391, Gladstone, Queensland 4680)

roger.horn@unisa.edu.au

We have developed an experiment enables the deformation of a fluid drop to be measured as it approaches a flat solid surface. The particular measurements described here are for a mercury drop approaching a smooth mica surface in aqueous electrolyte solution, but other fluid/fluid/solid combinations (such as air/water/silica) can also be investigated.[1,2] One benefit of using mercury is that its surface charge can be controlled by applying a suitable electrical potential, and hence the surface forces acting between the drop and the solid can be controlled [3].

When the drop and the solid are in relative motion, hydrodynamic pressures build up in the thin intervening aqueous film, sufficient to deform the drop measurably. For rapid approach, the pressure can be enough to invert the curvature of the drop near its point of closest approach to the solid, forming a “dimple” in the drop. This is a classic problem in thin film drainage that has been explored many times in the past, both experimentally and theoretically. In our mercury/water/mica experiment the water film thickness between the drop and the solid is determined with sub-nanometre resolution as a function of radial distance from the axis of symmetry (micron resolution) at video frame rates (20 ms resolution). This gives us a very comprehensive set of data on hydrodynamic deformation, with the particular feature that dimpling has been examined for a range of double-layer forces (from repulsive to attractive) acting between the surfaces [4]. Under some conditions we observe an unexpected reversal of the flow direction of fluid under the dimple.

In addition to the rapid-approach experiment that produces dimpling, we will show movies that illustrate hydrodynamic deformations observed in other situations where the drop was moved towards or away from the solid. The results are interesting and sometimes counter-intuitive.

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PREDICTION OF INTERESTING HYDRODYNAMIC EFFECTS ON A FLUID DROP CLOSE TO A SOLID WALL

Rogèrio Manica, Steven L Carnie and Derek Y C Chan

Particulate Fluids Processing Centre, Department of Mathematics & Statistics,
The University of Melbourne, Parkville, VIC 3010 Australia

D.Chan@unimelb.edu.au

The task of quantifying the nature of velocity or time dependent interactions that involve moving deformable particles or interfaces poses significant experimental and theoretical challenges. The complexities arise from the need to account for hydrodynamic effects, surface tension and possibility elasticity effects as well as the influence of short-ranged colloidal interactions. While inextricably related, these effects tend to have different characteristic time and length scales. Nonetheless, such interactions are fundamental in understanding key interaction mechanisms in settings that range from mineral flotation to emulsion stability to the adhesion and interaction of biological cells.

In a recent series of experiments, Connor and Horn [*Faraday Disc.* 123 (2003) 193-206] have recorded accurate data pertaining to the detailed temporal and spatial evolution of a fluid drop near a solid surface with sub-nanometre resolution over a spatial extent of micrometres. The behaviour of the fluid interface can be probed by using different programmed movements of the nearby solid surface and observing the resulting behaviour of the fluid interface under well controlled electrochemical environments for which the nature of colloidal surface forces are known.

Progress in quantitative modelling of the temporal and spatial behaviour of the fluid interface in such experiments requires the ability to treat time-dependent phenomena in a consistent matter over very different length scales. We have developed an accurate theoretical framework and computational schemes that can facilitate detailed exploration of this class of problems.

Comparisons between experimental results and theoretical predictions show very good quantitative agreement under a variety of experimental conditions and a number of counter-intuitive experimental observations can also be understood in terms of this model. This imparts confidence in using the theoretical model to understand the detailed and delicate interplay between static and dynamic effects. In parameter regimes in which it is very difficult to acquire experimental data, the theoretical model can further provide insight into behaviour of the fluid interfaces and the forces that control such behaviour.

CAVITATION BUBBLE TEMPERATURE IN AQUEOUS SOLUTIONS CONTAINING SURFACE ACTIVE SOLUTES

Franz Grieser, Envi Ciawi and Muthupandian Ashokkumar

Particulate Fluids Processing Centre, School of Chemistry, University of Melbourne,
VIC 3010, Australia

franz@unimelb.edu.au

Mean acoustic cavitation bubble temperatures have been measured by a method that relies on the distribution of hydrocarbon product yields produced from the recombination of methyl radicals generated on the thermal decomposition of volatile solutes within cavitation bubbles. It is generally observed that the mean bubble temperature decreases with increasing concentration of volatile solutes. The measured temperatures range from 4600±200 K to 2300±200 K in the presence of volatile, surface active aliphatic solutes. Further investigation has revealed that the effect of solutes on the cavitation bubble temperature also depends upon the nature of the solute's functional group. For example, the cavitation bubble temperature observed in solutions containing aliphatic solutes with an amino group is much lower than that observed in solutions containing aliphatic solutes with a carboxyl group. We have also observed that the measured temperatures in the presence of volatile, surface active aromatic solutes are in the range between 8000±200 K and 12000±200 K, which is significantly higher than the experimentally measured cavitation bubble temperatures reported in literature to date. Multibubble sonoluminescence (MBSL) intensities under similar conditions have also been measured and correlated with the cavitation bubble temperatures.

THE EFFECT OF SURFACE-ACTIVE SOLUTES ON BUBBLE COALESCENCE IN THE PRESENCE OF ULTRASOUND

Muthupandian Ashokkumar[1], Judy Lee[1,2], Sandra Kentish[2] and Franz Grieser[1]

Particulate Fluids Processing Centre, [1]School of Chemistry, [2] Department of Chemical and Biomolecular Engineering, University of Melbourne, VIC 3010, Australia

masho@unimelb.edu.au

The effect of different surface active solutes over a range of concentrations, on bubble coalescence in an ultrasonic field has been investigated. The sonication of an aqueous solution generates cavitation bubbles, which may coalesce and produce larger bubbles. A capillary system has been designed to measure the change in the total volume resulting from the sonication of aqueous solutions with 515 kHz ultrasonic pulses. This volume change is proportional to the amount of larger gas bubbles generated by coalescence during sonication. The total volume of the bubbles generated is reduced when surface active solutes are present. We have proposed that this decrease in the total bubble volume results from the inhibition of bubble coalescence by the surface active solutes. The observed results showed similarities with bubble coalescence data reported in the literature in the absence of ultrasound. It was found that for uncharged surface active solutes, the extent of bubble coalescence is affected by the surface activity of the solutes. The addition of 0.1 M NaCl to uncharged surface active solutes had no effect on the extent of bubble coalescence. For charged surface active solutes, the extent of bubble coalescence appears to be dominated by inter bubble electrostatic effects. The inhibition of bubble coalescence was completely negated when 0.1 M of NaCl was present in the solution containing charged surface active solutes. Multibubble sonoluminescence data measured under similar conditions to that of bubble coalescence measurements will also be presented. It reveals that there is a correlation between the bubble coalescence data and the cavitation activity.

DIRECT MEASUREMENT OF SURFACE FORCES BETWEEN REGENERATED CELLULOSE SURFACES IN AN AQUEOUS ENVIRONMENT.

Shannon M. Notley

Department of Fibre and Polymer Technology, Royal Institute of Technology (KTH),
SE-10044 Stockholm, Sweden.

The interaction forces between cellulose surfaces are of fundamental interest in a variety of natural and industrial systems. A knowledge of cellulose interaction forces responsible for micro-fibril aggregation is of particular importance when considering the structure and growth of such structures.

The properties of wood- based materials and composites will be greatly influenced by the interaction forces between cellulose surfaces. Hence a fundamental understanding of the adhesion, friction, swelling and properties in a material such as paper is dependant upon an understanding of the basic interactions between cellulose surfaces.

The significance of one such force, that due to the ubiquitous van der Waals interaction, for example, on the formation and strength of the wood based fibre network in a paper sheet, is still much debated. Interactions due to the overlap of electrical double layers of the fibres can also greatly influence the strength of the fibre-fibre joint. In this study, the interactions between cellulose surfaces have been measured using an Atomic Force Microscope (AFM). Model cellulose surfaces with varying surface charge have been specifically prepared to mimic real fibre systems. Both the van der Waals attraction and the electrostatic double-layer repulsion between the surfaces have been characterised. Furthermore, the interactions between surfaces with adsorbed polymer layers have been studied.

SURFACE HYDROXYL GROUPS ON SAPPHIRE (α-AL_2O_3) (0001) IN WATER: AN ATOMIC FORCE MICROSCOPY STUDY

Yang Gan and George V. Franks

Chemical Engineering, School of Engineering, University of Newcastle, Callaghan,
NSW 2308, Australia

The atomic arrangements of surface hydroxyl groups on bulk α-Al_2O_3 (0001) single crystals in water have been imaged by contact mode atomic force microscopy (AFM). Cleaned samples showed terraces with steps of monolayer high. On the terraces, hexagonal arrays of corrugations were revealed by AFM. The distance between the nearest corrugations was 4.70 Å after calibration with the lattice constant of mica. This value was nearly the same as the known bulk unit cell dimension (4.76 Å). But obtaining this value suggested that not all hydroxyl groups on the surface could be resolved for a fully hydroxylated α-Al_2O_3 (0001) surface. We explained this by postulating that only the unoccupied octahedral interstices surronding by three hydroxyl groups could be imaged by AFM.

Keynote Lecture

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DESIGNER MICROEMULSIONS FOR THE FOOD INDUSTRY

Nissim Garti

Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Israel

garti@huji.ac.il

Microemulsions have been known for over 50 years and have been studied extensively by theoreticians and applied scientists. The advantages which microemulsions provide (thermodynamic stability, high surface areas, clarity, cost, etc.) are not questionable, and yet their use in the food, cosmetic and pharma industries has been very limited.

Health authorities are restricting the use of common emulsifiers and solvents that are essential in making microemulsions, making it quite difficult to design a microemulsion for food systems. Yet, the need for high-solubilization capacities in nutraceuticals, along with requirements for the manufacture of clear beverages, and a strong demand for improved bioavailability of insoluble nutraceuticals, has created a new call for food-grade microemulsions.

We have learned to construct phase diagrams based on multicomponent ingredients – all food grade – which are progressively and fully dilutable in water or sugar solutions, and which exhibit large U-type isotropic regions.

We load the tightly packed reverse micelles (surfactant + oil phase) with nutraceuticals, allowing the "concentrates" to be further diluted with water by the consumer to form O/W microemulsions with high solubilization capacity, good oxidative protection, good permeability through human membranes (bioavailability), and high interfacial surfaces. Maillard interfacial reactions for generation of signature aromas can be carried out in the microemulsions as microreactors of aromas derived from the interfacial orientation of the amino acids at the interface, thus yielding new chemical species.

THE INFLUENCE OF INTERFACIAL MECHANICS ON THE CREAMING AND RHEOLOGY OF OIL-IN-WATER EMULSIONS

Peter J. Wilde, Alan R. Mackie, Graham R. Moates, Michael J. Ridout
and Margaret M. Robins

Institute of Food Research, Norwich Research Park, Norwich, NR4 7UA. UK.

peter.wilde@bbsrc.ac.uk

Stability and rheology of food emulsions are of paramount importance for consumer acceptability, shelf life, texture and mouthfeel. There has been much research on emulsion creaming and rheology, focussing mainly on the basic physical parameters such as density, viscosity, polymer concentration, ionic strength, pH etc. In the field of food colloids, interfacial rheology is a well developed area. The principal reason is because proteins, which are the most common food emulsifier, generally form a viscoelastic adsorbed layer. The physical and mechanical properties of this layer are critical for the coalescence stability of emulsions and foams. However, to date, there has been a lack of any systematic investigations into how the mechanical properties of protein stabilised interfaces influence interactions within emulsion systems.

From previous observations of foam drainage and emulsion rheology we designed some more highly controlled experiments. Pairs of emulsions were produced with near identical physical parameters (droplet size distributions, zeta potential, phase density and viscosity). The major difference between them was that one possessed a rigid interfacial layer (protein) and the other a fluid one (emulsifier).

Ultrasonic creaming experiments showed that their appeared to be little effect on the creaming rate of individual droplets, however, the cream layer showed differences in the packing density between the two emulsions. Confocal microscopy of the cream layer showed that the protein stabilised system maintained a slightly more open network structure containing voids whereas any voids in surfactant stabilised systems were filled by small droplets. Rheological investigations observed that the protein stabilised emulsions generally had a much greater elastic response. The influence of polydispersity and degree of flocculation were also investigated. Although the principal mechanism underlying these changes is not yet clear, the results are discussed in terms of the droplet deformability, polydispersity, and frictional interactions between droplets.

INTERFACIAL RHEOLOGY AS A TECHNIQUE FOR PROBING FOOD EMULSION AND FOAM STABILITY

Tim. J. Wooster

Food Science Australia, 671 Sneydes Road, Werribee 3030, Australia.

Timothy.Wooster@csiro.com

A significant number of food emulsions utilise proteins as stabilisers. The functional role of protein surfactants is complex and dependent on the system. Whilst the surface activity of proteins is important, the moderate reduction in interfacial (surface) tension does not itself explain the stability of protein-based emulsions and foams. Instead stability (in concentrated emulsions) might be explained by (Rehbinder's) structure-mechanical barrier concept. Essentially the stabilising function of proteins is that they enable the liquid interface to resist tangential stress along the interface. Therefore, it is important to understand the surface (interfacial) rheological properties of adsorbed protein layers.

The two main interfacial rheology techniques are shear rheology and dilatational rheology. Interfacial shear rheology can be used to examine the viscoelastic properties of adsorbed protein films, which are important in stabilising against coalescence. Dilatational rheology can be used to examine the relaxation properties of these films. The present paper outlines the underlying concepts of these two interfacial rheology techniques and also gives practical examples using milk proteins. It is also shows emulsion coalescence stability can be related to the mechanical properties of the protein film. Such correlations might be used to enhance the stability of food emulsions.

USE OF PROTEIN-SUGAR CONJUGATES FOR MICROENCAPSULATION OF OILS

Jenny Kartika Rusli[1], Luz Sanguansri[2] and Mary Ann Augustin[2]

1. Faculty of Land and Food Resources-Gilbert Chandler Campus, The University of Melbourne, Sneydes Road, Werribee, VIC 3030
2. Food Science Australia, 671 Sneydes Road, Werribee, VIC 3030

jenny.rusli@csiro.au

The utilisation of microencapsulated oil powder has grown in recent years. The process involves preparation and drying of oil-in-water emulsions into powders, which are easier to handle and stable against oxidation. Proteins alone or in combination with carbohydrates are commonly used for manufacture of oil powders. The use of protein-sugar conjugates formed by the Maillard reaction has been proposed as alternative encapsulants (International Patent WO 01/74175A1).

This study examined the use of conjugates formed by heating mixtures of proteins [soy protein isolate (SPI) or whey protein isolate (WPI)] and dried glucose syrup for microencapsulation of oil. The effectiveness of conjugates as encapsulants for production of oil powders containing different loads (20%, 40%, 50% and 60% w/w oil-in-powder) was assessed. The effectiveness of conjugates to encapsulate different oil types (tuna oil, palm stearin and 1:1 tuna oil and palm stearin blend) was also investigated at 50% oil loading. Microencapsulation efficiency (MEE), microencapsulation yield (MEY), and oxidative stability (propanal headspace analysis and peroxide value) of SPI- and WPI-based powders were examined. In addition, effect of altering formulation of aqueous phase solid (10% and 20%) and homogenization conditions (180/80 bar or 350/100 bar) on emulsion characteristics (particle size and viscosity) and final powder properties were evaluated.

The analysis of powders demonstrated that protein-sugar conjugates containing SPI and WPI could be used for efficient encapsulation of oils. Conjugates containing WPI were superior to corresponding systems containing SPI. This is evidenced by the higher MEE and lower peroxide value and headspace propanal level of the WPI-based microcapsules. Regardless of the oil types, MEE of >89% was obtained in microcapsules containing ≤50% oil load, prepared at higher homogenization pressure. Microcapsules containing lower oil load, lower tuna oil:palm stearin ratio, higher concentration of wall solids and those prepared using lower homogenization pressure were more stable to oxidation.

THE CHARGE ON THE PRISTINE OIL/WATER INTERFACE

James K. Beattie and Alex M. Djerdjev

School of Chemistry, University of Sydney, NSW 2006, Australia

j.beattie@chem.usyd.edu.au

The surfactant-free oil/water interface acquires a negative charge through the autolysis of water and the preferential adsorption of hydroxide ion. We have measured this charge in a pH-stat experiment by the simultaneous determination of the quantity of NaOH required to keep the pH constant (at pH 9 or 7) and the increase in surface area as a 2 vol% oil-in-water emulsion is homogenised (*Angew. Chem.* **43**, 3568 (2004)). The latter was calculated from the decreasing size of the emulsion droplets obtained from analysis of the dynamic mobility spectrum measured in an electroacoustic apparatus. The capability of the AcoustoSizer to measure concentrated emulsions means that the pH effect is significant and that trace contamination is not a problem.

The charge of 5-7 μC cm^{-2} (0.3-0.4 unit charges nm^{-2}) appears to be nearly independent of the nature of the oil, for oils less soluble in water than decane including hexadecane, squalane, squalene and perfluoromethyldecalin. The pH dependence of the zeta potential of these surfactant-free emulsions indicates an 'isoelectric' point of pH 3-4. This same value occurs at the air/water interface, which suggests that it reflects the structure of water at the surface of a low-dielectric medium.

Most of the hydroxide surface charge is compensated by alkali metal counterions in the Stern or stagnant layer. The magnitude of surface conduction is described by the dimensionless Dukhin number: Du = $K_s / (K^\infty a)$, where K_s is the surface conduction, K^∞ the conductivity of the bulk electrolyte and a is the radius of the droplet. The values of Du obtained independently by fitting the dynamic mobility spectra and from high frequency dielectric response measurements are in good agreement, and show only a small amount of stagnant layer conduction. The lack of difference among Li^+, Na^+ and Cs^+ implies that dispersion forces are not important.

OSTWALD RIPENING OF WATER-IN-OIL EMULSIONS

Nirmesh Jain, Jason S. Hong, Brian W. Hawkett and Gregory Warr

School of Chemistry and Key Centre for Polymer Colloids, The University of Sydney,
NSW 2006, Australia.

nirmesh@chem.usyd.edu.au

In this paper we present an experimental study of the ripening of water-in-oil emulsions as a function of emulsifier concentration, hydrocarbon chain length of the oil, and in the presence of various aqueous electrolytes. Ripening of dilute emulsions at low emulsifier concentrations is shown to follow the predictions of LSW theory as in oil-in-water emulsions. The ripening rate decreases with increase in hydrocarbon chain length, due primarily to lower water solubility. At higher emulsifier concentrations, the presence of reverse micelles and microemulsions droplets, studied using small-angle neutron scattering, changes ripening. Addition of simple electrolytes to the aqueous droplets retards the ripening rate and changes ripening behaviour significantly. This is shown to be consistent with the generation of osmotic pressure differences between droplets, and is also closely analogous to the effect of water-insoluble solutes in oil-in-water emulsion

SELF-INDUCED DEPLETION FLOCCULATION OF A POLYDISPERSE O/W EMULSION

Alex M. Djerdjev, Robert J. Hunter and James K. Beattie

School of Chemistry, University of Sydney, NSW 2006, Australia

a.djerdjev@chem.usyd.edu.au

When several vol% of an oil with a solubility in water of a few ppm or more is homogenised to form an oil-in-water emulsion stabilised by SDS, complex changes occur in the electroacoustic dynamic mobility spectra over a period of several hours. Initially the dynamic mobility spectrum is almost 'normal', with the magnitudes decreasing and the phase lag increasing with frequency. Over about an hour the magnitudes drop by more than half with a minimum at intermediate frequencies. The phase lags increase at low frequencies but show a large positive phase lead at high frequencies. Gentle sonication almost restores the original spectra, which then again show a similar time dependence. After a few days storage, however, the dynamic mobility spectra have the 'normal' shape and now there is no longer any time depenence.

We now recognise that the unusual spectra observed after a hour are characteristic of a floc, and ascribe the formation of the floc to depletion flocculation of the larger droplets of the polydisperse emulsion by the population of smaller droplets. The effect only occurs with slighly soluble oils such as toluene, hexane and tetralin, but not with less soluble oils such as decane, hexadecane and squalene. It is independent of whether the emulsion is formed by high pressure homogenisation or sonication.

The depletion flocculation explanation is consistent with the time required for floc formation, for the observation that sonication can remix the emulsion, after which the flocs form again, and for the disappearance of the effect after several days during which time the depletion-inducing small droplets have disappeared due to Ostwald ripening, leaving a dispersed emulsion with drops larger than the original mixture.

Keynote Lecture

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FOOD COLLOIDS: BRIDGING THE GAP BETWEEN FUNDAMENTAL RESEARCH AND COMPLEX APPLICATION.

Peter J. Wilde, Alan R. Mackie, Michael J. Ridout, A. Patrick Gunning, Paul A. Gunning and Victor J. Morris

Institute of Food Research, Norwich Research Park, Norwich, NR4 7UA. UK.

peter.wilde@bbsrc.ac.uk

Colloid science is a research field at the leading edge of fundamental research in physics and chemistry. In contrast, studies on food colloids are often regarded by purists as low quality research on a low grade commodity. However, food is something we all consume, and it is vital for our health and wellbeing. The importance of food cannot be over estimated, but perhaps it is taken for granted, and this may underlie the reason why quality science on food systems is not considered fundamental.

In contrast, the food community consider fundamental research on model systems to be irrelevant to real products. Hence measurements are often made on complex food systems without rational knowledge of the component interactions within the material. This can lead to misinterpretation of complex data resulting in conflicting opinions in the literature.

In our opinion, food systems should be considered a complex challenge to be solved, rather than a crude system to be ignored. Our approach has therefore been to apply a range of colloidal techniques and approaches to particular events or interactions known to occur within a food matrix. One of our principal aims, and the focus of this presentation, is the competitive adsorption behaviour of protein surfactant mixtures. This is an issue in both food and non-food applications, which can result in antagonistic effects on the stability of foams and emulsions. We will review a range of approaches that have been applied to understanding the behaviour of proteins and surfactants at fluid interfaces. Using a range of techniques including molecular dynamics, complex rheology, AFM force measurements and imaging, has allowed us to have a unique insight into the complex adsorption behaviour of protein-surfactant mixtures.

MILK CASEIN PROTEINS AS MOLECULAR CHAPERONES AND STABILISERS OF PROTEIN FOOD COMPONENTS

John A. Carver

School of Chemistry ond Physics, The University of Adelaide, Sa 5005

john.carver@Adelaide.edu.au

Caseins are the predominant milk proteins and comprise four unrelated subunits: α_{s1}, α_{s2}, β and κ of similar subunit mass (~ 20 kDa). They are relatively unstructured proteins with consequent inherent flexibility. In solution, they form large micelles of 50 to 300 nm in diameter comprising around 10,000 casein proteins. The flexibility, dynamism and aggregation properties of casein proteins have impeded their detailed structural characterisation, e.g. by x-ray crystallography or NMR spectroscopy.

Our recent research has characterised casein proteins as molecular chaperones whereby they potently prevent the aggregation and precipitation of a diversity of proteins, including whey proteins (α-lactalbumin and β-lactoglobulin) under stress conditions, e.g. elevated temperature. In doing so, casein proteins exhibit very similar properties to other molecular chaperones, i.e. the unrelated small heat-shock proteins and clusterin, proteins that we have studied extensively. In addition to their functional similarities, all three protein families share structural properties.

The chaperone (stabilising) ability of casein proteins rationalises the high temperature stability of milk, e.g. during pasteurisation and UHT treatment and has potential applications in a wide range of foods. In this presentation, I shall outline some of the results demonstrating the chaperone ability of casein proteins.

SOLUBILISED CASEINS AND THEIR EFFECT ON THE SURFACE PROPERTIES, FOAMABILITY AND FOAM STABILITY OF SKIM MILK

Ian R. McKinnon[1] Brent R. Ward[1] and Mary Ann Augustin[2]

1. School of Chemistry, Monash University , VIC 3800, Australia
2. Food Science Australia, 671 Sneydes Road, Werribee 3030 VIC

ian.mckinnon@sci.monash.edu.au

In the foaming of skim milk both the foam volume and the foam stability increase on addition to the milk of calcium chelating agents such as EDTA and citrate.

Skim milk is an aqueous dispersion of particles known as casein micelles. The so-called micelles are aggregates of rheomorphic phosphorylated proteins (caseins) and calcium hydrogen phosphate ranging in diameter from 50 – 300 nm. The aqueous serum phase contains solubilized caseins, globular whey proteins, minerals such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, $H_2PO_4^-$, and other minor components at pH of 6.6 and a total ionic strength of approximately 0.1M. It is well known that addition of calcium chelating agents to skim milk causes solubilization into the serum phase of caseins from the dispersed aggregates. In one example of milk containing 100 g solids/l addition of 10mM EDTA increased the casein component of the serum protein from 0.05 g/100 g milk to 1 g/100 g milk. The whey protein component was 0.6 g/100 g milk). Heat treatment at 85°C/30min rather than 72°C/30s resulted in the denaturation of 75% of the whey protein.

Time dependent measurement of the surface pressure of freshly formed drops showed a dependance on milk concentration but almost no dependence on the casein content of the serum phase or the denaturation of the whey proteins in spite of the known differences in their surface activities.

This paper will be concerned with the presentation of these results and their interpretation in understanding the foaming behaviour of skim milk systems.

ADVANCED NMR CHARACTERISATION OF MICROENCAPSULATED FOOD PRODUCTS

Matija. Iko Burgar[1], Pam Hoobin[1], Punsandani Udabage[2], Mary Ann Augustin[2]

1. CSIRO Maufacturing and Infrastructure Technology, Private Bag 33, Clayton South
2. CSIRO Food Science Australia, 671 Sneydes Road, Werribee, Vic 3030

Iko.Burger@csiro.au

The structure of food products is of primary importance in all aspects of its stability and functionality. Indeed, the microscopic organization of food components and additives govern the way the macroscopic architecture is taking place and the way this information can be observed. Nuclear magnetic resonance (NMR) is a unique technology in a sense that it measures non-destructively the magnetic properties of nuclear spins revealing structure as well as the physical and chemical properties of the materials.

In the early days of NMR physical applications to study molecular dynamics, partial alignment of macromolecules and phase separation were deduced from broad-line solid-state NMR. Only somewhat later, was high-resolution NMR in solution established as an important tool for elucidating the chain microstructure. According to top specialists in the field, the future should see these two methods merge for elucidation of new biodegradable bio-emulsifier materials using food ingredients as precursors (eg from protein, carbohydrate and lipids). We will demonstrate here the successful application of such non-destructive NMR experimental development for microencapsulated food products by including high-resolution solution NMR methods as well as the high-resolution solid-state NMR methods.

LIPOSOMAL DELIVERY SYSTEMS FOR NUTRACEUTICAL APPLICATIONS

Cindy Tran, Andrew Lawrence, and Shantha Kosaraju

Food Science Australia, Werribee, Victoria-3030, Australia

Shantha.Kosaraju@foodscience.afisc.csiro.au

Phospholipid based liposomes using pro-liposome technology were developed for the encapsulation and delivery of micronutrients such as iron. The phospholipid used was based on a composition containing primarily phosphatidylcholine with small quantities of charged lipids. Liposomal formulations were prepared by varying the concentration of phospholipid from 1.5 to 3.0%. Ferrous-sulphate ($FeSO_4$. $7H_2O$) as the iron source and ascorbic acid as the anti-oxidant were chosen for encapsulation in the liposomes. A range of 15- 45% of ferrous-sulphate and 10-30% of ascorbic acid was used for encapsulation. The preparation of liposomes was optimised by varying different parameters such as concentration of the lipid, concentration of ferrous-sulphate/ascorbic acid, time and type of stirring employed. Both the placebo and ferrous sulphate/ ascorbic acid loaded liposomes were characterised by the particle size distribution analysis and the electron-microscopy studies. The amount of the entrapped ferrous-sulphate in the liposomes was analysed by atomic-absorption spectroscopy. The particle size of liposomes prepared using 1.5% concentration of phospholipid were found to be the lowest when compared to the formulations with 2.25 and 3.0 % of phospholipid. The volume median diameter of 50% of particles of placebo and ferrous- sulphate loaded liposomes prepared using 1.5% of phospholipid concentration was around 0.7 μm and 5 μm respectively. The electron microscopic characterisation revealed the multilamellar nature of the formed liposomes with wider size distribution. The maximum entrapment efficiency of ferrous-sulphate achieved was around 11% for the liposomal formulation prepared using 15% of ferrous-sulphate as the initial loading concentration.

PHYSICAL AND OXIDATIVE STABILITY OF TUNA OIL-IN-WATER EMULSIONS STABILISED BY WHEY AND SOY PROTEINS

Cheryl Chung[1], Amirtha Puvanenthiran[2], and Mary Ann Augustin[2]

1. Faculty of Land and Food Resources, University of Melbourne, Gilbert Chandler Campus, Sneydes Road, Werribee, 3030, Victoria, Australia
2. Food Science Australia, 671 Sneydes Road, Werribee 3030, Victoria, Australia

Cheryl.Chung@csiro.au

There is increasing interest in the incorporation of omega-3 fatty acids into functional food products because of their health benefits. However, oils such as tuna oil that contain high levels of omega-3 fatty acids are unstable due to the high susceptibility of these polyunsaturated fatty acids (PUFA) to oxidation. This results in the development of undesirable flavours that affects the sensory properties of the food. Proteins, either alone or in combination with other ingredients can be used to stabilise polyunsaturated oil-in-water emulsions against oxidation.

This study examined the physical and oxidative stability of tuna oil-in-water emulsions stabilised with proteins (whey protein isolate (WPI) or soy protein isolate (SPI)). Emulsions (5 % w/w tuna oil) containing protein alone or in combination with sugars (glucose or oligofructose) were prepared by microfluidisation (800bar, 1 pass). Particle size distribution and the stability of the emulsion to centrifugation were used to assess the physical properties of the emulsions. Oxidative stability was assessed using peroxide value as an indicator of the primary oxidation and propanal in the emulsion headspace as the secondary oxidation indicator.

Increasing the protein content of the emulsion (from 1 to 5 % w/w protein) did not alter the particle size distribution when WPI was used but with the use of SPI, smaller particle sizes were obtained. Emulsions with higher protein content were more stable to oxidation overall. The addition of sugars had no effect on the properties of the WPI based emulsions, but had a minor effect on the properties of SPI based emulsions. Emulsions stabilised by WPI were superior in terms of physical and oxidative stability compared to those stabilised by SPI.

APPLICATIONS OF ULTRASOUND IN THE FOOD INDUSTRY

Sreeraj Balachandran[1], Shobha Muthukumaran[1], Sandra E. Kentish[1],
Muthupandian Ashokkumar[2], Raymond Mawson[3]

1. Department of Chemical and Biomolecular Engineering, University of Melbourne
2. School of Chemistry University of Melbourne, Victoria 3010, Australia;
3. Food Science Australia, Sneydes Road, Werribee, Victoria 3030, Australia

sandraek@unimelb.edu.au

There has been a growing interest in the industrial application of ultrasound, especially in the food industry. Power ultrasound can have a number of physical effects; it can increase turbulence through both the introduction of vibrational energy and through acoustic streaming, it can cause both particle agglomeration and particle dispersion, de-foam or de-gas liquids and clean surfaces with a scouring action.

Our current studies examine the use of ultrasound to enhance the extraction rate of soluble essences from a typical herb Ginger (Zingiber Officinale Roscoe) using supercritical carbon dioxide. Our results show that the extraction yield of gingerols from supercritical carbon dioxide can be enhanced by up to 30% through the application of ultrasound. The increase in extraction rate and yield is attributed to increased localised turbulence which in turn increases the external mass transfer coefficient.

In a similar manner, ultrasound-induced physical effects can be utilised for the enhancement of membrane processing. Our work in this area has focussed on the use of ultrasound to enhance dairy ultrafiltration. We have trialled low frequency ultrasound both during the ultrafiltration production cycle and the cleaning cycle. During the production cycle, the use of low intensity continuous ultrasonic exposure reduces both pore blockage and the specific resistance of the fouling cake layer. This leads to higher flux rates and the potential for longer production cycles. During the cleaning cycle, ultrasound systematically increases cleaning efficiency. The ultrasonic effect is consistent across a range of alkali pH levels and trans-membrane pressures. We observe no deterioration in cleaning effectiveness or membrane condition over experimental timeframes of some months. This implies that to date sonication has not damaged the membrane itself and that membrane life spans should be unaffected. We have also found little change to the properties of dairy whey solution exposed to such sonication.

RADICAL CHEMISTRY DURING THE ULTRASONIC TREATMENT OF FOOD MATERIALS

Raymond F. Mawson[1], Muthupandian Ashokkumar[2], Franz Grieser[2],
and Cornelis (Kees) Versteeg[1]

1. Food Science Australia, Sneydes Road, Werribee, Victoria 3030, Australia
2. School of Chemistry University of Melbourne, Victoria 3010, Australia

Raymond.Mawson@foodscience.afisc.csiro.au

High-intensity ultrasound has been increasingly employed in food processing. Ultrasonic extraction of gingerol from ginger, ultrasonic homogenisation of milk, dispersion of powdered ingredients and ultrasonic emulsification, are some examples that can be highlighted. These processes rely upon the physical effects of the ultrasound induced cavitation phenomenon. However, the potential restrictions and / or uses of the chemical effects generated by cavitation have either been ignored/overlooked or regarded as insurmountable. Our current research has been focussed upon three main issues: (i) to investigate the reaction sequences that can be initiated by the cavitation generated hydroxyl radicals during the ultrasonic treatment of food materials (e.g., milk and fruit juices) and during the extraction of bioactives from food materials (e.g., carotene, flavonoids, polyphenols), (ii) to minimise/eliminate undesired sonochemical reactions by the selection of suitable ultrasound frequencies, and the use of selective additives during the ultrasonic treatment and extraction of food materials and (iii) where hydroxyl radicals are found to be useful (e.g., enhancing the antioxidant activity of food materials), develop an ultrasonic treatment procedure for the enhancement of the degree of hydroxylation of food materials. Our investigation shows that the radical reactions can be minimised by selecting lower ultrasonic frequencies for food processing. However, high frequency ultrasound units can also be used for food processing if suitable radical scavengers are present in the solution. The sonochemical hydroxylation of phenolic compounds has been identified as an efficient way of enhancing the antioxidant properties of certain food materials (e.g., polyphenols, flavonoids). An overview of our recent findings on the above mentioned issues will be presented.

DEVELOPMENT OF A NOVEL INSTRUMENT COMBINING FLORESCENT MICROSCOPY AND SURFACE TENSION MEASUREMENT TOOLS TO STUDY LIQUID-FLUID INTERFACES

Eldon Pierce and Alidad Amirfazli

Department of Mechanical Engineering, University of Alberta, Edmonton, AB, T6G 2G8, Canada

a.amirfazli@ualberta.ca

Generally, to study rheological characteristics (or for biological systems, the biophysical function) of surfactants, a molecular layer of surfactant molecules are spread on a liquid-fluid interface. This molecular layer is exercised (i.e. expanded or compressed) to collect information regarding the dynamic surface tension response, module of elasticity, structural conformations, determination of the state of the monolayer phase, etc.

A new instrument is designed to allow study of surfactant layers or particles at liquid-fluid interfaces. For the first time, this instrument will enable researchers to simultaneously gather not only macroscopic information such as surface tension, module of elasticity and isotherm graphs, but also to microscopically observe the conformations of the surfactant molecules at an interface using fluorescent microscopy. It allows the liquid-air interface (a bubble formed in a chamber filled with liquid) to be observed using an inverted fluorescent microscope and at the same time an image of the air-bubble interface profile will be captured to measure surface tension based on bubble shape. The capabilities of this new instrument will be demonstrated by discussing measurements for DPPC, a common surfactant used for instance in lung surfactant studies.

A NOVEL METHODOLOGY USING LASER TO PATTERN SELF-ASSEMBLED MONOLAYER SURFACES

M. Reza Shadnam, Daniel Raso and Alidad Amirfazli

Department of Mechanical Engineering, University of Alberta, Edmonton, AB, T6G 2G8
Canada

a.amirfazli@ualberta.ca

The ability to engineer surface properties (e.g. wettability, adhesion) at micoscopic scale is the key to the emerging technologically important areas such as biosensors, tissue engineering, MEMS, and controlled delivery of liquids in microfluidics. A “Laser patterning” methodology has been developed to manipulate surface wetting properties using a chemisorbed self assembeled monolayer (SAM) on gold film (alkene-thiol type). In this methodology, direct irradiation of a continuous wave (CW) Laser is used to thermally desorb the SAM at specific regions. The bare gold regions is then back filled with a second desirable SAM (e.g. with a hydrophilic tail group). An Argon Laser beam in TEM_{00} mode is scanned at constant speed of 200 μm/s along straight lines on the surface to locally heat up the sample; the local rise in temperature triggers the endothermic reaction of SAM desorption. The Laser beam can be used similar to a free hand to generate shapes of arbitrary complexity.

The results will be discussed in terms of (a) spatial profile of SAM composition on surfaces patterned; (b) modeling of Laser induced SAM desorption process to theoretically predict the spatial profile of SAM coverage on surface; (c) comparing the theoretical results with associate experimentally obtained profiles (SEM contrast images was used for experimental analysis); and (d) the model calculations which combines temperature history of the surface as a result of Laser heating with a model describing kinetics of SAM desorption based on Eyring equation to predict the final composition of the surface in terms of fraction of various SAM coverage. The resulting theoretical chemical composition contours were also related to wetting properties of surface; it will be shown that the theoretical predictions are in agreement with experimental observations of liquid confinement in hydrophilic regions created by this technique. The results, for example, indicate good control over feature size to manipulate wetting properties of a surface (features in the order of a few micrometers to 100 micrometers were generated).

CORE-SHELL PARTICLES WITH pH-RESPONSIVE POLY(VINYLPYRIDINE) SHELLS FROM SILICA-MICROGEL HETEROAGGREGATES.

Rob Atkin, Melanie Bradley, Michael O'Sullivan, Brian Vincent.

School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK.

A new method has been developed for the preparation of core-shell particles with thick, pH responsive, polymer shells. In the first step, poly(vinylpyridine) (PVP) microgels are adsorbed to ~ 5 μm silica spheres. This step is performed at pH ~ 3.5, so the silica is negatively charged, while the microgels are oppositely charged and swollen with solvent. After adsorption reaches equilibrium, stirring of the solution is ceased, and the silica-microgel heteroaggregates settle. This allows the supernatant, containing non-adsorbed microgels, to be decanted. The heteroaggregates are then redispersed in pure water. At this ambient pH, the microgels become uncharged, hence de-swell and become hydrophobic. A solution of pure PVP monomer, 2 wt % divinyl benzene (a cross-linking molecule) and 2 wt % initiator is added to the aqueous suspension. This is attracted to the silica-bound microgels, leading to swelling as it is incorporated into the polymer matrix. Polymerisation is initiated, facilitating seeded growth of the polymer around the silica sphere, to form a complete layer. This polymer shell has been shown to swell and de-swell in response to pH variation *in-situ* using optical microscopy, and electron microscopy reveals that the polymer layer is thick and continuous.

A long term goal is to use the same particle coating technique to encapsulate oil-core silica-shell microcapsules. These particles are created by first depositing a thin layer of silica around a PDMS droplet, followed by "Stober-type" growth of the shell. The PVP layer will then be grown on the silica surface, using the heteroaggregation method described above, producing microcapsules with organic-inorganic composite shells.

STRUCTURE OF POLYMERISED SURFACTANT FILMS AT SOLID/SOLUTION INTERFACES

Robert Chan[1], Christopher M. Fellows[1,2] and Gregory G. Warr[1]

1. School of Chemistry, The University of Sydney, NSW 2006
2. School of Biological, Biomedical, and Molecular Sciences, The University of New England, Armidale, NSW 2351

robert.chan@usyd.edu.au

The aqueous self-assembly and adsorbed layer structure of a series of cationic surfactants incorporating polymerizable methacrylate and vinylpyridinium moieties with different chain lengths and counterions have been examined on a variety of substrates including mica, graphite, and quartz using conductivity, AFM, and neutron reflectometry. Critical micelle concentrations are consistent with expectations for similar, non-polymerizable surfactants, but adsorbed layers on mica are surprisingly, often found to be laterally-unstructured bilayers. Polymerization has been performed under a variety of thermal and photoinitiation conditions both ex-situ and in-situ, and the structure and stability of the films thus formed characterized by AFM, mass spectrometry and dilution studies. Low conversion of monomer to polymer frequently yields unstable films that are readily washed off by dilution, but under some conditions a stable permanent structure may be formed and preserved.

DISTINGUISHING BETWEEN SURFACE HYDROXYL GROUPS OF BOEHMITE USING ATR-IR.

Scott A. Dickie and A. James M^{c}Quillan

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin

sdickie@alkali.otago.ac.nz

Alumina is an important material used widely in a number of industrial applications, particularly as a catalyst support, in the ceramics industry and as a coating for pigments. The predominant crystal phase of alumina present in pigment coatings is believed to be boehmite (γ-AlOOH) and thus its surface chemistry is of great interest.

Adsorption processes on poorly crystalline boehmite (PCB) particles have been studied using the attenuated total reflection infrared (ATR-IR) spectroscopic method. This method allows the *in-situ* investigation of wet surface chemical processes. Thin films of aggregated particles of PCB that are stable between pH 4 and 11 have been prepared by drying aqueous boehmite dispersions. The adsorption of acetylacetone (acac) to the surface of PCB has been studied at the solid/liquid and solid/gas interface. The bidentate chelating nature of the acac ligand requires the presence of a surface Al^{3+} ion possessing two or more exchangeable OH groups for chemisorption to take place. By looking at the changes in the OH deformations of PCB surface OH groups upon chemical and physical adsorption of acac the differentiation between surface OH groups of PCB can be made.

DIVALENT AND TRIVALENT METAL ION ADSORPTION ONTO INORGANIC SUBSTRATES

Daniel S. Eldridge, Russell J. Crawford and Ian H. Harding

Environment and Biotechnology Centre, Swinburne University of Technology, P.O. Box 218, Hawthorn 3122, Australia

DEldridge@groupwise.swin.edu.au

Many studies have been performed where aqueous heavy metals have been adsorbed onto a variety of different colloidal substrates in an attempt to model aqueous metal ion removal from industrial waste-water. One challenge in this modelling process is that it is very difficult to vary the individual properties of the adsorbent, such as its iso-electric point, surface area or dielectric constant, whilst keeping the other properties constant. There are substrates, however, where select properties can be varied whilst maintaining the overall chemistry of that substrate.

Adsorption onto a sample of amorphous Fe_2O_3 shows that the order of divalent metal ion adsorption with respect to pH follows the pattern, $Sn^{2+} > Cu^{2+} \approx Pb^{2+} = Zn^{2+} > Ni^{2+} > Cd^{2+} > Mg^{2+} > Ca^{2+}$. Literature shows that this order of metal ion adsorption affinity is not uncommon, irrespective of the adsorbing substrate employed. Furthermore, analysis of the data shows a good correlation between the hydrolysis behaviour of the divalent metal ions and their adsorption affinity.

Analysis of trivalent metal ion adsorption onto the same substrates does not appear to closely follow the same trend.

These observations warrant the future study of the adsorption of a suite of both divalent and trivalent metal ions onto a variety of substrates, including TiO_2, SiO_2 and amphoteric polystyrene latex, to further investigate the correlation between adsorption affinity and metal ion hydrolysis behaviour. Such a study will allow insight into the processes that dictate metal ion adsorption, as well as the differences in adsorption efficiency between various metal ions.

MEASUREMENT OF FILM STRESS USING A CANTILEVER BENDING TECHNIQUE

Drew Evans and Vincent S. J. Craig

Department of Applied Mathematics, Research School of Physical Sciences and Engineering, Australian National University, Canberra ACT 0200, Australia

dre110@rsphysse.anu.edu.au

Thin films deposited by sputtering or applied as a coating, often exhibit film stress when cured. The degree of stress in these films is important in macroscopic samples, as well as many of the manufacturing processes important to the production of Micro-Electro-Mechanical devices (MEMS). The magnitude of this stress is important, given that excessive stress may delaminate the film or cause the substrate to buckle or curl.

The measurement of film stress using the Atomic Force Microscope and custom built instruments that employ macroscopic surfaces will be described. Correct evaluation of the film stress requires knowledge of the bending mode of the cantilever under the action of the stress. Here we demonstrate that a significant number of measurements in the literature are based on methods of analysis that yield values of the film stress that are incorrect. How this data may be corrected is described and some examples of film stress measurements discussed.

TITANIA PIGMENT DISTRIBUTION IN DRY WATER-BASED PAINT FILMS IN THE PRESENCE OF POLYMERIC DISPERSANTS

Saeed Farrokhpay[1], Gayle Morris[1], Daniel Fornasiero[1] and Peter Self[2]

1. Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095.
2. Adelaide Microscopy, University of Adelaide, Adelaide SA 5000.

Saeed.Farrokhpay@postgrads.unisa.edu.au

The influence of polymeric dispersants containing different functional groups on the titania pigment dispersion in both aqueous suspensions or the wet state and dry water-based paint films were investigated. The polymeric dispersants chosen were polyacrylic acid and polyacrylamide homo- and co-polymers modified with hydroxyl and/or carboxylate groups. A range of experimental methods including polymer adsorption, zeta potential, rheology and particle size measurements were used to assess the dispersion effect of the polymeric dispersants in the wet state. AFM and TEM were used to assess the distribution of the titania pigment particle in the surface and bulk of the dry paint films. Gloss and surface roughness of the dry films were also measured. The results of these measurements were all in agreement regarding the effect of the polymeric dispersants on the pigment dispersion properties. In the absence of dispersant, the pigment distribution in the paint film was non-uniform and relatively large pigment aggregates appeared at the surface, resulting in a rough surface. In the presence of dispersants, in general, the paint surface roughness decreased and the gloss increased. In the presence of polyacrylamide homopolymer, the paint gloss slightly increased and further increased when hydroxyl modified polyacrylamide copolymer was used. In the presence of polyacrylic acid or carboxylate and hydroxyl modified polyacrylamide, the paint gloss significantly increased. The type of polymeric dispersant considerably affected the pigment distribution in dry paint film, in agreement with the stabilisation effect of both anionic and non-ionic dispersants in aqueous pigment suspensions.

THIOL-BASED PLASMA POLYMER COATINGS AS PLATFORMS FOR BIOSCIENCE APPLICATIONS

Patrick G. Hartley[1], Sofia .K. Øiseth[2], Thomas .R. Gengenbach[1], Graham Johnson[3],
Keith M. McLean[1] and George Ganakas[1]

1. CSIRO Molecular Science, Bag 10, Clayton South 3169, Australia
2. School of Chemistry, Faculty of Science, Monash University, Clayton 3800, Australia
3. CSIRO Molecular Science, PO Box 184, North Ryde, NSW, 1670, Australia

george.ganakas@csiro.au

Radio frequency glow discharge plasma polymer coatings form robust thin films which contour and adhere strongly to the surfaces of polymeric and other materials. Their ability to modify surface properties, for example, to enhance biocompatibility or to introduce defined chemical functionalities at interfaces for the subsequent coupling of bioactive molecules, have seen their widespread application in the field of biomaterials research.

We report on the development of sulphur containing plasma polymers using ethanethiol as the feed monomer. In order to ascertain the influence of deposition conditions on the properties of the films, a range of protocols were employed. The films were characterised by X-ray photoelectron spectroscopy (XPS); atomic force microscopy; streaming potential and contact angle measurements. Since XPS data are not sufficiently specific to distinguish between similar carbon-sulphur functional groups (e.g. thiol vs. sulphides), the nature and density of the surface functionalities were quantified by using a thiol specific maleimide containing probe. The stability of the films was tested by assessing coating thickness and chemistry before and after autoclaving. The effects of ageing in air, particularly with respect to the chemical structure were monitored over several months. The incorporation of sulphur functionalities provide reproducible supports for the subsequent grafting of proteins and for the adhesion of gold nanoparticles. The coatings were also shown to act as supporters of cell attachment and growth.

A NOVEL MODEL OF DNA BASES

Nicola Lake[1], John Ralston[2] and Geoffrey Reynolds[2]

1. Madderns Patent and Trade Mark Attorneys, First Floor, 64 Hindmarsh Square, Adelaide, South Australia, 5000
2. Ian Wark Research Institute, Uni South Australia, Mawson Lakes, SA, 5095

nicola@madderns.com.au

A novel model of DNA bases has been developed by tethering DNA bases to a surface in a self-assembled monolayer [SAM], comprising thymine moieties standing normal to the surface. The ordered nature of the system, in conjunction with the close packing, means the thymine groups mimic DNA chemistry, enabling base stacking and immobilisation effects to be explored that solution studies simply cannot provide for. The physical properties of the individual molecules in the SAM, such as acidity constant, change quite markedly from bulk solution phase values.

Apart from an intrinsic, theoretical interest in the physical and chemical properties of DNA bases, the nucleic acids form permanent photoproducts in DNA, i.e. thymine-dimers, that result in biological inactivation. To that end a model that can be used to investigate the formation and cleavage effects of thymine-dimers is very important. Upon exposure to light radiation the monolayer exhibits an unexpected molecular reorganisation that is observed due to the nature of the biomolecules used. This intriguing phenomenon provides a route for further exploring the molecular structure of the thymine-dimer and in particular the different spatial requirements required for the photoproduct. Other uses of the system, for example, investigations into the strength of base pair bonding and how easily bases are replaced by contaminants, etc. will be discussed.

NOVEL SURFACE COATINGS FOR ARRAY BASED APPLICATIONS

Ben Muir[1], Patrick Hartley[1], Celesta Fong[1], Keith McLean[1], Kirby Siemering[2]

1. CSIRO Molecular Science, Bayview Ave, Clayton, Melbourne, Vic, Aus
2. Australian Genome Research Facility, Melbourne, Vic, Aus

ben.muir@csiro.au

There is a strong need to improve the immobilisation of bio-molecules such as oligonucleotides and antibodies, onto various formats for array based applications. Inherent challenges exist during the microarray spotting of bio-molecules including surface chemical inhomogeneity, spot reproducibility and poor background fluorescence of the slide substrate. These factors result in poor spot morphology and signal intensity which can lead to a reduction of the sensitivity (S/N) of the diagnostic assay.

The prohibitive expense of commercially available microarray slides along with current microarray challenges, indicates the importance of developing new surface coatings for the life sciences. By tailoring the substrate surface chemistry, structure, charge, wettability and morphology, CSIRO Molecular Science in conjunction with the Australian Genome Research Facility hope to utilise the power of High Throughput Surface Discovery (HTSD) to screen for novel oligonucleotide binding surfaces. In the early stages of this research, plasma polymer coatings and functional graft polymers are being used in an attempt to optimise cDNA binding on a glass slide format. Initial work has been aimed at developing functional plasma polymer films with low intrinsic fluorescence. The use of a wide range of surface analytical techniques including fluorescent scanning/detection, AFM, SIMS, MALDI and streaming potential measurements are being utilised in this research. The project aims to elucidate the important parameters required to successfully and reproducibly array cDNA.

SATELLITE HOLES FORMATION IN THIN POLYMER FILMS

Chiara Neto[1,2] and Karin Jacobs[2]

[1] Department of Applied Mathematics, RSPhysSE, Australian National University, Canberra ACT 0200, Australia
[2] Experimental Physics, Saarland University, 66041 Saarbrücken, Germany

chiara.neto@anu.edu.au

The spreading of a liquid on a solid surface and the stability of the resulting film are issues of major importance not only in a number of technological applications, such as paints, surface coatings, lubrication and textile dyeing, but also in fundamental studies of surface physics. The thermodynamic stability and the dynamics of thin films on solid surfaces have been addressed in numerous studies, both experimental and theoretical in the last decade. These films can decay either by nucleation events or by spinodal dewetting, essentially only depending on the interface potential describing the short- and long-range intermolecular interactions between the interfaces and the initial film thickness. In the present work we focus on dewetting of very thin, low molecular weight polystyrene films of thickness between 4 and 30 nm. In the experiments the film rupture is artificially triggered by scratching an initially flat film, resulting in dry channels in the film. The further rupture of the film occurs by the formation of a correlated pattern of holes ("satellite holes") along the liquid rims accumulating at the channel borders. We provide a direct comparison between experimental results, obtained by atomic force microscopy (AFM), and numerical results, obtained from simulations based on the lubrication equation. Results of experiments and simulations are in good agreement, in respect both to the particular patterns developed upon dewetting and to their temporal evolution. The artificial indentations provide a direct and easy means to study the connection between local curvature of the hole rims and the appearance of satellite holes. On the basis of experiment and simulation we elucidate the mechanisms involved in the formation of the satellite holes.

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AN INVESTIGATION OF pH-RESPONSIVE DIBLOCK COPOLYMER MICELLES ADSORBED ON SILICA PARTICLES BY CONFOCAL MICROSCOPY

Christophe Schatz, Erica J. Wanless

School of Environmental and Life Sciences, The University of Newcastle, N.S.W. 2308

christophe.schatz@newcastle.edu.au

Diblock copolymers based on dimethylamino-ethyl methacrylate (DMA) and diethylamino-ethyl methacrylate (DEA) form micelles in slightly alkaline conditions. In bulk solution, the micellisation is a fully reversible process driven by the pH of the media[1,2]. In this work, the adsorption of PDMA-PDEA copolymer micelles on silica particles was investigated by epifluorescence and confocal microscopy. The use of suitable fluorescent probes allows us to determine further characteristics of the adsorbed copolymer layer as a function of the solution pH. The encapsulation of a hydrophobic molecule in the core of adsorbed micelles and its subsequent release was also investigated as a function of the pH.

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EFFECT OF pH ON THE ASSEMBLY OF WEAK POLYELECTROLYTE MULTILAYER FILMS

Elvira Tjipto, John Quinn and Frank Caruso

Department of Chemical and Biomolecular Engineering, Centre for Nanoscience and Nanotechnology, The University of Melbourne, Victoria 3010, Australia.

e.tjipto@pgrad.unimelb.edu.au

The buildup of multilayers by the layer-by-layer (LbL) technique involves the alternating adsorption of oppositely charged polyelectrolytes. With each adsorption step, the surface charge is reversed and this allows adsorption of the next layer of polyelectrolyte. This versatile method allows multilayer construction with controllable thickness, composition and chemical functionalities.

When strong (largely pH-independent) polyelectrolytes are used in multilayer assembly, factors such as ionic strength and molecular weight have a significant effect on the properties of films. More recent work has shown that in weak polyelectrolyte systems, it is possible to have greater control over multilayer properties such as thickness, wettability, porosity etc. However, since weak polyelectrolytes have charge densities that are pH-dependent, their behaviour is less well understood.

In this work, a copolymer of styrene-sulfonate and maleic acid, PSSMA (4-styrenesulfonic acid-co-maleic acid) is assembled into thin films with a weak polyelectrolyte, PAH (poly(allylamine hydrochloride)). PSSMA is particularly interesting because it has styrene-sulfonate side groups that are strongly charged and maleic acid side groups that can be charged or uncharged, depending on pH conditions. Consequently, the styrene-sulfonate group may provide stability to the multilayer films while the carboxylic acid groups can be used to alter multilayer properties because the extent of ionization is pH-dependant. The multilayer films are characterized using QCM (Quartz Crystal Microgravimetry), UV-Vis spectrophotometry, AFM (Atomic Force Microscopy) and FTIR (Fourier Transform Infrared Spectroscopy).

The assembly pH is found to significantly influence multilayer thickness, and the stability of the films upon post-assembly treatments into different pH. The influence of the comonomer ratio in PSSMA, molecular weight of the polyelectrolyte and ionic strength of deposition solutions were also investigated. Another finding is that the ionization of the weak polyelectrolytes is significantly different in the film compared to in solution.

INVESTIGATION OF SELF-ASSEMBLED MONOLAYERS ON MERCURY USING A SURFACE FORCE APPARATUS (SFA)

Lucy Wang[1], Miao Chen[3], Wolfgang Knoll[2], Olga Vinogradova[2] and Roger Horn[1]

[1] Ian Wark Research Institute, University of South Australia, Mawson Lakes, Adelaide SA 5095, Australia;
[2] Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany;
[3] Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China.

wanyl001@students.unisa.edu.au

Study of self-assembled monolayers (SAMs) formed from long chain thiol compounds adsorbed to metallic surfaces (in particular, gold) has attracted considerable attention in recent years. However, SAMs formed on solid metals tend to have defects such as pinholes and steps. On the other hand, when SAMs are formed on mercury there are no defects in the substrate and there is no crystal structure to impose itself on the organization of the adsorbed monolayer. As a result the SAM can form with high uniformity, smoothness and integrity [1,2].

A surface force apparatus [3,4] has recently been modified to allow interactions between mica and a mercury drop in aqueous solutions to be explored. Applying an electrical potential to the mercury allows electrical double-layer forces between mercury and mica to be measured as a function of surface charge on the mercury. Our results show that a SAM formed from uncharged thiols (11-mercapto-1-undecanol, 11-mercaptoundecanthiol) change the dipole potential of the mercury/water interface without affecting the charging behaviour. On the other hand, SAMs of 11-mercaptoundecanoic acids are negatively charged due to the dissociation of the -COOH function group. This significantly influences the double-layer forces between the mercury and mica, whose measurement can be used to determine the amount of surface charge. The electrocapillary curves of SAM-modified mercury have also been measured using the sessile drop method, which shows that the formation of SAMs reduces the interfacial tension of the mercury/water interface by 20~30mN/m at the pzc of mercury. The SAMs can be desorbed by applying a large negative potential to the mercury. Desorption peaks in a cyclic voltammogram measured in situ are correlated with changes in force between mica and the SAM-modified mercury.

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UNDERSTANDING METAL ION ADSORPTION ONTO BIOLOGICAL SUBSTRATES THROUGH SURFACE CHARACTERISATION

Gordon D. Bewsell[1], Ian H. Harding[1], Marylou Molphy[1], William Skinner[2]
and Russell J. Crawford[1]

1 Environment and Biotechnology Centre, Swinburne University of Technology, P.O. Box 218, Hawthorn 3122, Australia
2 Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes Boulevard, Mawson Lakes 5095, Australia,

GBewsell@groupwise.swin.edu.au

Environmental damage caused by aqueous heavy metals is an increasingly important issue. Heavy metals released into the environment through industrial activities tend to persist indefinitely, accumulating through the food chain. This can ultimately lead to serious environmental and public health problems such as genetic malformation and/or death. One of the main causes of heavy metal pollution is the release of heavy metal-containing industrial effluent into waterways. This is often as a direct result of inefficiencies associated with existing heavy metal removal processes. Consequently, the efficient removal of heavy metals has become a significant problem for industry. Over the past few years, biological substrates such as fungi have been investigated as potential adsorbents. This study examined the adsorption of selected aqueous metals onto biological adsorbents of fungal origin (*Rhizopus stolonifer*, *Mucor rouxii* and *Pycnoporus cinnabarinus*).

The pH-dependent adsorption of various divalent metals onto the above substrates was investigated at constant substrate surface area. It was found that of all the substrates investigated, *M. rouxii* was the most effective. Further studies were conducted focusing on copper adsorption with both Langmuir and Freundlich isotherm models being fitted to the data, *M. rouxii* was again found to be the most effective of the substrates investigated.

Surface characterisation of all fungal substrates was carried out, in order to investigate the ‘unique’ surface properties of *M. rouxii* that resulted in this enhanced adsorption ability. The surface functionality of the fungi was investigated using both DRIFTS and XPS. Preliminary studies show amine functionality appears to play a key role.

COVALENT MODIFICATION OF FLAT SINGLE CRYSTAL AND POROUS SILICON SURFACES FOR BIOSENSOR APPLICATIONS

T. Böcking[1,2], K.A. Kilian[2], S. Ilyas[1], P. Reece[1], K. Gaus[3], M. Gal[1] and J.J. Gooding[2]

1. School of Physics, The University of New South Wales, Sydney 2052, Australia
2. School of Chemistry, The University of New South Wales, Sydney 2052, Australia
3. Centre for Vascular Research, The University of New South Wales, Sydney 2052, Australia

t.boecking@unsw.edu.au

The modification of flat single crystal and porous silicon surfaces with Si-C linked monolayers[1-3] is the first step in the development of biosensors based on changes in the space charge region at the semiconductor surface (for flat single crystal silicon) or changes of the optical properties (for porous silicon)[4]. The monolayers should passivate the underlying silicon against corrosion, allow the specific immobilisation of biological capture agents (to which the analyte can bind) and resist the non-specific adsorption of biomolecules.

We have synthesised a range of novel alkenes with ethylene oxide moieties (to impart anti-fouling properties) and reactive endgroups (for biomolecule attachment) and reacted these with hydride-terminated silicon surfaces in thermal hydrosilylation reactions. The structure and chemical composition of the resulting monolayers were characterised by X-ray reflectivity and contact angle measurements (for flat samples), infrared spectroscopy (FTIR) and reflection spectroscopy (for porous samples) and X-ray photoelectron spectroscopy (for all samples).

We have investigated the functional properties of these SAMs for biosensing applications. The anti-fouling properties of the monolayers were tested by monitoring the adsorption of fluorescent proteins to the surfaces. A number of model compounds and biomolecules were covalently immobilised on the organic monolayers to verify the reactivity of the terminal functional groups.

It was shown that the reaction of alkenes with dual functionalities form well-defined monolayers on flat single crystal and porous silicon surfaces to provide a platform for biosensing applications.

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A STUDY OF THE BIOLUBRICATING PROPERTIES OF MUCIN.

Adam Feiler

Centre for Surface Biotechnology, Uppsala Biomedical Centre (BMC), Box 577,
751 23 UPPSALA

adam.feiler@ytbioteknik.uu.se

Biocompatibility is crucial for successful implementation of prostheses, be it a bone replacement part or a contact lens. Any mismatch in biochemistry of the implant *in vivo* can quickly lead to encapsulation, rejection and/or infection. Design and control of the physical and chemical properties of the surface of an implant is therefore vital to ensure good biocompatibility and desired mechanical properties.

Mucins, a group of high molecular weight proteoglycans, together with water, salts, immunoglobins and secreted proteins, forms mucus, a viscous secretion that covers epithelial surfaces throughout the body. This gel layer is known to have important protective and lubricative properties, for example it protects the epithelial cells in the gastrointernal tract from digestive enzymes, hydrochloric acid and microorganisms. It is envisaged that a mucin-rich surface coating could be used to reduced protein and bacterial attack of prostheses.

In the current study the adsorption kinetics and conformation of purified mucin BSM (Bovine Submaxially mucin) onto polystyrene surfaces was measured by QCM and Ellipsometry. The influence of adsorbed layers of mucin on normal and frictional forces was measured by AFM. Mucin adsorbed slowly (hours) onto polystyrene and formed a fairly diffuse layer which showed very good lubricating properties. Competitive adsorption between mucin and the protein BSA (Bovine Serum Albumin) prevented mucin adsorption and its concurrent lubricating properties.

ON THE CHEMICAL CONTROL OF THE POLY(DIMETHYLSILOXANE) INTERFACE

Xin Gao, Flavio Mornaghini, Hans Jörg Mathieu

Ecole Polytechnique Fédérale de Lausanne (EPFL), Institute of Materials Science and Technology (IMX), Switzerland

Xin.Gao@EPFL.ch

Poly(dimethylsiloxane) (PDMS) is used in various biomedical applications [1, 2]. The aim of the present study is the controlled tailoring and analysis of the polymer biointerface with the change of chemistry and wetting behavior of the surface. We report on the reduction of the water contact angle studying the physico-chemical phenomena that govern oral mucosa when in contact with food. In this study the elastic commercial PDMS (Silflow, Davis Healthcare) is used as a model substance for simulation of the bio-interface in the mouth when eating.

The aim of the present study is to reduce the contact angle from its original hydrophobic value of 110° to more hydrophilic values over several days. Change of the chemical composition was obtained by applying a radio-frequency (rf)-plasma (O_2, Ar, and N_2) varying power and duration. In a follow-up process the PDMS was exposed to a wet-chemical treatment using hydrophilic polymers (e.g. PAA, PHEMA). The chemical composition of the surface layers was analyzed at various times after plasma using Angle Resolved X-ray Photoelectron-Spectroscopy (AR-XPS) at different take-off angles assessing a shallow layer between 3-10 nm from the surface. The topography was controlled by Atomic Force Microscopy (AFM). In addition, the PDMS surface was studied by tribological wear tests on PDMS and results are correlated with the surface modification. We show experimental evidence that the control of chemical and the topographical modifications at the surface are essential for the solid/liquid interface behavior.

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PHASE BEHAVIOR AND SMALL-SCALE STRUCTURE OF ONE- AND TWO-COMPONENT PHOSPHATIDYLCHOLINE LIPID BILAYERS

Thomas Kaasgaard[1], Chad Leidy[1], Ole G. Mouritsen[2] and Kent Jørgensen[3]

1. MEMPHYS Center for Biomembrane Physics, Dept. of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark.
2. MEMPHYS Center for Biomembrane Physics, Dept. of Physics, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark.
3. LiPlasome Pharma A/S, Technical University of Denmark, Bldg. 207, DK-2800 Lyngby, Denmark.

thomas.kaasgaard@email.dk

Atomic force microscopy (AFM) is a powerful technique for studying the small-scale structure of lipid bilayers. A major drawback of the technique, however, is the need to use solid supported lipid bilayers, because lipid bilayer behavior may be perturbed by the presence of the solid support. Indeed, studies have shown that both the phase transition temperature and the domain structure of solid supported bilayers differ from free-standing lipid bilayers. Consequently, there is a need to develop improved solid supported lipid bilayer systems.

In this study, atomic force microscopy has been employed to study the top bilayer of one- and two-component supported double bilayers. In contrast to more traditional supported single bilayers, the well-known ripple phase was observed in the top bilayer of both one-component DPPC, and two-component DMPC-DSPC supported double bilayers. This allowed us to visualize and study the formation and disappearance of ripples at the pretransition of DPPC lipid bilayers, as well as the impact of ripples on the domain structures in DMPC-DSPC lipid mixtures. Our AFM experiments showed intriguing angular domain structures that were similar to the domain structures in giant unilamellar vesicles reported by others. Moreover, the phase transition temperatures were in good agreement with differential scanning calorimetry measurements on bulk lipid vesicle samples. On this basis, it was concluded that the top bilayer of supported lipid bilayers shows free-standing behavior.

SELF-ASSEMBLY AND SURFACE MODIFICATION OF MULTILAYER MEMBRANES FOR CELL MICROENCAPSULATION

Celine Doeuk, Annie Chen, Andy Leung, Matt Trau and Gwen Lawrie

Nanotechnology and Biomaterials Centre, School of Microbial and Molecular Sciences,
The University of Queensland, 4072

g.lawrie@mailbox.uq.edu.au

Animal tissue can address the immediate and future short-fall in human transplant material for treatment of, for example, diabetes, liver failure, Parkinson's disease, and Alzheimer's disease. Isolating the foreign tissue from the immune system is the key to avoiding rejection without the need for immunosuppressive drugs. Microencapsulation of cell spheroids in a immunoisolative, highly biocompatible, immunoselective biomembrane offers an alternative to allograft or autograft implantation. We are developing innovative approaches to the bioencapsulation of cell clusters using complex membranes assembled from biopolymer hydrogels and polypeptides. As cell spheroids are time consuming to produce, these membranes have been developed and modified on collagen coated beads and empty alginate beads as model spheroids. Recent studies have resulted in the covalent modification of the outer polysaccharide membrane with polypeptides and proteins with the am of ultimately improving immunoisolation. We present evidence of these successful modifications and demonstrate the retention of activity of the molecules which are have been bound to the beads.

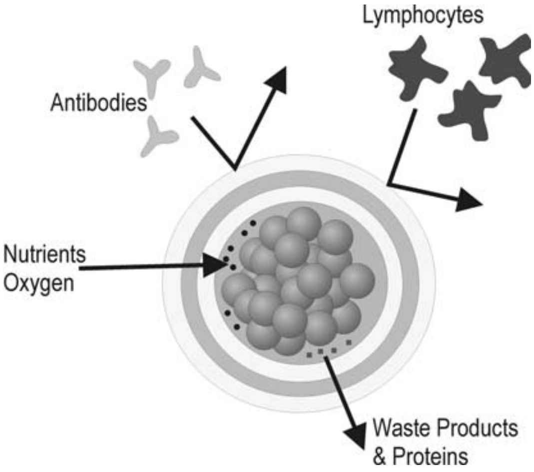

Fig 1: Cell spheroid encapsulated in a multilayer polyelectrolyte membrane.

A NOVEL CLASS OF SYNTHETIC CATIONIC LIPID VECTORS FACILITATING THE EFFICIENT DELIVERY OF GENES AND PROTEINS

Minoo Moghaddam[1], Fiona Cameron[2], Horace Drew[1] and Trevor Lockett[2]

1. CSIRO, Molecular Science, North Ryde, NSW 2113, Australia
2. CSIRO Corporate, North Ryde, NSW 2113, Australia

minoo.moghaddam@csiro.au

Cationic liposomes are used as synthetic vectors in human clinical trials for gene therapy purposes. Despite their relatively low efficiency compared to viral-based vectors, cationic lipids have several critical advantages: 1) low immunogenicity 2) large-scale production, 3) Low toxicity, 4) higher safety and, most importantly, delivery of varying lengths of DNA. Since cationic lipids are less efficient than viral-based delivery systems, considerable effort has been made in synthesis of new lipids, formulations and careful evaluation of transfection activities.

We have developed novel cationic lipids for use in gene therapy and delivery of proteins. These cationic lipids are based on cationic peptides linked to fatty acyl conjugates through the Tris molecule. The compounds are structurally similar to triglycerides, although with greater flexibility due to the nature of the Tris linkage, which allows simple alteration of the number and nature of fatty acyl groups, the number of positive charges and the spacing between the cationic head groups and the lipophilic domains. By systematic variation of these parameters we have synthesised some 130 different compounds. All of these compounds have been tested for their ability to introduce reporter gene cassettes into CHO cells and other mammalian cell lines in culture. In this way we have improved the transfection activity of our reagents some 30-fold over the original prototype molecule. Selected reagents routinely promote significantly higher levels of transfection than the commercial reagents lipofectamine (Gibco/BRL), TFX-50 (Promega) and DOSPER (Boehringer Mannheim). The best reagents have transfection activities of 7-20 fold over the commercially available reagent, lipofectamine in the cell lines tested.

One of the unique characteristics of Tris cationic lipids is their effective capability to deliver without formulation with added neutral lipids. In addition, a selected number of our reagents have been tested for delivery of proteins into mammalian cells. They have shown a several fold increase in activity compared to the commercially available reagent, Bioporter (Pierce).

KINETIC AND NANOSTRUCTURAL ANALYSIS OF PROTEIN ADSORPTION ON TAILORED SUBSTRATES

A. Quinn, H. Mantz, and K. Jacobs

Saarland University, Saarbrücken, Postfach 15 11 50, D-66041 Saarbrücken, Germany

a.quinn@physik.uni-saarland.de

The principal aim of this research is to identify the surface physicochemical properties that affect protein adsorption in the oral cavity, and ultimately to govern the structure and composition of the acquired salivary pellicle (the proteinaceous film that rapidly coats all intraoral surfaces). By controlling the composition of the pellicle on dental replacement materials via tailoring of their surface properties, it is anticipated that the rate and type of bacterial attachment can be reduced due to the highly specific nature of the bacteria/protein interaction. Hence the growth of dental plaque can be inhibited and the incidence of periodontal disease reduced.

A specific focus of this research is on the effect of long-range forces emanating from the bulk material beneath any surface coating. For extremely thin surface coatings, such forces contribute to the total interfacial force, and hence alter protein adsorption. Protein adsorption kinetics are presented for surfaces with identical surface chemistries, yet variable substrates. A combination of in-situ ellipsometry adsorption measurements, scanning probe microscopy, and wettability analysis are undertaken to investigate these effects.

SPONTANEOUS AGGREGATION AND DYNAMICS OF MIXED BILE SALT / PHOSPHOLIPID MICELLES AND LIPID FORMULATIONS USING MOLECULAR DYNAMICS SIMULATIONS

Dallas B. Warren[1], David K. Chalmers[2] and Colin W. Pouton[1]

[1] Department of Pharmaceutical Biology and Pharmacology, Victorian College of Pharmacy, Monash University, Parkville, Victoria 3052, Australia
[2] Department of Medicinal Chemistry, Victorian College of Pharmacy, Monash University, Parkville, Victoria 3052, Australia

dallas.warren@vcp.monash.edu.au

We report on the aggregation and dynamic behaviour of mixed bile salt (BS) / phospholipid (PL) micelles, mixed BS, fatty acid (FA) and lysophospholipid (LPL) micelles and glyceride lipid formulation systems using molecular dynamics (MD) simulations. MD simulations were performed using GROMACS 3.1.4 (www.gromacs.org). The mixed micelle simulation has similar structural and dynamic properties to those presented previously in the literature. The digested form presents some notable differences and provides some insight into the nature of mixed micelles within the small intestine as digestion occurs. Interesting results have been obtained for the two different lipid formulations, due to the micro structures observed for what are typically considered as a homogenous mixture. The lipid formulations consist of distinct regions of hydrophobic and hydrophilic character; they are essentially reverse micelles under low water content conditions.

PROBING POLYMER-MINERAL INTERACTIONS WITH VIBRATIONAL SPECTROSCOPY

Linh Chiem, Le Huynh, John Ralston and David Beattie

Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes Boulevard, Mawson Lakes 5095, Australia,

linh.chiem@postgrads.unisa.edu.au

Polymers are used in the minerals processing industry as surface modifiers for applications such as depression, flocculation and dispersion. To understand why particular polymers are more suitable than other polymers for a given mineral system and application, it is important to study the polymer-mineral interactions that govern the adsorption process.

In this study Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR) Spectroscopy was used *in-situ* to study the adsorption of two polyacrylamides at the talc surface using the particle film method[1]. Adsorption was evident by the increase in the absorbance maxima of infrared bands due to the polyacrylamides. The adsorption was studied as a function of concentration and time using the 1457 cm^{-1} band (due to the $–CH_2$ stretching vibration. The Gibbs free energy of adsorption ($\Delta G°$) and the rate constant of adsorption were found to be in the order of –45 kJ/mol and 0.030 min^{-1}, respectively. A shift in the 1425 cm^{-1} band due to the –CN stretching vibration was observed upon adsorption and attributed to either a direct interaction of the amide group with the talc surface or a change in polymer conformation after adsorption on the talc surface.

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ATOMIC FORCE MICROSCOPY STUDY OF SILICA-SILICA INTERACTION IN DODECYLAMINE SOLUTIONS

Glen McCann[1], Anh V. Nguyen[1], Geoffrey M. Evans[1] and Erica J.Wanless[2]

University of Newcastle, Callaghan, NSW 2308
1. School of Engineering
2. School of Environmental and Life Sciences,

Glen.McCann@studentmail.newcastle.edu.au

Dodecylamine is commonly used in industry to facilitate the flotation of quartz, (silica). This study examined interfacial conditions arising in the silica-dodecylamine flotation system. Atomic Force Microscopy (AFM) was used to determine the influence of dodecylamine solutions on silica particle-surface interactions. A 14.5µm diameter silica particle was attached to a microfabricated AFM cantilever to form a colloid probe. The interaction forces between the colloid probe and an identical silica planar substrate were measured and related to the separation distance. Dodecylamine solution concentrations were varied, ranging from 0.01mM to 8mM. The pH of the system was also varied.

Previous work undertaken in silica flotation demonstrated regions of micellisation of dodecylamine with respect to concentration and pH. Increases in pH corresponded to lower concentrations where micellisation occurred. Solutions with conditions below the micellisation range were used in this study.

Monotonic repulsive interaction forces were observed in deionised water. With increases in dodecylamine concentration attractive forces were detected, with the most ‘hydrophobic’ conditions seen at approximately 2mM. Further increases in concentration saw the attraction decrease, such that above concentrations of 4mM only repulsive forces were seen.

The extended DLVO theory was used to quantitatively justify measured interaction forces. At separation distances below approximately 10nm, the DLVO theory failed to adequately describe the system, hence indicating the presence of the strongly attractive (non-DLVO) hydrophobic force. DLVO and non-DLVO forces were considered additive, and were used to describe the total interaction forces for the silica-dodecylamine system.

THE EFFECT OF COAGULANT DOSE AND pH UPON DRINKING WATER SLUDGE DEWATERABILITY

David I. Verrelli, Peter J. Scales, David R. Dixon

Department of Chemical and Biomolecular Engineering, Particulate Fluids Processing Centre, The University of Melbourne, Victoria 3010, Australia

d.verrelli@pgrad.unimelb.edu.au

Drinking water treatment results in the formation of a sludge (waste by–product) of low solids concentration. Water companies increasingly wish to minimise the quantity and/or maximise the ‘quality’ of sludge they produce so as to reduce both financial and environmental costs.

Several influences on the formation and behaviour of flocs in sludge must to be considered, including raw water type (*e.g.* colouration, dissolved organic carbon), coagulation /flocculation conditions (*e.g.* chemical type, dose, pH), and shear history. Rheological data is analysed using phenomenological models, leading to prediction of sludge dewaterability, process optimisation, and, ultimately, evaluation of process ‘robustness’.

The presentation will focus on the influence of coagulant dose (aluminium sulfate) and pH on both the rate and extent of dewatering of drinking water treatment plant sludges.

It will be shown that sludges generated in the laboratory have dewatering properties that overlay those of sludges sampled in the field. Further, it will be shown that dose and pH significantly affect dewatering behaviour.

In particular, aside from producing a lesser amount of sludge, low coagulant doses were identified as producing sludge that is more dewaterable. Additionally, dewaterability was seen to deteriorate as the coagulation pH increased from 6 up to 8 and above.

A NOVEL METHOD FOR INVESTIGATING SOLID-LIQUID INTERACTIONS: INVERSE LIQUID CHROMATOGRAPHY

Pirre Ylä-Mäihäniemi and Daryl R.Williams

Imperial College of Science, Technology and Medicine, Department of Chemical Engineering and Chemical Technology, London, UK

p.yla-maihaniemi@imperial.ac.uk

Inverse Liquid Chromatography (ILC) is a physicochemical chromatographic technique for studying solid-liquid interactions and surface characteristics of particulate materials. The solid material to be studied is packed into a liquid chromatography (LC) column, and known solutes of relevance are introduced into liquid mobile phase which passes though the column as in a LC experiment. The retention behaviour of these solutes with the unknown solid packing is studied from the resultant chromatograms. This allows a detailed study of solid-liquid interactions to be thermodynamically described under real world conditions.

The technique provides information on both thermodynamic parameters, such as adsorption energy, and adsorption isotherms. The chromatographic experiments may be undertaken by either the pulse technique or the frontal analysis breakthrough curves, both provide the retention time and the height of the peak or plateau. The adsorption isotherms and other characteristics are determined from experimental solid-liquid adsorption chromatograms.

In this work solid-liquid interactions based on a surface adsorption mechanism have been investigated using a range of solid materials and solutes. Adsorption isotherms for cyclohexanone adsorption on silica powder have been measured by ILC and compared with isotherms achieved by classical static methods. Surface energy studies have been constructed using paracetamol as the solid material. Irreversible adsorption has been studied using an ILC system consisting of two detectors. This work shows ILC to be a useful tool for particulates characterisation.

SELF-ASSEMBLY OF NONIONIC SURFACTANTS INTO LYOTROPIC LIQUID CRYSTALS IN ETHYLAMMONIUM NITRATE, A ROOM-TEMPERATURE IONIC LIQUID

Miguel U. Araos, Gregory G. Warr

School of Chemistry, University of Sydney, Sydney, NSW, 2006,

miguel.araos@orica.com

The formation and stability of a variety of lyotropic liquid crystals by polyoxyethylene nonionic surfactants is reported in the room-temperature ionic liquid, ethylammonium nitrate (EAN). The pattern of self-assembly behaviour and mesophase formation is strikingly similar to that observed in water, even including the existence of a lower consolute boundary or cloud point. The only quantitative change from water is that longer alkyl chains are necessary to drive the formation of liquid crystalline mesophases in EAN.

NETWORK DEFORMATION OF COAGULATED COLLOIDAL SUSPENSIONS

Ainul A A Aziz, Jonathan Foong, Peter J Scales

Particulate Fluids Processing Centre, Department of Chemical and Biomolecular
Engineering, University of Melbourne, Parkville 3010, Victoria, Australia.

aaaa@unimelb.edu.au

The rheology of concentrated particulate suspensions is very sensitive to the nature and magnitude of the inter-particle forces, especially for colloidal sized particles. If the attractive forces dominate over the repulsion and Brownian forces, particles aggregate and form clusters. As the solids volume fraction increases the clusters form a three-dimensional network that spans entire suspension. Spanning network are sometimes referred to as 'gels' which exhibit a very complex flow behavior. Some phenomena observed include visco-elastic, yielding, shear thinning and shear thickening and the extent of each property is the manifestation of the particles interaction forces.

The network deformation of concentrated suspensions can be monitored in the presence of shear and this was investigated through the use of small amplitude dynamic oscillatory (SADO) tests. This method also allowed quantitative interpretation of the network deformation which involved the transition between solid-like behaviour (before elastic deformation) and liquid-like behaviour (after plastic deformation). Deformation can be characterised into two limits, brittle and ductile material failure. The observed phase transitions were examined using Lissajous figures.

These tests have been performed on coagulated AKP-30 alumina suspensions from pH 7.0 to 9.5. The variation of G', G" and Lissajous plots are presented and discussed. As the pH of the suspension moved away from the iso-electric point (pH 9.2) of alumina, there was a gradual change in the deformation of the network from brittle to ductile failure. The point at which the material begins to plastically deform using SADO measurements was found to compare favourably with yield stress measurements conducted using the vane technique. It has been demonstrated that SADO measurement provides a more sophisticated tool to observe the network deformation of a material.

GROWTH OF ADSORBED QUATERNARY AMMONIUM SURFACTANT FILMS ON MICA OBSERVED USING AFM.

Annabelle Blom[1], Gregory G. Warr[1], and Erica J. Wanless[2]

1. School of Chemistry, The University of Sydney, Australia
2. School of Environmental & Life Sciences, University of Newcastle, Australia.

a.blom@chem.usyd.edu.au

The structure of adsorbed quaternary ammonium surfactant films formed by different alkyl chain lengths and number has been observed using atomic force microscopy (AFM). The single chained surfactants DTAB and TTAB have an adsorbed cylindrical morphology on mica at concentrations above the cmc whereas CTAB initially adsorbs as cylinders but transforms to a bilayer over time. Below the critical micelle concentrations both DTAB and TTAB form spherical aggregates, which grow along one axis, first forming short rods and then long rods as the cmc is approached. CTAB behaves more unusually due to the slow kinetics of its adsorption and evidence for the formation of a bilayer at concentrations as low as half the cmc is obtained.

The double-chained, bilayer-forming surfactants di-C_{12}DAB (DDAB), di-C_{14}DAB and di-C_{16}DAB have also been examined. Both DDAB and di-C_{14}DAB form a cohesive bilayer immediately, which is observed to strengthen with equilibration time. The slow equilibrium of di-C_{16}DAB allows examination of the film at less than saturated coverage and reveals growth of the bilayer through the nucleation and coalescence of patches. The difference in height between higher and lower regions is insufficient to result from bilayer and monolayer regions and the postulated structure is that of regions of bilayer with different packing densities. The regions with greater packing density force the alkyl chains into a more extended formation resulting in a slightly thicker bilayer. As further adsorption occurs more monomers pack into the less densely populated regions and the film becomes more uniform.

TEMPERATURE-DEPENDENCE OF ADSORBED LAYER STRUCTURE OF NONIONIC SURFACTANTS ON SILICA.

Annabelle Blom[1], Gregory G. Warr[1] and Erica J. Wanless[2]

1. School of Chemistry, The University of Sydney, Australia
2. School of Environmental & Life Sciences, University of Newcastle, Australia.

a.blom@chem.usyd.edu.au

Using atomic force microscopy (AFM), the adsorbed layer morphology of dilute solutions of nonionic ethylene oxide surfactants on hydrophilic silica has been determined as a function of temperature. Observations of the adsorbed layer morphology for the surfactants $C_{12}E_5$, $C_{14}E_6$ and $C_{16}E_6$ were made from 20ºC up to temperatures above the cloud point. For all surfactants studied, adsorbed structures were globular at 20ºC and reduced in curvature to cylinders and then a mesh structure[1] with increase in temperature. At temperatures close to their respective cloud points, all the surfactants studied were observed to form meshes. The film was never observed to transform to a bilayer even above the cloud point.

The loss in hydration of the polyoxyethylene headgroups with increase in temperature results in a reduction in the area occupied at the micelle surface. This increases the surfactant packing parameter (decreases aggregate curvature) from globules to a mesh, analogous to branched micelles recently reported in bulk solution[2] near the cloud point. That the film never transforms into a bilayer is significant and may provide insight into the mechanism of clouding in solution.

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NON- DLVO BEHAVIOUR AT THE OIL- WATER INTERFACE:
A SPECIFIC ION EFFECT

Tam T. Chau[1], Raymond R. Dagastine[1], Derek Y. C. Chan[2], Franz Grieser[3],
Geoff W. Stevens[1]

Particular Fluid Processing Centre, The University of Melbourne, Victoria, 3010, Australia
[1]Department of Chemical and Biomolecular Engineering
[2]Department of Mathematics and Statistic,
[3]School of Chemistry

t.chau@pgrad.unimelb.edu.au

Emulsions in general play an important role in many industrial processes and therefore controlling the interaction between droplets is often crucial for enhancing the efficiency of many processes. For example, liquid-liquid extraction, in applications such as hydrometallurgy, is a process where droplet coalescence is commonly controlled without added stabilisers. Some previous studies on droplet coalescence behaviour have shown a dependence on the polarity of the oil, but the reasons behind the effect have not been elucidated. In order to understand the previous effects, colloidal probe AFM was used to study the interaction between a silica sphere and polar organic droplets of both butyl and octyl acetate in a range of inorganic electrolyte solutions in the absence of any added stabilisers.

A series of electrolytes was used to vary both the anion and cation according to a Hofmeister series in the concentration range of 0.1mM to 10mM. The observed force behaviour was found to be dependent on the type of inorganic electrolyte in solution. The anionic sequence used in this study was iodide, nitrate, iodate, perchlorate and thiocyanide. The cationic sequence used in this study was ammonia, potassium, sodium, calcium and aluminium. It was observed that chaotropic (structure breakers) ions resulted in attractive force behaviour between the interacting surfaces whereas kosmotropic ions (structure makers) resulted in repulsive force behaviour. This behaviour cannot be completely described by DLVO theory. Separate experiments using a sequential series of electrolytes, on the same droplet, suggest that the effect is due to some type of interfacial phenomenon. These results will be discussed with respect to the possible origin of this specific ion effect.

INVESTIGATING SLIP BOUNDARY CONDITIONS WITH SQUEEZE FILM MEASUREMENTS IN THE SFA AND AFM

Jarred Clasohm and Roger Horn

Ian Wark Research Institute, University of South Australia, Mawson Lakes, Adelaide
SA 5095, Australia;

clajn002@students.unisa.edu.au

It is often assumed in hydrodynamic calculations that a no-slip boundary condition applies at the interface between a Newtonian liquid and a solid. In other words, the flow velocity of liquid at the interface is taken to be that of the solid. In recent years, as fine-scale experimental techniques have developed, questions have been raised about the validity of the assumption and whether the velocity-matching condition applies exactly at the liquid solid interface or at another position close to it, either to the liquid or to the solid side. The latter case would correspond to liquid slipping over the solid surface, and the amount of slip is characterised by a "slip length" which is the distance between the interface and the (virtual) position of the velocity match.

Two decades ago, measurements of squeeze-film lubrication using a surface force apparatus and simple liquids between mica [1,2] or silica [3] surfaces were analysed in terms of hydrodynamic lubrication theory. The theory was found to represent the data very accurately. In particular, the no-slip boundary condition was placed at the solid boundary [2,3], or about one molecular diameter into the liquid [1]. More recently, similar experiments have been conducted using colloid-probe AFM, and have concluded that slip does occur in simple liquids, with slip lengths of tens or even hundreds of nm [4-6]. It is not obvious why slip should be found in AFM measurements of hydrodynamic forces and not in SFA ones.

We present simulations of AFM experiments which suggest a possible difficulty in interpreting hydrodynamic AFM data to calculate the true thickness of the liquid film. Uncertainties in this quantity lead to uncertainty in the slip lengths established from this technique. There is no such uncertainty in the SFA measurements, in which the distance between the solid surfaces is determined absolutely.

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EVANESCENT WAVE AFM

Spencer Clark[1], Clayton McKee[1], John Walz[2] and William Ducker*[1]

1. Department of Chemical Engineering, University of Melbourne, Melbourne, Australia and Department of Chemistry, Virginia Tech, VA, USA.
2. Department of Chemical Engineering, Yale University, New Haven, CT, USA

*wducker@vt.edu

We describe the use of evanescent wave scattering to measure the separation between the surface of a solid and a particle that is attached to an Atomic Force Microscope (AFM) cantilever. Termed evanescent wave AFM (EW-AFM), our approach involves measuring the intensity of the light scattered from an evanescent field formed by the total internal reflection of a laser beam at a solid/fluid interface. In a conventional AFM 'colloid probe' measurement, this separation must be inferred from an examination of the surface forces. Direct measurement of this separation with EW-AFM removes some ambiguity in surface force measurement and, in addition, allows new types of measurements. Our evanescent scattering apparatus is essentially identical to that used in Total Internal Reflection Microscopy (TIRM), except that we collect the light that scatters back into the incident medium, because the AFM partly obscures the forward scattered light (*i.e.*, light scattered into the transmitted region). Compared to a conventional TIRM measurement, where the particle moves freely, attaching the particle to the cantilever in EW-AFM gives much greater control of the particle position.

We discuss applications of this technique to surface measurement and imaging. We also discuss how the scattering profile is a not always the same as the evanescent profile, and how the scattering depends on the radius and refractive index of the particle, as well as the polarization of the incident light.

THE INFLUENCE OF IONIC LIQUIDS ON EMULSION SYTEMS

Simon Ferguson[1], Erica Wanless[1], and Simon Biggs[2]

1. School of Environmental and Life Sciences, University of Newcastle, Callaghan 2308, Australia.
2. Institute of Particle Science and Engineering, University of Leeds, Houldsworth Building, Leeds LS2 9JT. United Kingdom.

simon.ferguson@newcastle.edu.au

Ionic liquids have raised substantial interest in both academia and industry over the past decade, and developed into a keen focus in green chemistry. These new liquids boast the ability to dissolve a range of solutes, have high thermal stability, negligible vapour pressure and a seemingly limitless range of compositions. The variety of applications for these new solvents spans all disciplines of chemistry to include catalysis, synthesis, polymerisation, and phase separations to name a few.

A frequently exploited class of ionic liquids is that based around the 1-alkyl-3-methylimidazole $[C_nMIM]^+$ cation. These ionic liquids are produced by the quaternisation of 1-methylimidazole with an alkyl halide to produce a cation of variable alkyl chain length and corresponding anion. Possible anions include hexafluorophosphate $[PF_6]$, tetrafluoroborate $[BF_4]$, nitrite $[NO_2]$, nitrate $[NO_3]$, tetrachloropalladate(II) $[PdCl_4]$, tetrachloroaluminate $[Cl\text{-}AlCl_3]$, ethanoate $[O_2CCH_3]$ and bis[(trifluoromethyl)sulfonyl]imide $[(CF_3SO_2)_2N]$. We have synthesised and investigated the series $[C_{4\text{-}8}MIM][X]$ ionic liquids, measuring physical properties such as density, viscosity, phase behaviour, thermal stability, melting point and temperature of decomposition. The c.m.c. of these ionic liquids in water was also determined, and rheology of emulsions containing ionic liquids investigated.

MÖSSBAUER SPECTROSCOPY INVESTIGATION OF THE ELECTROCHEMICAL BEHAVIOR OF NONTRONITE- AND MONTMORILLONITE-MODIFIED CARBON ELECTRODES

Tamar L. Greaves[1], Will P. Gates[2] and John D. Cashion[3]

1. CSIRO Molecular Science, Bag 10, Clayton South, Victoria 3169
2. Soil Physical Chemistry, Rutherglen Research Centre, Primary Industries Research Victoria, RMB 1145 Chiltern Valley Road, Rutherglen, Victoria 3685, Australia
3. School of Physics and Materials Engineering, Monash University, Clayton, Victoria 3168, Australia

tamar.greaves@spme.monash.edu.au

There has been considerable discussion in the literature over the past 20 years on the assignment of the peaks in the Mössbauer spectra of clay minerals to different crystallographic iron sites.

We have taken Mössbauer spectra of a range of nontronite and montmorillonite samples at room temperature and 80K. In addition, some of the clay samples were ground with carbon powder and bound with a Teflon binder to make working electrodes for use in an in-situ Mössbauer electrochemical cell. Mössbauer spectra were acquired over a few days while a reducing potential was applied to the cell.

From the Mössbauer spectra it was determined that in some of the clays a fraction of the structural iron underwent reduction, while in others no reduction was observed. In the case where reduction was observed, a direct correlation could be made between the decreased intensity in the Fe^{3+} contribution and the new Fe^{2+} intensity. Further correlations can be made by considering which of the samples did not undergo any reduction. These findings are providing useful information on the classification of the iron sites present in these clay minerals.

NANORHEOLOGY USING A MODIFIED COMMERCIAL ATOMIC FORCE MICROSCOPE

Jason Kilpatrick[1], Erica Wanless[1] and Simon Biggs[2]

1. Chemistry, School of Environmental and Life Sciences, University of Newcastle, Callaghan, NSW 2308, Australia
2. Institute of Particle Science and Engineering, University of Leeds, Leeds LS2 9JT, UK

jason.kilpatrick@newcastle.edu.au

The behaviour of fluids in confined geometries is increasing in importance due to the recent trend for the miniaturisation of systems. With the advent of microfluidic devices an understanding of the key factors that influence the behaviour of fluid flow in confined channels is of increasing relevance and this is reflected in the volume of literature reporting recent research in this area. Our main interest is in extending the capabilities of AFM technologies to allow relevant measurements of confined fluids. In so doing, we aim to take advantage of the increased sensitivity that the low inertia design of the instrument affords us.

By applying small amplitude high frequency oscillations to the substrate surface, we are able to extend the capabilities of the AFM to measure the hydrodynamic forces applied to a single colloidal particle attached to a cantilever whilst *simultaneously* collecting the normal static interaction potential data *without* it being influenced by the dynamic nature of the experiment. This is achieved through the use of Lock-in amplifiers for driving and detection, high speed data acquisition, and custom control and analysis software.

Through the utilisation of this technique we can also begin to investigate colloidal interactions on much smaller timescales then previously possible with AFM. In this presentation we will outline the development of this new technique and demonstrate some of the results that can be achieved through its application.

AFM MEASUREMENTS OF HYDRODYNAMIC FORCES BETWEEN DEFORMABLE DROPS: THEORY

Rogério Manica, Raymond R. Dagastine, Steven L. Carnie and Derek Y.C. Chan

Particulate Fluids Processing Centre, Department of Mathematics and statistics,
The University of Melbourne, Parkville VIC 3010 Australia

r.manica@ms.unimelb.edu.au

The Atomic Force Microscope (AFM) has been used successfully to measure the interaction between two deformable oil drops. The drops size (radius about 40 microns), interfacial tension, and approach velocities (about 10 microns/s) are in a regime where surface forces, hydrodynamic effects and drop deformation are all significant. A theoretical model taking into account these features as well as AFM cantilever deflection has been developed. Using matched asymptotic expansions, a new boundary condition for moving drops under AFM experimental conditions has been derived. This boundary condition is necessary to obtain results that are independent of the size of the computational domain. There is good agreement between theory and experiment in characteristic effects such as velocity dependent repulsion on approach and long-ranged attraction of hydrodynamic origin on retraction. Animated results of calculations will be presented to illustrate non-intuitive findings in the evolution of the drop surface during collision.

METALLOMICELLES AS CATALYSTS FOR ESTER HYDROLYSIS

John Christie[1], Andrew B Hughes[1] and Anastasios Polyzos[2]

1. Department of Chemistry, La Trobe University, Bundoora, Victoria, Australia 3086.
2. CSIRO Molecular Science, Bag 10, Clayton South, Victoria, Australia 3169.

tash.polyzos@csiro.au

Metallo-surfactants are an emerging class of functionalised surfactant that possess a transition metal complex forming a cationic head-group. In aqueous solution, the spontaneous self-assembly of metallo-surfactants results in the formation of metallomicelles that have been shown to be catalytically active toward the hydrolysis of phosphate and carboxylate esters at neutral pH and ambient temperatures. Metallomicelles have shown potential utility in important industrial processes including the detoxification of stockpiles of phosphorus(V) containing pesticides and chemical warfare agents such as GD or 'Soman'. Consequently, there is interest in the preparation of novel metallo-surfactants and the elucidation of the factors which determine the catalytic activity of metallomicelles toward ester hydrolysis.

This work investigated the influence of ligand structure, transition metal ion, surfactant concentration and substrate structure on the rate and mechanism of carboxylate ester hydrolysis in the presence of metallomicelles and co-micelles. A series of metallo-surfactants were prepared and the relative rates (k) of hydrolysis of a number of nitro-activated aryl esters were studied at neutral pH using UV spectrophotometry. The metallo-surfactants were prepared *in situ* by the complexation of transition metal ions (Cu(II), Zn(II), Cd(II) and (Ni(II)) with appropriate hydrophobic triaza ligands.

All metallomicelles studied significantly increased the rate of hydrolysis compared to the rate in buffered water (k_0) and non-functionalised micelles such as myristyltrimethylammonium bromide (MTAB) and Triton X-100. The substrates contained a carboxylate anion (nitroaspirins) or pyridine ring (picolinates) and catalysis was attributed to the co-ordination of the substrate to the metallo-surfactant head-group to form a reactive ternary complex (ML_nS) between transition metal (M), ligand (L) and substrate. Rate data from the study of the hydrolysis of picolinate structural isomers, suggests that the mechanism involves the pseudo-intramolecular nucleophilic attack of a metal bound hydroxyl within the ternary complex.

THE IMPORTANCE OF AROMATIC RINGS ON THE FORMATION OF WATER-SOLUBLE POLYMER - LOW MOLECULAR-WEIGHT MOLECULE COMPLEXES

Ignacio Moreno Villoslada[1], Susan Hess[1], Felipe Oyarzún[1], Marlen Jofré[1]
and Bernabé L. Rivas[2]

1. Instituto de Química, Facultad de Ciencias, Universidad Austral de Chile, Valdivia, Chile
2. Departamento de Polímeros, Facultad de Ciencias Químicas, Universidad de Concepción, Concepción, Chile

imorenovilloslada@uach.cl

The study of aqueous systems containing water-soluble polymers (WSP) is interesting in order to understand biological processes from both a structural and a functional point of view. These polymers undergo interactions with low molecular-weight species or with other polymers in solution. The interactions of low molecular-weight molecules (LMWM) with WSP are normally weaker and very dependent on the pH and ionic strength conditions. Interactions between surfactants and WSP are specially interesting due to the high ability to form supramolecular ordered sturctures. Apart from the study of the different structures and architectures involving WSP by means of their intermolecular interactions, the dynamics of these systems when different variables are changed provide with complementary information to system analysis. As is normally the case when long range electrostatic interactions are dominant, the absence of spectroscopical differences do not allow concluding the absence of interaction. Separation techniques may contribute to the detection, evaluation, and application of intermolecular interactions. Diafiltration allows obtaining the interaction constants between WSP and LMWM.

The binding features of poly(sodium 4-styrenesulfonate) (PSS) with π system-containg molecules such as methylene blue (MB), Rodamine B (RB), 2,3,5-triphenyltetrazolium chloride (TTC), or chlorpheniramine maleate (CPM) differ from other negatively charged polyelectrolytes. Seen by diafiltration, the interactions appear to be more intense, and a residual binding is found under high ionic strengths. Spectroscopical changes have been found for PSS-TTC, PSS-MB, and PSS-RB. In the case of the system PSS-RB, flurescence is strongly decreased.

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OLIGOMERIC SURFACTANTS THROUGH POLYMERISATION

Kathryn A. Topp[1], Gregory G. Warr[1], Christopher Barner-Kowollik[2]

1. School of Chemistry, University of Sydney
2. CAMD, School of Chemical Engineering, University of New South Wales

topp@chem.usyd.edu.au

Oligomeric (sometimes known as 'gemini') surfactants consist of several ordinary surfactant units joined by short chains linking the hydrophilic heads. They display interesting and unusual rheological and self-assembly properties. Since their synthesis can be a lengthy and difficult process, we are investigating polymerisation techniques as a way of producing a range of oligomeric surfactants.

Two classes of polymerisable surfactant (‘surfmer’) are being utilised: one based on a methacrylate group, the other on a vinylpyridinium group. Several of these, particularly in the latter class, are novel surfactants, and the self-assembly of the monomers is also being characterised.

The oligomeric surfactants are produced through free-radical polymerisation, which is carefully controlled in order to limit the degree of polymerisation and polydispersity. Two techniques have proven most suitable in this regard: catalytic chain transfer (CCT) and RAFT (reversible addition-fragmentation chain transfer). CCT uses less catalyst and leaves no end groups on the oligmers that might disrupt the surfactant behaviour, but is oxygen-sensitive and difficult to do in water. RAFT agents (e.g. cumyl dithiobenzoate) are a special class of chain transfer agent, provide excellent control over molecular weight and can be used in aqueous systems, but attach bulky end-groups to the oligomers and have only been well characterised in high molecular weight systems.

SILICA SURFACES NANOTRIBOLOGY IN AQUEOUS SOLUTIONS

Ivan U. Vakarelski, Bogdan C. Donose, Elena Taran and Ko Higashitani

Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan

vakarelski@cheme.kyoto-u.ac.jp

Understanding of nanotribological phenomena has a critical importance for the fast development of existing and emerging technologies, such as the chemical mechanical planarization (CMP) and the microelectromechanical systems (MEMS). Using Lateral Force Microscopy (LFM) we have investigated the frictional interaction between micron size silica particles and silica wafers in solution conditions characteristic for these technologies: high applied loads; extreme pH and electrolyte concentration. Two types of phenomena were demonstrated to play a determining role for the frictional force between the surfaces at these conditions. One of them was related to the microstructures of the layer of surface adsorbed cations and water molecules and the other to the mechanical properties of the silica surfaces change when in contact with water. For high electrolyte concentrations the layers of hydrated cations adsorbed on the surfaces were found to act as efficient boundary lubricants. Thus the smaller and more hydrated cations like Li^+ were having a higher lubrication capacity than the larger and less hydrated cations like Cs^+. With respect to the pH of the solutions no significant change in the frictional force was found for pH between 2 and 8. However at pH higher then 9 there was an initial region of significantly decreased frictional force. That region was suggested to indicate a softening in the upper layer of the silica surface due to increased silica dissolution at high pH. The phenomenon is expected to play an important role in understanding the basic mechanisms behind the CMP process.

HYDROCARBON SOLVENCY AND REVERSE MICELLE FORMATION IN MICROEMULSIONS

Krisztian J. Baranyai, Philip A. Reynolds, Mark J. Henderson and John W. White

Research School of Chemistry, The Australian National University, Canberra ACT 0200, Australia.

baranyai@rsc.anu.edu.au

We have measured and modelled small angle neutron scattering patterns from a polyisobutylene-based surfactant dissolved in six different oils (hexadecane, cyclohexane, toluene and the three equivolume binary mixtures), in contact with saturated ammonium nitrate solution, at 25 and 55 C. The measurements have been done for three different isotopic contrasts. Quantitative fitting of the scattering functions gives the amount and structure of reverse micelles in these microemulsions. All of the micelles contain negligible amounts of water, a core of the surfactant head group of radius about 10Å, surrounded by a shell of surfactant tail mixed with large amounts of oil solvent. The oil solvent content increases in the shell of the micelle as the free oil region is approached. The core's head content and innershell's tail content are generally relatively independent of oil nature. However, there are strong trends in other micelle parameters. As the oil solvency parameter increases, surfactant molecules of lower molecular weight increasingly aggregate to micron scale structures; while the tails of the remaining higher molecular weight surfactant molecules in the micelles become less coiled and stretch out straighter into the surrounding oil as the solubility of the tail in the oil solvents increases. These both cause the micellar external radius to increase, the micellar polydispersity decreases, and the percentage of surfactant in the outer region of the micelle decreases.

REVERSIBLE PHASE TRANSITIONS OF NANOSTRUTURED LIPID SYSTEMS IN CONFINED GEOMETRY

Liliana de Campo[1,2], Anan Yaghmur[1], Laurent Sagalowicz[3] Martin E. Leser[3],
Heribert Watzke[3], and Otto Glatter[1]

1. Institute of Chemistry, Colloids & Polymers, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria
2. University of Sydney, School of Chemistry F11, NSW 2006, Australia
3. Nestlé Research Center, Vers-Chez-Les-Blanc, 1000 Lausanne 26, Switzerland

liliana.decampo@uni-graz.at

Aqueous sub-micron sized dispersions of the binary monolinolein/water system, which are stabilized by means of a polymer, internally possess a nano-structure[1]. Taking this as our starting point, we were able to demonstrate that this internal structure can be tuned by temperature in a reversible way[2]. Upon increasing the temperature, this internal structure undergoes a transition from cubic via hexagonal to a fluid isotropic, so-called L_2-phase and vice versa. This means that upon cooling there is also a back transformation of the internal structure from L_2 via hexagonal to cubic. We found that these internal structures depend only on the current temperature and there is no hysteresis or other change after such a heating/cooling cycle. In addition to the structural changes in topology, the particles exhibit a "breathing mode": they expel (take up) water to (from) the aqueous continuous phase when increasing (decreasing) the temperature in a reversible way. At each temperature, the internal structures of the dispersed particles correspond very well to those in non-dispersed binary monolinolein-water phase with excess water, which proves that they actually remain in thermodynamic equilibrium even though the particles themselves are kinetically stabilized.

The internal structure of such dispersed particles can also be tuned by the addition of hydrocarbons with the main goal to arrive at an *emulsified microemulsion* EME system[3]: Depending on the used conditions, the addition of hydrocarbons might either lead to an emulsified emulsion (double emulsions, both emulsions are kinetically stabilized), or to an emulsified microemulsion (EME), in which the interior of the kinetically stabilized emulsion droplets is in thermodynamic equilibrium.

Small angle X-ray scattering (SAXS), cryogenic transmission electron microscopy (Cryo-TEM), and dynamic light scattering (DLS) allow these systems to be investigated in detail.

[1] J. Gustafsson, H. Ljusberg-Wahren, M. Almgren, and K. Larsson, Langmuir **12** (20), 4611 (1996).

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QUOKKA: THE SMALL ANGLE NEUTRON SCATTERING INSTRUMENT AT THE AUSTRALIAN REPLACEMENT RESEARCH REACTOR

Elliot P. Gilbert, Terry Noakes, Peter Abbeywick, Peter Baxter, Alain Brule, Frank Darmann, Nick Hauser, Eno Imamovic and Jamie C. Schulz

Bragg Institute, Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW, 2234, Australia.

epg@ansto.gov.au

A small-angle neutron scattering (SANS) instrument is being designed as part of the initial instrument suite for the 20-MW Australian Replacement Research Reactor. The new instrument, receiving neutrons from a large liquid-D_2 cold source, will be in the spirit of the world's best facilities and will greatly build upon the Australian Nuclear Science and Technology Organisation's existing expertise and facilities. Scheduled for completion in July 2006, it will provide Australian and international researchers with opportunities to access state-of-the-art SANS instrumentation. The details of the new SANS will be presented.

[1] E. Gilbert, C.J. Garvey, J.C. Schulz and R.B. Knott, Neutron News, **14**, 27 (2003)

WHAT DO YOU WANT TO KNOW ABOUT NANOSTRUCTURE?

Michael James, Robert Knott, Jamie Schulz, Andrew Nelson, David Sutton, Tracey Hanley and Elliot Gilbert

Bragg Institute, Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW, 2234, Australia.

epg@ansto.gov.au

Small-angle scattering and reflectometry are ideal techniques for structural characterisation in the size range between 1 nm and 1 micron and are applied widely to the study of colloidal systems as well as polymer physics, biomembranes and natural fibres. Building upon ANSTO's existing expertise and facilities, we are constructing, at the new 20 MW Australian research reactor, a world-class small-angle neutron scattering instrument and a neutron reflectometer, scheduled for completion in July 2006. Additionally, we will provide complementary state-of-the-art laboratory-based X-ray instruments, access to synchrotron radiation facilities combined with extensive experience in innovative product development. ANSTO offers academia, industry and government a unique capability not only in Australia but internationally.

Small angle scattering offers the possibility of investigating the structure, on the molecular scale, of colloids and proteins in solution and monitor their response to environmental change. For example the response of a colloid to an applied shear, or the response of a protein to denaturation conditions.

Reflectometry offers the possibility of investigating the organisation of thin films of materials on a flat surface. For example, the organisation of lipids on a liquid or solid surface, and changes induced by temperature or lateral pressure.

SANS STUDY OF NOVEL DENDRITIC POLYMERS PREPARED USING RAFT POLYMERIZATION

Tracey L. Hanley[1], Robert B. Knott[1], Xiaojuan Hao[2], Martina Stenzel,[2] Thomas P. Davis,[2]
Eva Malmström[3] and Christopher Barner-Kowollik[2]

1. Bragg Institute, Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW, 2234, Australia.
2. Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Sydney, NSW, 2052, Australia.
3. Royal Institute of Technology, Fibre and Polymer Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden

Tracey.Hanley@ansto.gov.au

Dendritic polymers are of significant interest because of their well-defined structure and globular architecture that give rise to innovative applications (eg drug delivery, biosensors, molecular batteries etc). Novel synthetic procedures can be used to produce polymers of very well defined architecture and molecular weights, and one such method is reversible addition fragmentation chain transfer (RAFT). Multifunctional, mono-disperse dendritic RAFT agents have previously been employed to prepare star polymers of *poly*butyl acrylate (PBA) and *poly*styrene (PS) of very narrow molecular weight distributions ($1.4<PDI<1.1$ for PBA and $1.5<PDI<1.3$ for PS) via bulk free radical polymerization. While the star shaped structure of the generated polymers was established by cleaving the pendant arms off the core of the star-shaped polymeric materials, the behaviour of the dendrimer based star polymers in solution is largely unknown. Potential end use of these dendrimers is defined by their behaviour in solution environments with respect to their specific shape in varying solvent environments. SANS experiments were conducted to confirm the star structure of the dendimers and the cleaved pendant arms, as well as their behaviour in solvent environments.

SANS experiments on dilute solutions of the PS and PBA dendrimers and the subsequently cleaved pendant arms were conducted at the NIST Centre for Neutron Research (Gaithersburg, USA) using the 8m NG-1 SANS instrument. Hydrogenated dendrimer and cleaved arm samples were dissolved in deuterated-THF solvent to produce the dilute solutions of interest; THF is a good solvent for PS and PBA. The results of these experiments on PS and PBA dendrimers produced by RAFT will be discussed.

Hao, X.; Nilsson, C.; Jesberger, M.; Stenzel, M. H.; Malmström, E.; Davis, T. P.; Östmark, E.; Barner-Kowollik, C. *J. Polym. Sci. - Chem*, **2004**, in press.

WHEN THIN IS SEXY – THE FUTURE OF NEUTRON REFLECTOMETRY IN AUSTRALIA

Michael James, Jamie Schulz and Andrew Nelson

Bragg Institute, Building 58, ANSTO, PMB 1, Menai, NSW 2234.

mja@ansto.gov.au

Neutron reflectometry is used to probe the structure of surfaces, thin-films or buried interfaces as well as processes occurring at surfaces and interfaces. Applications cover adsorbed surfactant layers, self-assembled monolayers, biological membranes, electrochemical and catalytic interfaces, polymer coatings and photosensitive films. Contrast variation and selective deuteration of hydrogenous materials are important aspects of the neutron-based technique. Neutron reflectometry probes the structure of materials normal to the surface at depths of up to several thousand Å, with an effective depth resolution of a few Å. Neutron reflectometry experiments have been performed by a number of Australian researchers at overseas facilities for more than a decade, however this capability has previously been absent in this country. We report instrument details as well as experiment results from Australia's first neutron reflectometer at the 10MW HIFAR facility at Lucas Heights. This instrument has now become part of the AINSE User Program and is accepting beam time proposals from Australian and International researchers. A neutron reflectometer has been recognised as one of the highest priority instruments to be constructed at the new 20MW research reactor facility at Lucas Heights (due for completion in 2006). In this presentation we also report the design of the horizontal sample, time-of-flight reflectometer to be constructed at the new research facility.

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