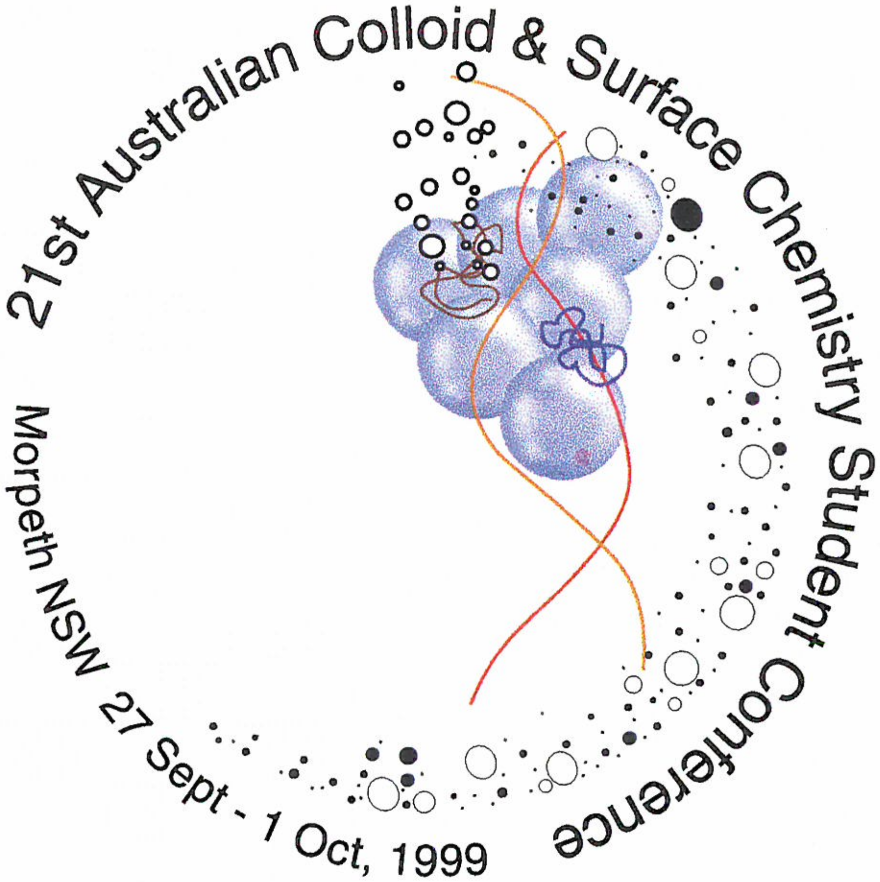


21st Australian Colloid & Surface Chemistry Student Conference

Morpeth NSW 27 Sept - 1 Oct, 1999

PROGRAMME & ABSTRACTS

TABLE OF CONTENTS

PREAMBLE

With hope in Hunter, the Colloid community is constituted as a democracy with a unique system of conferences to serve the common good with colloid and surface chemistry.

We the members of the Australian colloid and surface chemistry community commit ourselves to the 18-monthly student conference, proud that our national unity has been forged by a tradition that began with a handful of students back in 1967;

Never forgetting the sacrifices of those at each conference that make it to the first talk every morning despite the events of the preceding evening;

Upholding freedom, tolerance and individual dignity when it comes to questioning the speakers.

Honouring the conference founders, Bob Hunter and Tom Healy through the Hunter-Healy award for the best talk, first presented at the 20th conference held in Hahndorf in February 1998 under the auspices of the University of South Australia. Our nation's first colloid scientists are honoured for their ancient and continuing research culture, which enriches the life of our country;

Recognising the community-building contribution of generations of international visitors;

Mindful of our responsibility to nurture our unique research environment;

Supportive of achievement as well as equality for all growing researchers;

And valuing informality as clearly as the national colloid spirit which binds us together in both adversity and success.

Welcome to Morpeth and the 21st Australian Colloid and Surface Chemistry Student Conference hosted by the University of Newcastle. This year we have nearly 150 delegates, but we hope to maintain the traditional informal nature of the conference. There will be 47 student talks from senior research students and 30 poster presentations from junior research students. A particular welcome to the visiting international students: John Enlow from Otago (NZ), Nicola Woodward & Lisa Benee from Greenwich (UK), Valeria Tohver from Illinois (USA) and Natalia Panova from Waikato (NZ). We also welcome our plenary speakers, Laurent Michot from the CNRS Laboratory "Environnement et Minéralurgie" (France), and Mike Bevan lately from Carnegie Mellon University in the USA. Both speakers are currently researching at the AMPC in Melbourne.

The sessions are deliberately not grouped by subject, university of origin, gender or any other obvious category. The committee used a creative algorithm to timetable the talks and their decision is final. The abstracts are listed in chronological order. The organising committee encourages students to promote discussion and will therefore call for the speakers to be questioned initially by other students.

The conference has many strong traditions, not all of which are academic. In keeping with this we have timetabled a free afternoon on Wednesday. The staff vs student cricket match will be held on the St John's oval during this time. Others may choose to sample the local wineries or potter around the delights of Morpeth village. On Wednesday night the talent quest will be held. The conference dinner will be held on Thursday night after all the student presentations. We thank our plenary speakers for speaking on the final morning following the dinner.

We hope that you find everything to your satisfaction from the science to the location. If it is your first student conference, take heart from the confirmed addicts around you and we hope to see you all at the next conference in the next millennium.

Have fun.

Barry Fleming Shannon Notley Erica Wanless Simon Biggs

SPONSORS

The 21st Australian Colloid and Surface Chemistry Student Conference Organising Committee would like to extend their sincere thanks for the generous support that the following sponsors have provided.

ALBRIGHT
& WILSON

Albright & Wilson Australia

HUNTSMAN

Huntsman Surfactants

GS Group Scientific

SOLA
International
Sola Optical

AUSTRALIAN RESEARCH COUNCIL
Centre for Multiphase Processes
UNIVERSITIES OF NEWCASTLE, NEWSOUTH WALES & QUEENSLAND

R L A
...the Name behind the Names...
RESEARCH LABORATORIES
OF
AUSTRALIA

PASMINCO
GROUP
TECHNICAL
SUPPORT

Royal Australian Chemical Institute

CONFERENCE DELEGATES

Albright & Wilson
John O'Donnell

Australian National University
Ana-Suncana Barisic
Vincent Craig
Nobuo Maeda

CSIRO Minerals
Greg Allan
Joseph Muscat
Theo Rodopoulos

CSIRO Molecular Science
Robert Considine
Celesta Fong
Calum Drummond
Peter Harbour
Patrick Hartley
Marco La Rosa
Sally McArthur
Laurence Meagher
Orla Wilson

Dulux Australia
Michelle Carey

Huntsman Corporation Australia
Julie Brennan

Kodak (Australasia) Pty Ltd
Deirdre Murphy

La Trobe University
Rod Harris
Kurt Lackovic
John Wells

Monash University
Ian McKinnon
Niem Tri
Dorothy Attard

RMIT University
Ning Li

Swinburne University of Technology
Carolyn Burns
Russell Crawford
Jacinta Gorman
Ian Harding
Sonja Jenkinson
Mary-Lou Molphy
Tamna Woolcock

University of Greenwich
Lisa Benee
Nicola Woodward

University of Illinois
Valeria Tohver

University of Melbourne
Muthupandian Ashokkumar
Michael Bevan
Melanie Bradley
Kristen Bremmell
Jamie Chamberlain
Yu Chen
Antje Daehler
Tai Du
Dave Dunstan
Sam Gason
Michelle Gee
Diana Goodall
Franz Grieser
Tom Healy
Daniel Horrobin
Luisa Jayme
Malin Jonsson
Jenny Kisler
Daniel Lester
Christine Mangelsdorf
George Maurdev
Laurent Michot
Heide Mielke
Ineke Muir
Sarah Nespolo
Andrea O'Connor
George Oldfield
Simon Petris
Boris Poliak
Andrew Rodd
John Sader
Rob Salvatore
Peter Scales
Jim Stankovich
Rohan Tronson

Shane Usher
Millie Wan
Dallas Warren
Janine Wehrenbrecht
Yalin Wei
Annabel Wood

University of New South Wales
Siew Wei Goh
Andreas Hartmann
Wilhelm Holzschuh
Ashley Jones
Robert Lamb
Everett Lee
Antonella Petrella
Juniwaty Thomas
Hua Zhang

University of Newcastle
Rob Atkin
Simon Biggs
Janine Burns
Rob Cain
Barry Fleming
George Franks
Sharna Glover
Brett Macaulay
Shannon Notley
Mark Reitsma
Erica Wanless
Grant Webber
Yaode Yan

University of Otago
John Enlow

University of Queensland
Geoff Barnes
Ian Gentle
Linh Tran
Barry Wood

University of South Australia
Jonas Addai-Mensah
Phil Attard
Tim Barnes
Wuge Briscoe
Adam Feiler
Sarah Harmer
Roger Horn
Paul Jenkins
Roland Keir
Ian Larson
Jun Li
Andrew Michelmore
Michael Moody
Tim Muster
Clive Prestidge
Peter Pullman
Suparno
Matthew Taylor
Minh-Uyen Trinh
Bianca van der Zande
Christopher Weisener
Elaine Wightman
Ying Zhang

University of Sydney
James Beattie
Gordon Burns
Helge Hodne
Laszlo Kovacs
Greg Warr
Paul FitzGerald
Bob Hunter
Linggen Kong
Gregory Nash
Miles Page
Jamie Schulz
Asaph Widmer-Cooper

University of Waikato
Natalia Panova

GENERAL PROGRAMME

Sunday		Monday		Tuesday		Wednesday		Thursday		Friday	
		7.30	**Breakfast off-site**	7.30	**Breakfast**	7.30	**Breakfast**	7.30	**Breakfast**	8.00	**Breakfast**
				9.00	Session # 3	9.00	Session # 7	9.00	Session # 9		
			On-site registration	10.30	**Morning Tea**	10.30	**Morning Tea**	10.30	**Morning Tea**	9.30	Plenary Speakers
				11.00	Session # 4	11.00	Session # 8	11.00	Session # 10	11.00	Conference ends
		12.30	**Lunch**	12.30	**Lunch**	12.30	**Lunch**	12.30	**Lunch**		
		2.00	Session # 1	2.00	Session # 5			2.00	Session # 11		
3.00	On-site registration	3.20	**Afternoon Tea**	3.20	**Afternoon Tea**		Free Afternoon	3.20	**Afternoon Tea**		
		3.50	Session # 2	3.50	Session # 6			3.50	Session # 12		
6.30	**Dinner off-site**	6.30	**BBQ Dinner**	6.30	**Dinner**	6.30	**Dinner**	6.30	**Conference Dinner**		
				7.30	Albright & Wilson Poster Session # 1	7.30	Huntsman Surfactants Poster Session # 2		Entertainment		
						9.00	Talent Quest				

SCIENTIFIC PROGRAMME

Monday 27th September 1999

1.50pm **Welcome** **Barry Fleming**

2.00 – 3.20pm **Session 1** **Chair: Erica Wanless**

2.00 Extremely Hydrophobic Thin Films - Preparation and Characterisation
Hua Zhang

2.20 Kinetics and Mechanisms of Vesicle Self-Assembly
Millie Wan

2.40 Counterion Effects on Hexadecyltrimethylammonium Surfactant Self-Assembly on Silica
Barry Fleming

3.00 Flocculation and Dewatering of Bauxite Residues
Janine Wehrenbrecht

3.50 – 5.10pm **Session 2** **Chair: Laurence Meagher**

3.50 Development of a Spreading Formulation using Methyl Anthranilate
Sonja Jenkinson

4.10 Photochemical Behaviour of Zinc Oxide Quantum Dots
Annabel Wood

4.30 The Primary Electroviscous Effect and the Motion of Hematite Particles
Sam Gason

4.50 PEO-PPO-PEO Block Copolymers at the Emulsion Droplet-Water Interface
Tim Barnes

Tuesday 28th September 1999

9.00 – 10.20am **Session 3** **Chair: Michelle Gee**

9.00 Small Amplitude Oscillatory Rheometry and Dynamic Light Scattering of the Stoichiometric and Thermal Dependence of a Polysaccharide Gelling System
Andrew Rodd

9.20 Creeping Flow of a Concentrated Emulsion
Brett Macaulay

9.40 Adsorbed Layer Structure of Cationic Surfactants on Quartz
Jamie Schulz

10.00 Kinetics of Polymorphism in Photographic Coupling Agent
Ning Li

11.00 – 12.20pm Session 4 Chair: Paul Jenkins

11.00 The Characterisation of Pharmaceutical Powders: Crystal Habit and Wettability
Tim Muster

11.20 Hot Flocs and Cool Dispersions
Lisa Benee

11.40 Minimal Surface Modelling of Surfactant Liquid Crystals: Comparison of Theoretical and Experimental X-Ray Diffraction Patterns
John Enlow

12.00 AFM Tip Deformations Under an Oscillatory Loading Regime
Shannon Notley

2.00 – 3.20pm Session 5 Chair: Patrick Hartley

2.00 Optimisation of the Washing and Dewatering of Flocculated Suspensions: The Influence of Temperature
Shane Usher

2.20 The Role of Colloid Science in Bitumen Emulsion-Aggregate Interactions
Jacinta Gorman

2.40 Single Bubble Sonoluminescence
Rohan Tronson

3.00 Formation and Flocculation of Calcium Phosphate Phases - Precipitates from Heated Whey Permeates
Natalia Panova

3.50 – 5.10pm Session 6 Chair: Kristen Bremmell

3.50 Dielectric Response of a Porous Particle
Boris Poliak

4.10 The Effect of Crosslink Density on the Phase Transition Behaviour of Colloidal Microgel Particles
Nicola Woodward

4.30 Interactions of Cryptosporidium Oocysts and Filtration Media (typical of the drinking water treatment process) assessed by Colloid Probe AFM Measurements
Rob Considine

4.50 A Phase Transition in Adsorbed Layers of an n-Alkane on Mica
Nobuo Maeda

8.00pm Albright & Wilson Poster Session 1

A Reflectometry Study of the Adsorption Kinetics of CTAB to the Silica-Water Interface
Rob Atkin

Cu(II) Adsorption Mechanism on Pyrite: An XAFS & XPS Study
Christopher Weisener

Hydrophobic Thin Films Based on TiO_2 and Silica Based Crosslinking Sol-Gel Technology
Juniwaty Thomas

Accessibility and Kinetics of Adsorption in Mesoporous Molecular Sieves
Antje Daehler

Self-Assembly of Cationic Surfactants at the Graphite-Solution Interface
Paul FitzGerald

Surface Layer Control for Improved Copper Recovery for Chalcopyrite Leaching
Sarah Harmer

Molecular Structure of a Weak Gelling System
Heide Mielke

Tailoring Selective Surfaces for Metal Ion Uptake
Linh Tran

Phase Behaviour in Colloidal Dispersions
Simon Petris

Stabilization of Cubic Phases
Gregory Nash

Semiconductor Nanobubbles and Coated Metal Nanoparticles
George Oldfield

Depletion Interactions in Charged, Binary Suspensions
Valeria Tohver

Polarised Attenuated Total Reflection Spectroscopy in Protein Adsorption Kinetic Studies
Luisa Jayme

Rheological Study of Kappa-Carrageenan and Locust Bean Gum System
Yu Chen

Wednesday 29th September 1999

9.00 – 10.20am Session 7 Chair: Ian Gentle

9.00 The Influence of Cations on the Crystallization of Colloidal $Al(OH)_3$ from Synthetic, Self-Nucleating Bayer Liquors
Jun Li

9.20 Non-Equilibrium Forces Between Polyelectrolyte-Coated Surfaces
George Maurdev

9.40 Surfactant Design by Molecular Simulation
Marco La Rosa

10.00 Can You Hear Me? Ultrasonic Forces for Particle Separation
Niem Tri

11.00 – 12.20pm Session 8 Chair: Russell Crawford

11.00 Imaging the Surfactant Self-Assembly Shape Transition at the Solid-Liquid Interface Using Atomic Force Microscopy
Laszlo Kovacs

11.20 The Role of Electrostatic Interactions in Protein Adsorption on Polysaccharide Surfaces
Sally McArthur

11.40 The Effect of Interfacial Properties on the Reaction of Nickle Ion Extraction by LIX 84 in a $G_{12}A_8$ Micelle Model System
Dallas Warren

12.00 An Electrokinetic Study of CN-Silica in a Non-Polar Colloidal System
Suparno

8.00pm Huntsman Surfactants Poster Session 2

Removal of Aqueous Heavy Metals by Biosorption onto Fungi
Tamna Woolcock

Reversible Wetting of Photo-Responsive Surfaces
Peter Pullman

Adsorption of Amphiphilic Block Copolymers at the Solid/Liquid Interface
Grant Webber

Investigation of Paint Film Formation by Atomic Force Microscopy
Gordon Burns

Polymer Adsorption onto the Different Surfaces of Kaolinite Clay
Matthew Taylor

The Effect of Citric Acid on the Adsorption of Cadmium to the Clay Mineral Illite
Kurt Lackovic

Characterisation and Stabilisation of Lipid-DNA Complexes for Gene Therapy
Minh-Uyen Trinh

The Colloid Science of Pasta Filata Cheese
Dorothy Attard

Glass Formation in Microemulsions
Asaph Widmer-Cooper

Syneresis in Carrageenan Gels
Rob Salvatore

Novel Methods of Dewatering of Colloidal Suspensions
Daniel Lester

Sonoluminescence from Ethylene Glycol-Water Mixtures
Melanie Bradley

Absorption of Oppositely Charged Polyelectrolyte and Surfactant onto α-Alumina Fibres
Ineke Muir

Growth of ZnO Films - a Several Variable Problem
Antonella Petrella

The Origin of the Hydrophobic Interaction
Ana-Suncana Barisic

Thursday 30th September 1999

9.00 – 10.20am Session 9 Chair: Vincent Craig

9.00 Forces Involving a Deformable Surface using the Atomic Force Microscope
Sarah Nespolo

9.20 Growth of Piezoelectrical ZnO Films using Single Source Chemical Vapour Depostion
Everett Lee

9.40 Structure and Dynamics of Aluminium Alkoxide / Phosphate Surfactant Organogels
Miles Page

10.00 Nanotribology in Soil and Granular Systems
Mark Reitsma

11.00 – 12.20pm **Session 10** **Chair: George Franks**

11.00 Mesoporous Silicates and Protein Adsorption
Jenny Kisler

11.20 Bridging Flocculation of Alumina Particles Using Dual Polymers
Sharna Glover

11.40 Interparticle Forces Modified by Adsorbed Polyphosphate
Adam Feiler

12.00 Incipient Failure of a Yield Stress Material
Jamie Chamberlain

2.00 – 3.20pm **Session 11** **Chair: Clive Prestidge**

2.00 A Proposed Mechanism of Polyphosphate Adsorption onto Titanium Dioxide and their Effect on Interparticle Forces
Andrew Michelmore

2.20 The Effect of Solution Conditions on Film Drainage from between a Droplet and a Solid Surface
Dianna Goodall

2.40 Growing Gallium Nitride Films the Easy Way
Wilhelm Holzschuh

3.00 Acid/Base Properties and Cadmium Adsorption of Carbonaceous Substrates
Carolyn Burns

3.50 – 4.50pm **Session 12** **Chair: Ian Larson**

3.50 Measuring Long Range Repulsion in a Nonpolar Liquid
Wuge Briscoe

4.10 The Effect of Natural Organic Matter on the Rheology of Concentrated Alumina Suspensions
Peter Harbour

4.30 The Influence of Adsorbed Polymers on Galena Particle Interactions
Elaine Wightman

Friday 1st October 1999

9.30 – 10.50am **Plenary Speakers** **Chair: Simon Biggs**

11.00am **Closing Remarks** **Simon Biggs**

NOTES

Extremely Hydrophobic Thin Films - Preparation and Characterisation

Hua. Zhang, R. Lamb and B. Gong

Surface Science & Technology, School of Chemistry, University of New South Wales, Sydney, 2052
E-mail: hz@student.unsw.edu.au

The development of thin films based on cross-linking of nanosize particles is discussed.[1] A remarkable property of these films is the enhanced hydrophobic properties. Water contact angles as high as 170° are possible.

The fabrication of such films involves binding silica powder using polydimethyl siloxane (PDMS). This results in a surface comprised of silanol and methyl silane groups. Variations in this surface chemistry were evaluated using time-of-flight second ion mass spectrometry (TOFSIMS). The resulting surface roughness was assessed with both AFM and SEM.

While the ratio of hydrophobic to hydrophilic groups is important there is a limit. Above this, where the remarkably enhanced hydrophobicity is observed, only variations in roughness are important. Some ideas based on a simple capillary model of the films are examined

References:
1. R.Lamb and H.Zhang, Int. Pat./PCT/AU98/00185, 1998

The Kinetics and Mechanisms of Vesicle Self-Assembley

Millie Wan and Andrea O'Connor

Department of Chemical Engineering, University of Melbourne, Parkville VIC 3052
E-mail: m.wan@pgrad.unimelb.edu.au

There is a need to understand the fundamentals of the self-aggregation or self-assembly behaviour of surfactants. This will help researchers to better understand complex phenomena, such as detergency, and to optimise conditions for vesicle applications such as drug or flavour encapsulation. This research project is focussing on the kinetics and mechanisms of vesicle self-assembly in surfactant mixtures that form vesicles spontaneously. Vesicles are closed single-bilayer shells made of surfactants that enclose a separate aqueous phase from the bulk aqueous phase.

The specific surfactant mixtures being investigated are sodium octyl sulfate(SOS) and cetyltrimethyl-ammonium bromide (CTAB), and sodium dodecyl sulfate (SDS) and dodecyl trimethylammonium bromide (DTAB), from the cationic-anionic surfactant class of vesicle forming mixtures and the 4, 5 and 6-isomers of sodium dodecyl benzene sulphonate (SDBS). The SOS/CTAB and SDS/DTAB surfactant pairs form equilibrium vesicle phases when the correct ratios of cationic surfactant and anionic surfactant are mixed. The SDBS system undergoes a micelle to vesicle transition when the ionic strength of the solution is increased.

A major approach that is being used to elucidate the mechanisms of the vesicle self-assembly process in these mixtures, is the time-resolved solvatochromic probe method. This is a method in which changes in the absorption spectra of interfacially solubilized solvatochromic probes are measured. These changes in the absorption spectra reflect the change in the interfacial microenvironment that the probes sense as the vesicle self-assembly process is taking place.

Preliminary investigation of the kinetics of the SDS-DTAB system with ET(30) (Reichardt's dye) appear promising. However the use of this probe requires that the ionic strength of the surfactant solutions be increased and currently the effects of this change in solution conditions are being investigated. As well as continuing this line of investigation, it is envisaged that the kinetics and mechanisms of vesicle self-assembly will be studied by dynamic light scattering, video enhanced microscopy and other relevant methods.

Counterion Effects on Hexadecyltrimethylammonium Surfactant Self-Assembly on Silica

Barry D. Fleming[1], Stephanie M. Butler[2], Erica J. Wanless[1], Simon Biggs[1] & Robert D. Tilton[2]

[1]Department of Chemistry, University of Newcastle, Callaghan, NSW 2308 Australia
[2]Department of Chemical Engineering, Colloids Polymers and Surfaces Program,
Carnegie Mellon University, Pittsburgh, Pennsylvania 15213 U.S.A.
E-mail: cpbf@paracelsus.newcastle.edu.au

We have studied the effects of the surfactant counterion on the adsorbed layer structure for cationic hexadecyltrimethylammonium ($C_{16}TA^+$) surfactants on negatively charged silica surfaces using AFM. Above the CMC, increasing the binding affinity of the counterion (from chloride to bromide) increased the surface excess surface concentration by approximately 60% and changed the structure of the adsorbed surfactant layer from aggregates with circular projections to worm-like micelles. Below the CMC, the counterion has only a small effect on the structure of the adsorbed layer. A change in adsorption mechanism is suggested by differences observed in the state of interfacial self-assembly on either side of the critical micelle concentration (CMC) for CTAB. By quantitatively analyzing the AFM images and comparing this to the surface excess concentration measured by reflectometry, we determined that surfactants pack differently in adsorbed aggregates than they do in similarly shaped aggregates formed by self-assembly in solution.

Flocculation and Dewatering of Bauxite Residues

Janine Wehrenbrecht, Peter J. Scales and Thomas W. Healy

Advanced Mineral Products Research Centre, School of Chemistry, The University of Melbourne, Parkville, Vic 3052
E-mail: j.wehrenbrecht@pgrad.unimelb.edu.au

Flocculants are used in many aqueous mineral beneficiation processes as a means of hastening solid/liquid separation. One such example is the Bayer process, which is used to extract alumina from bauxite. In this process flocculants are utilised in the separation and washing of an insoluble residue, known as red mud, from a pregnant liquor containing valuable sodium aluminate.

The aim of the project is to optimise the separation and washing processes used in the Bayer process, and ultimately obtain maximum dewaterability. This is to be achieved by developing a clear understanding of the structure-function relationship between red mud particles and flocculants under Bayer liquor conditions. Of particular interest are the effects of chemical structure and conformation of the polymers, as well as Bayer liquor conditions (e.g. high sodium hydroxide concentration, carbonates, calcium, organics etc.). All of these variables will be related to the permeability and compressibility of red mud sludges.

Adsorption studies undertaken using hematite as a model surface have indicated that adsorption of sodium polyacrylate and co-polymers of sodium acrylate and acrylamide is heavily dependent upon charge density, ionic strength and carbonate concentration.

Development of a Spreading Formulation Using Methyl Anthranilate

Sonja E. Jenkinson[1], Russell J. Crawford[1], Ian H. Harding[1], Ian C. Bowater[1] & Linton Staples[2]

[1]Centre for Applied Colloid and BioColloid Science, Swinburne University of Technology,
P.O. Box 218, Hawthorn 3122.
[2]Applied Biotechnologies Pty Ltd, Unit 1, 56-60 Export Dr., Brooklyn 3025, Australia
E-mail: SJenkinson@swin.edu.au

Methyl anthranilate (2-aminobenzoic acid, methyl ester, MA) is a well-known non-lethal primary bird repellent. Its effectiveness results from the irritation of a bird's trigeminal and olfactory nerves and does not require ingestion to be effective. MA is also used as a food additive, with low mammalian toxicology. MA is, therefore, an ideal reagent for use as a repellent in areas where bird activity is not desirable such as food storage areas, factory roofs, golf courses, airports and mining tailing dams.

MA has a density greater than water. It is hydrophobic, freezes at around 25°C, has oil like consistency, and possesses some unusual physical properties. This presentation will discuss the development of a MA formulation that can be used to spread over water and solid surfaces. A novel method for the measurement of spreading rate has been developed.

Photochemical Behaviour of Zinc Oxide Quantum Dots

Annabel Wood

Advanced Mineral Products Research Centre, School of Chemistry, University of Melbourne, Parkville, Victoria, 3052
E-mail: a.wood@pgrad.unimelb.edu.au

Quantum dots (nanosized colloids) exhibit unusual properties as a result of spatial electron confinement within the particles, including an increased band gap energy and blue-shifted fluorescence. An increased surface area makes these species potentially useful as catalysts. An improved method of preparing zinc oxide quantum dots (Q-ZnO) has allowed ultra-small, stable particles to be formed without the use of stabilizing agents, which would otherwise complicate studies. The simplicity and narrow particle size distribution of this system makes it almost ideal for studying the electron-hole dynamics of the particles. A range of particle sizes has been characterized using absorbance and fluorescence spectroscopy and x-ray diffraction. Experiments investigating the enhanced semiconductor properties will be described.

The Primary Electroviscous Effect and the Motion of Hematite Particles

Sam Gason, Dave Dunstan and David Boger

Department of Chemical Engineering, The University of Melbourne, Parkville, 3052.
E-mail: s.gason@chemeng.unimelb.edu.au

Colloidal rod-like particle suspensions, such as hematite (Fe_2O_3), are of both an industrial and fundamental interest. Commonly used in the coating of polymeric substrates, such as digital tape manufacture, an understanding of the suspensions microstructural properties, under shear, is of paramount importance in controlling the properties of the final product. Hematite rod-like particles provide a system whereby the effect of surface potential, solvent composition and viscosity on the Brownian and hydrodynamic motion of a particle can be investigated. The use of flow birefringence and shear spectroscopic techniques allows the measurement of the particle's orientational order under shear. Results for the measurement of the hematite particle relaxation time and Jeffery orbit period with varying solvent properties are presented and discussed in terms of the Primary Electroviscous Effect.

PEO-PPO-PEO Block Copolymers at the Emulsion Droplet-Water Interface

Timothy J. Barnes & Clive A. Prestidge

Ian Wark Research Institute, University of South Australia, Mawson Lakes,
SA 5095, Australia
E-mail: bartj001@students.unisa.edu.au

Block copolymers are widely used as emulsion stabilisers, however, little is known concerning their conformation at the oil droplet-water interface. This study aims to characterise adsorbed copolymers at the emulsion droplet interface and to determine the role of copolymer structure and droplet deformation on adsorbed layer structure and emulsion droplet stability.

The adsorbed layer thickness of polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) block copolymers at the surfaces of polydimethylsiloxane emulsion[1] droplets were determined from zeta potential variation due to the shear plane shift away from the surface. Complementary studies on silica and latex particles are also reported. PEO block size, as well as the physical and chemical nature of the droplets or particles, has been shown to control the adsorbed copolymer conformation.

For all substrates the maximum adsorbed layer thickness (d_{max}) is in the range 2 to 20 nm and is directly proportional to the PEO block length. d_{max} for PDMS emulsion, latex and silica corresponds to 30-40%, 20% and 10% of the fully extended PEO segment length. These findings are discussed with respect to differences in the adsorption mechanism and the adsorbed conformation of the copolymers at the substrate surface.

References:
1. Obey, T.M. and Vincent, B. J. Colloid and Interface Science, 1994, 163, 454.

Small Amplitude Oscillatory Rheometry and Dynamic Light Scattering of the Stoichiometric and Thermal Dependence of a Polysaccharide Gelling System

Andrew B. Rodd, Dave E. Dunstan and David V. Boger

CRC For Industrial Plant Biopolymers, Dept. of Chemical Engineering, The University of Melbourne, Parkville VIC 3052
E-mail: a.rodd@pgrad.unimelb.edu.au

The process of gelation as applied to polysaccharide systems has been the subject of great interest in the recent literature. Two of the most important physical characteristics of a polysaccharide gelling system are the gel point and the thermal reversibility of the system. Presented in this work are results following the gelation of a xanthan gum based chemical gel. Xanthan gum is well known to form strong gels as in addition to its inherent 'weak gel' structure with the addition of trivalent metal ions such as Cr^{3+} ,Fe^{3+} and Al^{3+}. Xanthan – Al(III) chemical gels at low polymer concentrations form a strong transparent gel ideal for studying with both rheological and optical techniques. The gel point as observed through the Winter and Chambon[1] technique is compared to the analysis of Time Correlation Functions obtained from Dynamic Light Scattering. The complications associated with studying gelling systems both rheologically and through spectroscopic techniques are discussed. In addition rheological characterisation of the thermal reversibility of the gelling system is presented in terms of the effect of thermal history on small amplitude oscillatory properties. A 'dangling ends' model[2] for gelation is presented as a possible qualitative explanation of the observed thermal dependence.

References:

1. Winter, H.H. and Chambon, F. Analysis of Linear Viscoelasticity of a Crosslinking Polymer at the Gel point. *Journal of rheology* 30(2):367-382, **1986**.
2. Discussion with Prof. Walther Burchard, Institute of Macromolecular Chemistry, University of Freiburg, Germany, June 1999.

Adhesion and Creeping Flow of a Concentrated Emulsion

Brett Macaulay[1], Simon Biggs[1] and Kevin Galvin[2]

The Centre for Multiphase Processes, Departments of [1]Chemistry and [2]Chemical
Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia
E-mail: cpbm@paracelsus.newcastle.edu.au

A specifically designed tube rheometer is used to examine the critical conditions necessary to induce motion in a highly concentrated water-in-oil emulsion plug. The apparatus was initially pressurised to approximately 100 kPa. The creeping flow of the emulsion plug is induced via a pressure differential. Before the plug flows an adhesion value must be exceeded, once past this point the plug accelerates until some point where the differential pressure value plateaus to a steady state where the plug flows at a constant velocity. Once the gas outflow is ceased, the differential pressure decays until another steady state value is attained. At this point the plug has decelerated to rest and the static value is maintained indefinitely. The static value is also known as the adhesion value. Measurements for a certain emulsion (94% dispersed phase) have revealed a variety of properties, which appear to be independent of the bulk properties of the emulsion. The single most important component appears to be the viscosity of the continuous phase oil used in the emulsion. The emulsion plug is modelled as a solid that is surrounded by a thin lubricating oil film. The thickness of these lubricating layers has been calculated for a variety of different viscosity oils.

Adsorbed Layer Structure of Cationic Surfactants on Quartz

Jamie C Schulz[1], Gregory G Warr[1], William A Hamilton[2], Paul D Butler[3]

[1]School of Chemistry, University of Sydney, Sydney, New South Wales, 2006, Australia
[2]Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6393, USA
[3]Centre for Neutron Research, National Institute of Standards and Technology, REACT E151, Gaithersburg, MD, 20899, USA
E-mail: j.schulz@chem.usyd.edu.au

Atomic force microscopy has emerged as a unique tool for studying the structure of adsorbed surfactant films. However, this technique lacks the ability to accurately determine the composition, surface coverage and thickness of the adsorbed surfactant film. We have utilised the complimentary nature of two surface analysis techniques: Neutron Reflectivity and Atomic Force Microscopy to investigate the structure and composition of adsorbed cationic surfactant films on the quartz solid mineral surface. Results from the two techniques indicate that the surfactant phase behaviour and film structure on the surface mimics the bulk solution behaviour.

Kinetics of Polymorphism in Photographic Coupling Agent

Ning Li[1], R. A. Shanks & D.M.Murphy[2]

[1]Applied Chemistry, RMIT University, Melbourne, Australia
[2]Research Laboratory, Kodak Australasia Pty Ltd
E-mail: nli@bunyip.ph.rmit.edu.au

The phenomenon of polymorphism plays an important role in many industries including food, cosmetic, pharmaceutical and photographic. Compounds that exist in two or more solid phases (polymorphs) can offer some distinct advantages in the end use of the product[1]. However, they may cause serious problems during processing[2,3]. In this work, the polymorphism of a photographic coupling agent has been studied using differential scanning calorimetry (DSC) and optical microscopy with polarized and transmitted light.

A DSC thermogram at a heating rate of 5 °C/min is shown in Fig.1. The coupling agent exhibits two polymorphs: polymorph I with lower melting temperature (168 °C) and polymorph II with higher melting temperature (181 °C). Optical micrographs show that polymorph I has needle-like crystals and polymorph II has cubic-like crystals. The DSC thermograms of isothermal transition I to II are shown in Fig.2. Peak I is dominant at the initial time under isothermal conditions. After for 100 min, peak I is decreased and peak II is beginning to increase. The enthalpies of peak I decrease while enthalpies of peak II increase with an increase in annealing time. The crystal transform has been described using a phase diagram of time-temperature-transformation, TTT diagram.

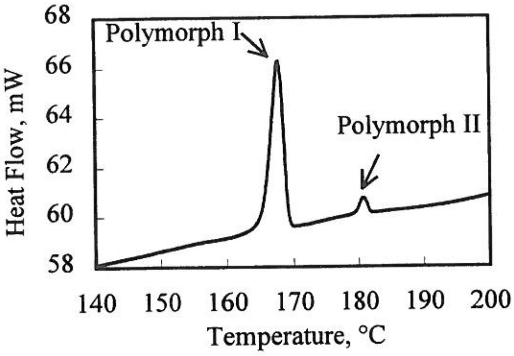


Figure 1. DSC thermogram on heating at rate of 5 °C/min.

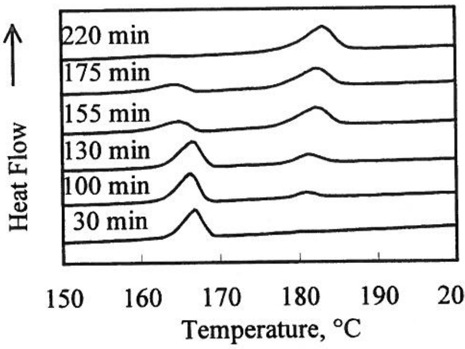


Figure 2. DSC thermograms for the polymorphic a transformation at 145 °C.

References
1. Bavin, M. 1989, Chemistry & Industry, 21, 527.
2. Nass, K. 1990, AIChE Annual Meeting, Nov., 11.
3. Garti, N. and Sato, K. 1988, Crystallization and Polymorphism of Fats and Fatty Acids, New York, Wiley.

The Characterisation of Pharmaceutical Powders: Crystal Habit and Wettability

Tim Muster & Clive Prestidge

Ian Wark Research Institute, University of South Australia, Mawson Lakes,
SA 5095
E-mail: musth001@students.unisa.edu.au

In the quest to advance drug delivery technology, there is a need for improved characterisation and control of the surface energetics of pharmaceutical powders in both their raw and processed forms. This study aims to: 1. develop improved methods to determine the dynamic and equilibrium wetting behaviour of pharmaceutical powders, and 2. determine the influence of polymorphic and crystal habit changes in pharmaceutical contact angles.

Both video enhanced sessile drop and packed capillary penetration techniques have been used to determine contact angles of two polymorphic forms (I and III) of sulfathiazole, an anti-bacterial drug. Single crystals and powder compacts have been studied with AFM being used to probe surface morphology and surface roughness.

Sessile drop spreading kinetics over dry sulfathiazole compacts were inhibited by high surface roughness and the presence of pores. For reliable sessile drop equilibrium contact angles to be determined, compacts were pre-saturated with the test liquid prior to measurement. Powder contact angles determined by packed capillary penetration were consistently higher than those measured by sessile drop, however, both techniques reported the contact angle of form I as greater than form III. Measured trends in powder surface energies were confirmed with single-crystal contact angle measurements using sessile drop and Wilhelmy balance approaches.

Polymorphic induced crystal habit changes are reflected in contact angle variations of both large single crystals and bulk powders. Due to surface energy changes as a result of crystal habit alteration, variations in particle-particle and particle-liquid interactions are likely to change processing and drug delivery performance. Insight into the characterisation of powder surface energy has enabled the contact angle dependence on polymorphic induced crystal habit changes to be studied.

Hot Flocs and Cool Dispersions

Lisa S. Benee, Martin J. Snowden, & Babur Z. Chowdhry

University of Greenwich, London, England, SE18 6PF, UK
E-mail: lisa_benee@hotmail.com

The stability of positively and negatively charged latex particles has been studied by turbidity in the presence of sodium, magnesium and lanthanum chloride. The critical flocculation concentration for both latexes decreases as electrolyte cationic valency increases.

The particles have been stabilised with a cellulosic polymer (hydroxypropyl methyl cellulose). The stability of the mixed latex system has been investigated, and the particles were found to undergo reversible incipient flocculation when heated. Addition of sodium chloride resulted in a decrease in the LCST and CFT.

Light scattering has been used to measure the adsorbed layer thickness and electron spin resonance was used to measure the adsorption isotherms for HPMC onto each latex. More polymer was found to adsorb onto the cationic surface than the anionic.

Minimal Surface Modelling of Surfactant Liquid Crystals: Comparison of Theoretical and Experimental X-ray Diffraction Patterns

J.D. Enlow[1], Dr K.M. McGrath[2], Dr R.L. Enlow[1], Dr M.W. Tate[3],

[1]Dept of Mathematics and Statistics, University of Otago, NZ
[2]Dept of Chemistry, University of Otago, NZ
[3]Dept of Physics, Cornell University, Ithaca, NY, USA
E-mail: j@earthlight.co.nz

A mathematical model for surfactant liquid crystals is presented here, in which an electron density distribution is specified in the vicinity of an appropriate "minimal surface". Diffraction patterns resulting when a hypothetical X-ray beam is focused on the surfactant model are calculated for a nearby detector screen, and the peaks of constructive interference are determined in detail in both magnitude and location. The resulting intensities are compared with experimental results, giving further evidence for the minimal surface nature of surfactant liquid crystals.

AFM Tip Deformations Under an Oscillatory Loading Regime

Shannon Notley[1], Vince Craig[2] and Simon Biggs[1]

[1] The Centre for Multiphase Processes, Department of Chemistry, University of Newcastle,
Callaghan NSW 2308
[2] Department of Applied Mathematics, Research School of Physical Sciences and
Engineering, ANU, Canberra ACT 0200
E-mail: cpsn@paracelsus.newcastle.edu.au

The Atomic Force Microscope (AFM) has previously been applied to the measurement of surface forces (including adhesion and friction) and to the investigation of material properties, such as hardness. A commercial AFM has been modified to allow direct measurements of the "stiffness" of any interaction between two surfaces on colloidal length scales. On top of the normal loading conditions in an AFM force experiment is a small amplitude, high frequency oscillatory signal. The detected oscillatory signal is compared to the input signal and a rheological phase and amplitude is calculated. Data presented here are for the interaction of a silica tip with a silica substrate under high applied loads. Force and amplitude data indicate the breaching of the compressive yield stress and the onset of strain softening.

Optimisation of the Washing and Dewatering of Flocculated Suspensions: The Influence of Temperature

Shane P. Usher, Ross De Kretser and Peter Scales

Advanced Mineral Products Special Research Centre, School of Chemistry, The University of Melbourne, Parkville, VIC 3052
E-mail: s.usher@pgrad.unimelb.edu.au

Optimum washing and dewatering of mineral wastes is important for the maximum recovery of expensive process chemicals and timely rehabilitation of tailings disposal areas. Washing and dewatering of waste suspensions is achieved in trains of separation equipment employing filtration and gravity thickening. The compressibility and permeability of these suspensions determine their dewaterability. The compressibility expressed as a compressive yield stress, Py (0), allows identification of the maximum extent of dewatering for any compressive stress. In process equipment, the maximum extent of dewatering is rarely attained due to high throughputs. Thus, the extent of dewatering is dominated by the permeability of the suspension. Flocculants and other filter aids are added in these processes to increase the rate of solid-liquid separation and are often assumed to dominate the rate of filtration. Temperature however, is another process variable that has a large influence on the rate of filtration. Temperature however, is another process variable that has a large influence on the rate of filtration. Temperature strongly influences liquor viscosity, which inturn, plays and important role in determining the permeability and rate of filtration. Experimental characterisation of dewaterability for zirconia suspension as a function of temperature is used to show the influence on the rate of filtration. The implication for designing and optimising industrial processes is that head losses must be minimised through initiatives such as effective insulation and in some cases adding heat will be beneficial.

The Role of Colloid Science in Bitumen Emulsion-Aggregate Interactions

Jacinta L. Gorman[1], Russell J. Crawford, Paul Stannard[2] and Ian H. Harding

[1]Centre for Applied Colloid and BioColloid Science, Swinburne University of Technology,
P.O. Box 218, Hawthorn 3122
[2]BP Bitumen, BP Australia Ltd, Altona Regional Research and Development Laboratory,
Kororoit Creek Road, Altona North 3025
E-mail: JGorman@swin.edu.au

Road making bitumen products are typically applied in conjunction with a mineral aggregate. The bitumen acts as a binder and the aggregate provides mechanical strength. One way of applying the bitumen phase is as a bitumen-water emulsion that must break in a controlled manner upon laying. The efficiency with which the bitumen emulsion breaks is strongly influenced by the surface characteristics of the aggregate substrate and the emulsion formulation itself.

The current study employs colloid and surface chemical techniques to investigate the properties of both the mineral aggregates and bitumen emulsions commonly used in roadmaking processes, for example slurry surfacing and sprayed sealing. A selection of mineral aggregates, ranging from those found to be too "reactive" to obtain a satisfactory slurry surfacing mixture too "unreactive" (those that have been successfully used in slurry surfacing) have been studied. In addition, the solution behaviour of the cationic surfactant used for preparation of the bitumen emulsion has been studied, and will be compared to similar systems prepared using model surfactants.

Standard slurry surfacing characterisation techniques such as the cohesion test (determination of set and cure) have been performed on slurry surfacing mixtures using the range of aggregates, the results of which have been interpreted in terms of the surface characteristics of the aggregates.

Single Bubble Sonoluminescence

Rohan Tronson, Muthupandian Ashokkumar, Franz Grieser

Advanced Mineral Products Special Research Centre, School of Chemistry, The University of Melbourne, Parkville, VIC 3052
E-mail: r.tronson@pgrad.unimelb.edu.au

Given the correct conditions, samples of water or other liquids can be observed to luminesce blue-green under insonation. This luminescence has been termed sonoluminescence and is known to be due to the rapid compression of bubbles in the liquid.

By acoustically suspending a single bubble in a glass cell and adjusting conditions until we observe sonoluminescence we can measure the intensity and spectra of emitted light from a single bubble. In addition we can use both visual imaging and Mie scattering theory to observe the bubble dynamics during sonoluminescence.

We are particularly interested in the behaviour of surface active molecules at the bubble-liquid interface, and whether these surface active molecules also effect the bubble dynamics.

Formation and Flocculation of Calcium Phosphate Phases Precipitates from Heated Whey Permeates

Natalia.N. Panova, M.R. Mucalo, K.N. Pearce

Chemistry Department, University of Waikato, Private Bag 3105, Hamilton NZ
Dairy Research Institute, Palmerston North, Private Bag 11029
E-mail : np10@waikato.ac.nz

Calcium phosphate (CaP) precipitates are formed when ultrafiltration permeate (a solution of milk salts, lactose and lactic acid) from casein whey is heated to 75°C and neutralised with sodium hydroxide. Low-angle light scattering measurements were used to determine the effect of stirring rate on CaP precipitate particle size. Bench-scale precipitation reactions where agitation rate was varied from 3 to 150 rpm were performed. The particles size distributions became more mono-disperse and shifted to larger particle diameters as the stirring continued. After 30 minutes, the mean particle diameter D[4, 3] was 29 μm for an agitation rate of 3 rpm, and 55 μm at 150 rpm- faster agitation produced larger particles indicating that orthokinetic agglomeration process was occurring.

There was a fall in pH as the CaP precipitate forms. The pH versus time curves show two inflections associated with phase transformations. CaP precipitates from supersaturated solutions in accordance with Ostwald's Law of Stages with metastable solid phases forming before more thermodynamically stable solid phases. The first inflection may represent transformation of the initially formed colloidal amorphous CaP intermediate to semi-crystalline octacalcium phosphate (OCP) and the second the final transformation of OCP to thermodynamically stable apatitic CaP. Fourier Transform Infrared (FTIR) and Transmission Electron Microscopy (TEM) of the evolving precipitating phase confirms that phase transformations are taking place. A useful adjunct to these studies are computer speciation calculations which predict, using published acidity, stability and solubility constants, the equilibrium distribution of ionic species and occurrence of precipitating phases as a function of pH in permeates of known composition.

Dielectric Response of a Porous Particle

Boris Poliak

Department of Mathematics and Statistics, University of Melbourne, Parkville VIC 3052
E-mail: boris@mundoe.maths.mu.oz.au

Dielectric response measurements for a suspension of porous particles provide information essential for calculating the dynamic mobility of a porous particle. Interpretation of dynamic mobility measurements has attracted a considerable interest recently. It is customary to represent the dielectric behaviour of entities having a complicated internal structure (e.g. cells) in terms of macroscopic parameters according to a model which can be solved analytically. In this talk an empirical model of this kind will be presented. The silica porous particle is represented as a conductive interior enclosed by a thin capacitive layer. Then the Clausius-Mossotti factor is calculated and fitted to experimental measurements.

The Effect of Crosslink Density on the Phase Transition Behaviour of Colloidal Microgel Particles

Nicola C. Woodward[1], Babur Z. Chowdhry[1] and Martin J. Snowden[1] & Peter Griffith[2]

[1]School of Chemical & Life Sciences, University of Greenwich, Wellington Street, London, SE18 6PF, United Kingdom
[2]Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff, CF10 3TB, United Kingdom
E-mail: WN10@gre.ac.uk

A series of poly(N-isopropylacrylamide) microgels, prepared having varying degrees of crosslinker density (0.25-30% of total monomer concentration), have been investigated by a number of physicochemical techniques. Turbidimetric analysis has shown that the transition temperature of the dispersions increases as a function of crosslinker density. Furthermore this technique has indicated that the microgels conformational transition becomes broader at increasing crosslinker densities. Both of these observations are in good agreement with thermodynamic data obtained by high sensitivity differential scanning calorimetry (HSDSC) which has shown an increase in both the transition temperature and breadth of transition. HSDSC also shows a decrease in the calorimetric enthalpy of the transition, with increasing crosslinker density. These systems have also been investigated by using fluorescence probe analysis and nuclear magnetic resonance studies.

Interactions of Cryptosporidium Oocysts and Filtration Media (typical of the drinking water treatment process) Assessed by Colloid Probe AFM Measurements

Rob Considine, David R. Dixon, Calum J. Drummond

CSIRO Molecular Science, CRC For Water Quality and Treatment, Private Bag 10,
Clayton South MDC, Vic 3169
E-mail: robert.considine@molsci.csiro.au

Ingestion of a quantity of oocysts may result in the development of cryptosporidiosis, an important cause of enterocolitis and diarrhoea in humans. The oocysts of cryptosporidium parvum are resistant to conventional disinfection and must be physically removed (typically by sand or membrane filtration) from waters to be used for human consumption. An Atomic Force Microscope (AFM) has been used to measure the force of interaction between individual oocysts of cryptosporidium parvum and amorphous silica particles of diameters around 5micron. Measurements have been performed in the aqueous environment, under conditions typical of the drinking water treatment process. The hope is that the conditions for which oocysts attach (and detach) to filtration media can be assessed.

A Phase Transition in Adsorbed Layers of an n-Alkane on Mica

Nobuo Maeda, Hugo K. Christenson

Department of Applied Mathematics, Research School of Physical Sciences and Engineering, Australian National University, CANBERRA ACT 0200, Australia
E-mail: nma110@rsphysse.anu.edu.au

Films of n-octadecane adsorbed on mica surfaces from saturated vapour in the vicinity of bulk melting point (Tm) have been studied using a Surface Force Apparatus (SFA). The mobility and thickness of the adsorbed n-octadecane films are found to undergo a transition a few degrees above Tm. Below the transition temperature, the films are slightly thicker and much less mobile than above. This suggests that the adsorbed films undergo a transition similar to that found in "surface freezing" of liquid n-alkanes.

The Influence of Cation on the Crystallization of Colloidal $Al(OH)_3$ from Synthetic, Self-Nucleating Bayer Liquors

Jun Li, Jonas Addai-Mensah and Clive A. Prestidge

Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia
E-mail: Liyjy002@students.unisa.edu.au

Homogeneous nucleation of $Al(OH)_3$ crystals from synthetic, optically-clear, pregnant Bayer liquors and the influence of solution cation (Na^+ versus K^+) have been investigated under isothermal batch crystallization conditions. The nucleation kinetics showed a seventh order dependence upon Al(III) relative supersaturation and a strong temperature effect. An activation energy of 160 kJ $mole^{-1}$ and interfacial energy of 33 mJ m^{-2} were estimated and found to be independent of liquor cation. The nucleation rate, however, was faster in sodium than potassium aluminate solutions. Furthermore, significant differences in the level of cation incorporation, morphology and composition (bayerite to gibbsite dimorphic ratio) of the crystalline product were observed. The results indicate that $Al(OH)_3$ nucleation involves a chemical reaction-controlled, polyaluminate condensation process, that is cation-mediated. Na^+ ions provide greater interactions, higher stability and faster growth for the nuclei-forming, polyaluminate clusters and nuclei than do K^+ ions.

Non-Equilibrium Forces Between Polyelectrolyte-Coated Surfaces

George Maurdev[1], Laurence Meagher[2], Michelle Gee[1]

[1] University of Melbourne, Parkville 3052, Victoria
[2] CSIRO, Clayton 3168, Victoria
E-mail: g.maurdev@pgrad.unimelb.edu.au

The use of the Surface Forces Apparatus, which incorporates a magnetic force transducer, has allowed us to investigate hysteresis on the forces measured between adsorbed polyelectrolyte layers as a result of series of compressions and decompressions. We have also investigated how surface adhesion is affected by (a) the length of time that layers are in contact and (b) the compressional loads applied to the layers. Such studies are important to our understanding of high volume fraction colloidal suspensions in the presence of polyelectrolyte, particularly under dynamic conditions. We have found hysteresis effects, where a result of the initial compression/decompression. It was found that a close range repulsion due to overlap of the adsorbed polyelectrolyte layers on adjacent surfaces was significantly reduced after the first approach, not reappearing over times of up to several days. Found also upon compression of layers for times ranging between 1 to 30 minutes (even with loads ≥ 1 mN/m) is that polyelectrolyte entanglement increases between adjacent layers. This leads to increased adhesion between the layers, i.e., an increase in bridging attraction.

Surfactant Design by Molecular Simulation

Marco La Rosa

Private Bag 10, Clayton South MDC, Vic 3169
E-mail: Marco.LaRosa@molsci.csiro.au

Molecular simulation is now widely accepted as a complementary tool to experiment. With the continual increase in computing power, it is now feasible to study all sorts of different phenomena including protein conformation in solution, polymer melt properties and liquid dynamics. The two most widely used simulation techniques are Molecular Dynamics (MD) and Monte Carlo (MC).

In this work, both MD and MC are being used to study surfactant self-assembly over both short and long timescales. The aim of this is to develop a screening process which can be used to assess surfactant behaviour as a function of architecture; a technique which would be useful in the design of specialty surfactants. Molecular dynamics simulations of a decane/water system containing 50 decane and 500 water molecules have shown that the bulk liquid densities of both the decane and water phases are comparable to the experimentally measured densities and that the interface formed between the two phases is molecularly sharp. Simulations of systems containing decane, water and alkyl ethoxylate surfactants are currently running. Simulation of the same composition system in cells with different interfacial areas is being used to try and find an accurate measure of system equilibration.

Can You Hear Me? Ultrasonic Forces for Particle Separation

Niem Tri & Ron Beckett

CRC for freshwater Ecology; Water Studies Centre, Department of Chemistry
Monash University, Clayton, Victoria, Australia 3168
E-mail: Niem.Tri@sci.monash.edu.au

Field-Flow Fractionation and SPLITT channels are versatile and readily adaptable to new force fields. In the current study a relatively novel field, caused by acoustic pressure is considered. Consider a FFF or SPLITT channel where one wall is attached to a piezo ceramic transducer capable of generating ultrasonic frequencies. Further, consider the situation where the frequency is tuned such that a single standing wave is generated across the thickness of the channel.

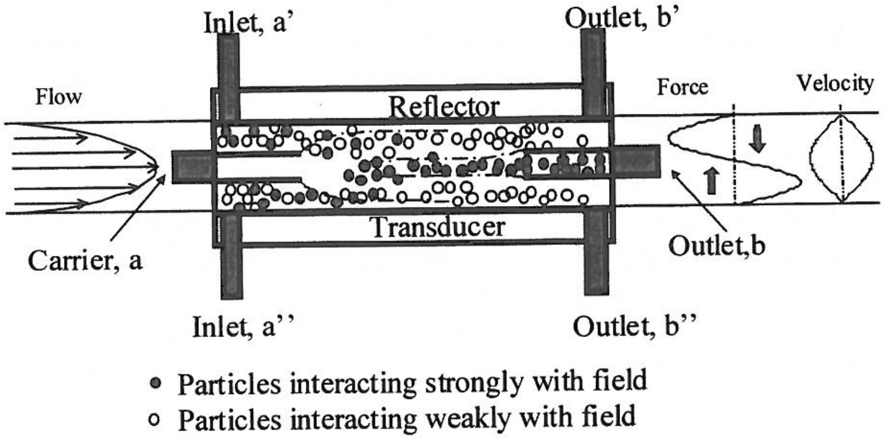


Figure 1. Dual SPLIT thin channel separation achieved using an ultrasonic standing wave.

Unlike conventional FFF and SPLITT where the force across the channel is constant, particles in the standing wave will experience an acoustic force (*F*) depending on its position, *x* given by:

$$F = 4\pi r^3 \kappa E_{ac} A \sin(2\kappa x) \tag{1}$$

where *r* is the particle radius, κ the wave number, E_{ac} the time averaged acoustic energy density and *A* the acoustic contrast factor and is given by

$$A = \frac{1}{3}\left[\frac{5\rho_p - 2\rho_l}{\rho_l + 2\rho_p} - \frac{\gamma_p}{\gamma_l}\right] \tag{2}$$

where ρ_p and γ_p are the particle density and compressibility and ρ_l and γ_l the carrier density and compressibility.

Due to the nature of the acoustic fields, the distribution of the particles will depend on particle size and the compressibility and density of the particle relative to the carrier. Closer examination of the acoustic contrast factor shows that is may be negative (usually applicable to biological cells which are more compressible and less dense relative to the surrounding medium) or positive (as is in many inorganic and polymer colloids). Therefore Acoustic FFF (AcFFF) has tremendous potential in separating cells from sediments samples where separation based on compressibility is anticipated.

References:

1. Yosioka, K. and Kawasima, Y. (1995). Acoustic Radiation Pressure on a Compressible Sphere, *Acustica*, 5: 167-173.

Imaging the Surfactant Self-Assembly Shape Transition at the Solid-Liquid Interface using Atomic Force Microscopy

Laszlo Kovacs

School of Chemistry F11, University of Sydney, Sydney NSW 2006
E-mail: kovacs_l@alf.chem.usyd.edu.au

There has been intensive research of surfactant aggregation from aqueous solutions at the solid-liquid interface in the last five years. Numerous interfacial structures have been determined for several ionic surfactants on both hydrophilic substrates, such as mica and silica; and on hydrophobic solid surfaces, such as graphite and molybdenumsulfide. A phase transition of cationic surfactants (DTAB, TTAB, and $C_{14}NEt_3Br$) is investigated at the interface of mica and surfactant solution using Atomic Force Microscopy. Modifications of the surface aggregates are induced by the addition of naphthalene or 2-naphthol and/ or a salt (NaBr). Light scattering and cryo-TEM are used for the determination of the micelle aggregate shapes in the bulk aqueous phase.

The Role of Electrostatic Interactions in Protein Adsorption on Polysaccharide Surfaces

Sally L McArthur[1,2], Keith M McLean[1,2], Patrick G Hartley[1], Heather AW St John[1,2] &
Hans J Griesser[1,2].

[1]CSIRO Molecular Science, Bag 10 Clayton Sth MDC, Clayton, 3169, VIC and
[2]CRC Eye Research and Technology, UNSW, Sydney, 2052, NSW, Australia.
E-mail: sally.mcarthur@molsci.csiro.au

The adsorption of proteins from biological fluids onto the surface of materials used in biomedical implants is a key event controlling the long and short-term performance of the device. In the design of improved biomedical polymeric coatings, one of the aims is the control of these protein/surface interactions. In this study, we investigate the role of electrostatic interactions in protein adsorption using hydrophilic grafted carboxymethyldextran. The carboxyl density of the dextran can be varied over a wide range and thus residual charge of the resultant surface can be controlled. The electrokinetic properties of the modified surfaces were assessed using streaming potential measurement. The surfaces were then incubated in a variety of single and mixed protein solutions selected as representative components of tears and serum. The resultant protein adsorption was monitored using a combination of X-ray photoelectron spectroscopy (XPS) and matrix-assisted laser desoption/ionisation mass spectrometry (MALDI-MS). Adapted recently by Kingshott et al [1], surface mode MALDI-MS detects surface adsorbed protein species via their molecular weight, allowing differentiation of multiple species adsorbed from complex solutions. This data was then correlated with the known isoelectric points of the adsorbed proteins and data ascertained from streaming potential measurements with a view to determining the influence of electrostatic interactions on protein adsorption at carboxymethyldextran surfaces.

References:
1. Kingshott et al, J. Biomed. Mater.Res. In press

The Effect of Interfacial Properties on the Reaction of Nickle Ion Extraction by LIX 84 in a $G_{12}A_8$ Micelle Model System

Dallas Warren[1], Franz Grieser[2], Jilska Perera[1], Geoff Stevens[1]

[1]Department of Chemical Engineering, The University of Melbourne, Parkville, VIC 3052
[2]Advanced Mineral Products Special Research Centre, School of Chemistry, The University of Melbourne, Parkville, VIC 3052
E-mail: d.warren@chemeng.unimelb.edu.au

Solvent extraction is an important metal ion separation process that is used in a variety of metal processing industries. Gaining detailed kinetic information about the extraction mechanism will allow an improvement in metal ion separation. The majority of extractants that are utilised are interfacially active and almost totally insoluble in the aqueous phase. As a result the reaction between the metal ion and the extractant in most cases occurs in the interfacial region.

The kinetics of the extraction of nickel by the active ingredient in LIX84, (2-nonyl-5-hydroxyacetophenone oxime) in a micelle model system ($G_{12}A_8$,poly-dispersed form of $C_{12}E_8$, octa-ethyleneglycol mono-n-dodecyl ether) was used to emulate the interfacial region between oil/water phases. Using a stopped flow apparatus and a UV-visible spectrophotometer the reaction was followed in the micelle phase, and the reaction rate constant determined.

Surface active components have been added to alter the physical properties of the interfacial region and the location of the extractant molecule at the oil/water interface. NMR spectroscopy has been used to determine the location and type of environment that the extractant molecule is found in at the micelle/aqueous solution interface. This is achieved by measuring the shift in the peak resonance location of various protons due to the proximity of the aromatic ring contained in the extractant molecule.

Collectively, the experimental results have allowed for a detailed understanding of the reaction taking place at the model oil/water interface. Work is currently being extended to a true oil/water interface using a TIR (total internal reflectance) static transfer cell to test the kinetic model developed to date.

An Electrokinetic Study of CN-Silica in a Non-Polar Colloidal System

Suparno, J. C. Thomas, Roland Keir, & Gary Bryant

School of Physics and Electronic Systems Engineering, University of South Australia, The Levels Campus, Mawson Lakes SA 5095
E-mail: supyy001@unisa.edu.au

Phase Analysis Light Scattering (PALS) and Atomic Force Microscopy (AFM) have been used to study the electrokinetic phenomena of a colloidal system consisting of CN-terminated silica particles suspended in decane in the presence of the surfactant AOT. The effect of AOT concentration on the mobility of the particles is reported. Furthermore, the electric field dependence of the mobility was measured using the PALS system. Finally, complementary force-distance measurements using an AFM of CN-Silica in decane are presented.

Forces Involving a Deformable Surface using the Atomic Force Microscope

Sarah A. Nespolo[1], Franz Grieser[2], Geoffrey W. Stevens[1]

[1]Department of Chemical Engineering
[2]Advanced Mineral Products Special Research Centre
School of Chemistry, The University of Melbourne, Parkville, VIC 3052
E-mail: s.nespolo@chemeng.unimelb.edu.au

The immobilisation of droplets of a hydrocarbon liquid (n-decane) on a flat solid surface has allowed the forces of interaction between a silica colloidal particle and the hydrocarbon-aqueous interface to be measured using the Atomic Force Microscope.

The effects of surface potential and interfacial tension on surface forces were investigated. In previous experiments, both the surface potential and interfacial tension change. To gain an understanding of the interactions occurring, there is a need to isolate these two components and assess their individual effect on the surface forces. An analysis of the interplay between the electrostatic forces and deformation is presented.

Force-distance relationships for different anionic surfactants have been measured for a variety of concentrations. The results presented show how different chain length anionic surfactants effect the force-distance relationship between the hydrocarbon and solid interface.

The presence of trace quantities of an anionic surfactant, sodium dodecyl sulfate (SDS) radically alters the forces between the two surfaces. For smaller chain length anionic surfactants, higher concentrations are required to have the same effect. The presence of anionic surfactants alters the forces between the two surfaces, which results in a 'softening' of the fluid interface.

It has been found that when this effective interfacial spring constant and interfacial tension are plotted as a function of surfactant concentration, the agreement is significant. This indicates that there is a connection between the bulk interfacial tension and the 'microelasticity" of the interface.

A theoretical model has been developed based on a force balance at the interface allowing for surface deformation of the oil drop as the colloid approaches.

Growth of Piezoelectrical ZnO Films using Single Source Chemical Vapour Deposition (SS CVD)

Everett Y Lee, A J Hartmann and R N Lamb

School of Chemistry, University of New South Wales, Sydney NSW 2052
E-mail: z2119347@student.unsw.edu.au

Piezoelectric crystals are used in a wide variety of applications from ultrasonic baths in laboratories to speakers in headphones for Walkman stereos. The lifetime of such devices is directly related to the nature of the active crystalline film. In this work we look at the physiochemical properties of Polycrystalline zinc oxide films. In particular the fabrication of these using the novel single source CVD approach in which extremely low density but nevertheless active (long lifetime) films can be produced.

Unlike other techniques, SS CVD provides exceptional control of film chemical compositions, crystallinities (size and orientation) and morphology.

Zinc oxide films with a variety of chemical compositions, crystallinities and morphologies were grown and characterised using X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The piezoelectrical properties of these films were also measured. The relationship between this and crystal structure and packing density are examined

Another advantage of SS CVD is that it allows films to be grown on highly curved surfaces. An example of films grown on optical fibres as part of a novel photonic device is described. Films were found to be continuous on all parts of the fibre and exhibited a long piezoelectrical lifetime.

Structure and Dynamics of Aluminium Alkoxide / Phosphate Surfactant Organogels

Miles Page & Gregory G Warr

School of Chemistry F11, University of Sydney, NSW 2006
E-mail: page_m@chem.usyd.edu.au

Addition of aluminium alkoxide to a solution of alkyl phosphate ester in a nonpolar solvent induces formation of giant wormlike particles (so-called "living polymers"), causing gellation at very low (<0.5% w/v) surfactant concentrations. This has a range of industrial applications such as agrochemical delivery and offshore oil extraction. The properties of these organogels are highly dependent on the aluminium alkoxide to surfactant ratio, as well as the surfactant volume fraction. However the relationship between gel composition and behaviour is not well understood. The growth of the particles results from coordination of aluminium forming bridges between neighbouring phosphate headgroups. Preliminary studies suggest that coordinated alkoxide groups in the particles may be the cause of greater than expected dependence of gel properties on the alkoxide / surfactant ratio, and that branching in the micelles could be occurring.

Rheological studies allow quantification of gel properties including relaxation time and zero shear viscosity. Information on possible branching in the structure is obtained by comparison with theoretical predictions of the rheology of branched and entangled micellar solutions, and expected small angle neutron scattering results.

Nanotribology in Soil and Granular Systems

Mark Reitsma[1], D.Smith[1], R.Cain[2], S. Biggs[3], and N. Page[2]

[1]Department of Civil Engineering, [2]Department of Mechanical Engineering and
[3]Department of Chemistry, The University of Newcastle, Callaghan, NSW 2308, Australia.
E-mail: cpmgr@paracelsus.newcastle.edu.au

In one mode of use, the Atomic Force Microscope is able to induce well-defined forces between two surfaces, as well as being able to 'sense' them (in the case of imaging, for example). To this end the instrument is capable of measuring surface properties such as friction (viz.LFM) and adhesion (viz.AFM) under different loading conditions. As contact between soil particles plays an important role in the overall strength of a soil, the focus of work is to investigate 'point' contact interactions of quartz surfaces as a function of load, temperature and humidity.

Mesoporous Silicates and Protein Adsorption

Jenny M. Kisler, Geoffrey W. Stevens & Andrea J. O'Connor

Department of Chemical Engineering, University of Melbourne
E-mail: j.kisler@chemeng.unimelb.edu.au

In the food and pharmaceutical industries the selective separation and purification of biological macromolecules such as proteins and vitamins is important. Successful adsorption of smaller molecules onto molecular sieves has been demonstrated, but the pore size range available has prevented their application for separation of larger species like proteins. A recently discovered mesoporous molecular sieve, MCM-41, greatly extends this pore size range and also has other properties which make it suitable for use as an adsorbent, including a regular hexagonal array of uniform pores and a large internal surface area. The pore size can be tailored during synthesis and the surface chemistry can also be modified to provide selectivity for a particular separation by attaching ligands to the surface silanol groups to form functional coatings.

The application of these materials for protein purification relevant to the food industry is currently being investigated. The pore size range, composition and surface chemistry of MCM-41 can be tailored to suit particular separations, so it is expected to have advantages for certain applications over currently used adsorbents, such as bentonite and activated carbon. Adsorption experiments involving proteins and a vitamin have been conducted to assess the potential of MCM-41 as a selective adsorbent for food processing.

Bridging Flocculation of Alumina Particles Using Dual Polymers

Sharna M. Glover, Yao-de Yan, Graeme J. Jameson and Simon Biggs

Centre for Multiphase Processes, The University of Newcastle, Callaghan, NSW 2308, Australia
E-mail: swaters@mail.newcastle.edu.au

Polymers are routinely used in many industrial solid-liquid separation processes to enhance the separation efficiency. In some industries the use of more than one polymer has been found to result in improved separation. In particular, studies performed in the papermaking industry have shown that dual polymers are able to improve the retention and lower the chemical costs when compared to a single polymer system. This is thought to be due to a synergistic effect that arises from the great difference that the segments of the two polymers have for the particle surface. This work investigates the structural characteristics of the aggregates of colloidal alumina particles formed using a low molecular weight polyacrylic acid and a high molecular weight cationic polymer. A video imaging technique, which is well suited to these aggregates owing to their large size and settling velocity, was used to determine the structural compactness of the aggregates formed using a range of polymer combinations. The flocculation kinetics and the size distribution of the aggregates were monitored using small-angle static light scattering. Attempts have been made to explain the mechanism by which these systems flocculate.

Interparticle Forces Modified by Adsorbed Polyphosphate

Adam Feiler

Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095
E-mail: feiay001@students.unisa.edu.au

The desorption of nanosized silica particles from oppositely charged titania wafers with the addition of polyphosphates were measured using stagnant point Reflectometry. The desorbed amount was seen to increase with increasing phosphate chain length and concentration.

In an attempt to rationalise the desorption processes, Atomic Force Microscopy (AFM) was used. The effect of adsorbed polyphosphate on the interparticle forces between a silica sphere and a titania wafer and also between a titania sphere and titania wafer were measured. It was seen that polyphosphates change the diffuse layer potential of the titania, rendering the surface negatively charged at all pH values. The diffuse layer potentials obtained with the AFM show good agreement with streaming potential measurements on the same substrates. A short-range repulsive force was detected. The range of this force compares well to the dimensions of a polyphosphate chain established with molecular modelling. Qualitative measurements indicate that the lateral-force between the substrates decreases with increasing polyphosphate concentration and chain-length.

The use of polyphosphates to desorb unwanted particles from surfaces could have applications in the high-tech electronics industry for wafer cleaning and in the minerals processing industry for slimes management.

Incipient Failure of a Yield Stress Material

Jamie Chamberlain

Department of Mathematics and Statistics, University of Melbourne, Parkville VIC 3052
E-mail: J.Chamberlain@ms.unimelb.edu.au

The incipient failure of a yield stress material deforming under its own weight corresponds to the point where the material is on the verge of flowing. A knowledge of this point is vital in understanding the basic mechanisms of the slump test, which is used to determine the shear yield stress of mineral tailing slurries. In this talk, I will present results of a detailed investigation of the incipient failure of a 2D rectangular block and a 3D circular cylinder of yield stress material. The material is modeled as a perfectly rigid-plastic body obeying the Tresca yield condition. Slip-line field theory is used to determine the point of incipient failure. A critical assessment of the commonly used uniform stress model due to Murata will be presented. Furthermore, new experiments for determining the yield stress of a slurry will be proposed.

A Proposed Mechanism of Polyphosphate Adsorption onto Titanium Dioxide and their effect on Interparticle Forces

Andrew Michelmore

Ian Wark Research Institute, University of South Australia, Mawson Lakes, 5095
E-mail: micap001@students.unisa.edu.au

Polyphosphates are utilised in many industrial applications including detergents, fertilisers and as dispersants and rheological modifiers in mineral processing. In this investigation we have studied the adsorption of polyphosphates onto the surface of a model mineral substrate, titanium dioxide. Through zeta potential determinations and adsorption isotherms, polyphosphates were shown to specifically adsorb onto the surface of titanium dioxide over a wide range of pH values. A strong dependence on polymer chain length with the maximum adsorbed amount and the zeta potential was observed. The nature of the specific chemical bond formed was determined by in situ attenuated total internal reflectance infra red spectroscopy. A mechanism for the adsorption is proposed based on the groups present in the adsorbing molecule, and the effect of the adsorption on the interparticle forces is discussed.

The Effect of Solution Conditions on Film Drainage From Between a Droplet and a Solid Surface

Dianna Goodall, Michelle Gee, Geoff Stevens

Advanced Mineral Products Special Research Centre, School of Chemistry, The University of Melbourne, Parkville, VIC 3052
E-mail: d.goodall@pgrad.unimelb.edu.au

The quality of many food and industrial products such as margarine, salad dressings and paints, depends on the quality of the emulsion system. When two droplets approach each other in an emulsion system, a thin liquid film forms between the droplets. If the system is unstable, this film then thins to a critical thickness at which point film rupture occurs and the two droplets coalesce. For the stability of emulsion systems to be properly controlled, an understanding of the properties that effect coalescence is necessary.

The objective of this study was to examine the effect of solution conditions on film drainage from between an organic droplet and a silica substrate in a continuous aqueous medium. The technique employed to monitor this behaviour was imaging ellipsometry/ reflectometry. This technique is advantageous in that it has high vertical resolution, enabling the study of both thick and thin films, and, allows the entire profile of the droplet to be monitored simultaneously. From monitoring the film drainage from between the droplet and the substrate using the technique of Imaging ellipsometry/reflectometry, the effect of additives on the evolution of the droplet profile as film drainage occured, has been studied. Droplets were observed to form a dimple (ie, reverse curvature) in most cases investigated.

Growing Gallium Nitride Films The Easy Way

Wilhelm. J. Holzschuh, A. J. Hartmann & R. N. Lamb

School of Chemistry, University of New South Wales, Sydney NSW 2052
E-mail: wilhelm@student.unsw.edu.au

Due to its direct band-gap of 3.4eV and chemical stability, the semiconductor GaN has shown great promise for use in electro-optical devices such as blue LEDs and laser diodes. However, these applications all require thin films of GaN deposited on a substrate to build these devices. At present the techniques commonly used to grow these films have separate sources for the gallium (eg. trimethylgallium) and the nitrogen (eg, ammonia or nitrogen ions) and require high substrate temperatures (600-1200°C) to encourage the reaction of the two components and produce crystalline films.

A different, and simpler, method of GaN film growth is presented here. Single Source Chemical Vapour Deposition (SS-CVD) uses a precursor that contains the Ga-N bond at its core. Sublimation of the precursor in a vacuum deposition chamber produces a vapour that transports this Ga-N core to the substrate which is heated enough (~400°C) to decompose the precursor and leave behind a GaN film. This lower substrate temperature allows a wider variety of substrate materials to be used that would not survive the higher temperatures used with other the methods, or have problems with thermal expansion mismatch.

However, initial studies showed that the films deposited contained a large amount of oxygen and little nitrogen. This was found to be due to residual air and the preferential formation of gallium oxide over gallium nitride. This problem is being overcome by the use of a low pressure of ammonia gas as a background in the vacuum chamber. Latest results, including description of a novel precursor and interpretations of mechanisms involved in the decomposition of precursors and film growth will be presented.

Acid/Base Properties and Cadmium Adsorption of Carbonaceous Substrates

Carolyn A. Burns, Ian H. Harding and Russell J. Crawford

Centre for Applied Colloid and BioColloid Science, Swinburne University of Technology,
P.O. Box 218, Hawthorn 3122
E-mail: CBurns@swin.edu.au

An experimental investigation of proton binding to Loy Yang coal (a brown coal) and Collie coal (a sub-bituminous coal) was conducted in 0.6 M, 0.1 M and 0.05 M NaNO3 using automated potentiometric titration techniques. The proton affinity constants were determined and the acid base properties of each coal have been modelled using electrostatic approaches.

The adsorption of Cd(II) to the coal surface was also investigated as a function of initial metal ion concentration using continuous batch experiments in 0.1 M NaNO3. The initial Cd(II) concentrations used in this study were: 0.5 mM, 2.5 mM, 5.0 mM and 7.5 mM. Potentiometric titrations were also carried out for all of the above initial Cd(II) concentrations. Proton data for each individual batch experiment compares favourably with proton data obtained from automated potentiometric titrations.

pH Static experiments at three different pH values have been conducted on both coal systems in 0.1 M NaNO3. The adsorption capacity for Cd(II) of each coal at a given pH has been obtained, with Loy Yang coal having a considerably higher adsorption capacity than Collie coal.

Measuring Long Range Repulsion in a Nonpolar Liquid

Wuge H. Briscoe

Ian Wark Research Institute, University of South Australia, The Levels Campus, Mawson Lakes, SA 5095
E-mail: wuge.briscoe@unisa.edu.au

Ample evidence exists that a solid can be charged in a nonpolar liquid, and an electrical double layer (EDL) would develop at the solid / nonpolar liquid interface consequently. The possible existence of this EDL has been previously probed by electrophoretic and light scattering studies, allowing a number of charging mechanisms at the solid / nonpolar liquid interface to be speculated. The detection of the EDL repulsion between surfaces immersed in a nonpolar liquid can also provide evidence that surfaces are charged and a double layer exists, but there has been no direct measurement of such a repulsion.

The extension of the aqueous EDL theory into the nonpolar liquid predicts an extremely diffused double layer. This diffuse characteristic imposes some significant difficulties on the detection of a double layer force in a nonpolar liquid, as the force, if present, would be extremely long ranged and probably very weak. In this study, a vertical magnetic force apparatus has been constructed, based on the Surface Forces Apparatus (SFA), in which the surfaces are suspended vertically with a soft double cantilever spring and positioned with a magnetic driving mechanism. Some preliminary results obtained with this apparatus will be presented, indicating the likely presence of a long range EDL repulsion between two mica surfaces immersed in decane with added di-(2-ethylhexyl) sodium sulfosuccinate (AOT). This enables the proposition of a charging mechanism which takes into the consideration many underlying factors such as inverse micelles and water.

The Effect of Natural Organic Matter on the Rheology of Concentrated Alumina Suspensions

Peter Harbour[1,2], D. R. Dixon[1] & P. J. Scales[2]

[1]*CSIRO Molecular Science, Private Bag 10, Clayton South MDC*
[2]*The University of Melbourne, School of Chemistry, Gratton St, Parkville, VIC 3052*
E-mail: peter.harbour@molsci.csiro.au

Natural organic matter (NOM) is present in most natural aquatic systems. NOM consists of a heterogeneous mix of compounds, with a continuous and polydisperse range of chemical structures and molecular weights. They are characterised by a high level of aromaticity and acidic carboxylate and phenolic groups. Historically aquatic NOM has been divided into humic acids and fulvic acids, the main distinction being an arbitrary evaluation of solubility. Humic acids are insoluble below pH 2 whereas fulvic acids are soluble at all pHs. It is also possible to fractionate the material on the basis of molecular size using ultrafiltration or, as we have done, on the basis of chemical functionality using ion exchange resins. The NOM fractions were isolated into three fractions: very hydrophobic (humic) acid, slightly hydrophobic (fulvic) acid and hydrophillic (charge and neutral) fractions.

The effect of aquatic NOM samples and fractions of NOM, on the rheology and surface chemistry of concentrated alumina suspensions has been examined. The Boger[1] vane method of shear yield stress determination was chosen to study the rheological properties of the suspensions, in particular shear yield stress. The surface charge properties of the alumina with and without NOM were monitored using a Matec Acoustosizer.

The Influence of Adsorbed Polymers on Galena Particle Interactions

Elaine Wightman

Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095
E-mail: WIGEM001@students.unisa.edu.au

In the minerals industry, ultrafine (< 5 micron) particles can represent a significant portion of the feed to flotation circuits. The poor flotation of these essentially liberated particles is generally attributed to a low probability of bubble-particle collision, which is related to physical variables and in particular particle size. In this work, increasing the collision probability is achieved through the formation of aggregates i.e. ultrafine particles are adsorbed onto coarser carrier particles which have been pre-coated with polymer.

Interactions between galena mineral surfaces have been found to be influenced not only by the presence of an adsorbed polymer but also the polymer molecular weight. Particle-particle interactions were probed by measuring the rate of removal of colloidal particles from suspension as a function of polymer molecular weight and amount adsorbed. The adsorbed amount was found to have a significant impact on the kinetics of removal of colloidal particles. The molecular weight determined the nature of the interaction i.e. the use of high molecular weight polymer resulted in an attractive interaction (aggregation) whereas use of a low molecular weight polymer resulted in a repulsive interaction (dispersion).

ABSTRACTS: POSTER PRESENTATIONS

ALBRIGHT & WILSON POSTER SESSION # 1

A Reflectometry Study of the Adsorption Kinetics of Cetyltrimethylammonium Bromide to the Silica-Water Interface

Rob Atkin[1], Vincent Craig[2] & Simon Biggs[1]

[1]*Centre for Multiphase Processes, Department of Chemistry, The University of Newcastle, Callaghan NSW 2308*
[2]*Department of Applied Mathematics, Research School of Physical Sciences and Engineering, ANU, Canberra ACT 0200*
E-mail: cpra@paracelsus.newcastle.edu.au

The adsorption kinetics of the cationic surfactant Cetyltrimethylammonium Bromide (CTAB) to the silica-water interface are investigated using optical reflectometry. This technique enables the rate of adsorption to be determined experimentally with a time resolution of approximately 1 millisecond. The experimental values are compared to those predicted by the theoretical diffusion limited flux of surfactant; the quotient being the "sticking ratio". Analysis of the sticking ratio as a function of CTAB concentration reveals that the adsorption process is cooperative above the critical micelle concentration (CMC), indicating that micelles adsorb directly to the silica-water interface. Surprisingly, at the Critical Surface Aggregation Concentration (CSAC) adsorption proceeds slowly in the absence of salt and takes hours to reach an equilibrium value. At all other concentrations and when salt is present the adsorption is complete within minutes.

Cu(II) Adsorption Mechanism on Pyrite: An XAFS & XPS Study

Christopher Weisener and Andrea Gerson

Ian Wark Research Institute, University of South Australia, The Levels, SA 5095, Australia
E-mail: Weicy001@students.unisa.edu.au

The surface of a <38μm ground fraction of pyrite was analysed by extended x-ray adsorption fine structure spectroscopy (XAFS) after Cu (II) adsorption under different pH and Cu (II) concentration conditions. It has been shown that a reducing mechanism occurs on the pyrite surface with Cu (II) reduction to Cu (I) with direct adsorption of Cu (I) ions attached to three sulfur ions on the surface. Copper is three-fold co-ordinate to sulfur on the surface of pyrite with an average bond length of 2.27A. A Cu-O bond with a length of 2.0A due to $Cu(OH)_2$ precipitation was also observed for a sample with Cu adsorbed at pH 8.5. XPS analysis was carried out on ground, polished and fractured pyrite samples with adsorbed copper. The Cu 2p signals show the presence of Cu(I) ions adsorbed on the pyrite surfaces in all cases. Both polished and fractured pyrite samples behaved similarily when exposed to a pH 5.5 with Cu (II) 10-4M solution. Both showed increases in polysulfide signals with minor increases in Fe (III) oxy- or hydroxy- species observed on the polished surface. It is possible that the reduction of Cu (II) to Cu (I) on the surface of pyrite is accompanied by the oxidation of the S22- species present in the pyrite surface, as suggested by the observation of oxidised sulfur species present.

Hydrophobic Thin Films Based on TiO_2 and Silica Based Crosslinking Sol-Gel Technology

Juniwaty. W. Thomas, H. Zhang and R. N. Lamb

School of Chemistry, University of New South Wales, Sydney NSW 2052
E-mail: juniwaty@hotmail.com

The behaviour of TiO_2 network based on crosslinked silica powders sol-gel technology is investigated. The continuous phase chemical binding particles between silica particles is formed. This is achieved by using TiO_2 as a crosslink agent and PDMS (Polydimethylsiloxane) as polymers to connect the silica particles. A macromolecular network is obtained as a result of hydrolysis-condensation reactions and the microstructure on the substrate surface depends on the experimental procedure.

TEOT (titanium tetrapropylorthotitanate) is used instead of TEOS (tetraethyloxosilicate), the most commonly used precursors in sol-gel processing, because TEOT is more reactive since Titanium is less stable toward hydrolysis-condensation reactions.

The uniformity, stability, hydrophobicity, roughness and molecular orientation of the TiO_2 film were studied by the measurement of dynamic contact angle, XPS and SEM techniques. The contact angle of water on the thin film ranges from 170-175°.

XPS results show that the contact angle is largely independent of small changes in chemical composition, and seems to depend on the physical structure of the film. The morphology of these films is examined further.

Accessibility and Kinetics of Adsorption in Mesoporous Molecular Sieves

Antje Dähler & Andrea O'Connor

Department of Chemical Engineering, University of Melbourne, Parkville VIC 3052
E-mail: a.daehler@chemeng.unimelb.edu.au

The selective separation of large biopolymers via adsorption is important for a number of applications, for example in the food and the pharmaceutical industries. The application of existing molecular sieves for adsorption of large biopolymers is limited. While the pores in conventional molecular sieves (e.g. zeolites) are often too small to allow access for large biopolymers, the smaller surface area of non-porous materials limits their capacity. Further concerns for some of the currently used adsorbents are lack of selectivity, swelling and leaching of undesirable materials out of the adsorbent.

Novel adsorbents that address these problems can be developed on the basis of molecular sieves of the M41S family. M41S, a group of molecular sieves with pore sizes in the range of 20 – 100 Å, has unique properties that are desirable for adsorbents, e.g. uniform pore size distributions, tunable pore sizes, mechanical and thermal stability, rigid structure and large surface areas (> 1000 m^2/g).

Since the development of these materials, applications research has concentrated mainly on MCM41, a molecular sieve with a parallel array of hexagonal pores, not unlike honeycomb. The first results of successful adsorption of proteins and vitamins on MCM41 have been reported. There are, however, limitations to accessibility of the pores and adsorption kinetics due to the geometry of the material (long, parallel, unconnected pores). The accessibility of the pores and kinetics of adsorption are potentially more favourable in another member of the M41S family, the cubic mesoporous molecular sieve MCM48, due to a more open pore structure (entwined, branching pores).

In this presentation, synthesis and characterisation of MCM 48 will be described, results on pore accessibility, adsorption capacity and kinetics will be presented for model biopolymers and potential developments involving different templated porous structures and functionalising of the pore surface will be proposed.

Self-Assembly of Cationic Surfactants at the Graphite-Solution Interface

Paul Fitzgerald

School of Chemistry F11, University of Sydney, Sydney NSW 2006
E-mail: fitzge_p@chem.usyd.edu.au

An Atomic Force Microscope (AFM) was used to study the self-assembly of cationic surfactants at the solution/graphite interface. The single tail surfactants dodecyltrimethylammonium bromide (DTAB) and dodecyltrimethylammonium chloride (DTAC) as well as the double tail surfactant didodecyldimethylammonium bromide (DDAB) were all studied as a function of concentration. DTAB and DTAC were found to form hemicylinders on the graphite at both low and high concentrations. Force curves revealed that additional structures formed over these hemicylinders at higher concentrations (approaching the phase boundary), however, these structures could not be imaged. DDAB was found to form stripes on the surface at both high and low concentrations. The addition of electrolyte (about 1M KCl) caused the formation of bilayers normal to the surface. After sufficient equilibration time the formation of large featureless structures over the stripes were also observed.

Surface Layer Control for Improved Copper Recovery for Chalcopyrite Leaching

Sarah Harmer

Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095
E-mail: harsl001@students.unisa.edu.au

Copper extraction via the leaching of chalcopyrite and other low-grade ores is of great interest to the minerals processing industry. Chalcopyrite leaching has been shown to be dependent on the surface layers that form during the dissolution process. XPS, ToF-SIMS, SEM and XRD are all techniques that are used to characterise the surface layers of varying materials. These surface analytical techniques have enabled the study of the evolving surface layers at selected stages in the dissolution process of chalcopyrite. Previous studies have shown that these inhibiting layers are ferric oxides / hydroxides and metal deficient polysulfide / elemental sulfur species. The identification and removal of these inhibiting surface layers may prove essential to improve the copper leaching rate.

Molecular Structure of a Weak Gelling System

Heide Mielke

Advanced Mineral Products Special Research Centre, School of Chemistry, The University of Melbourne, Parkville, VIC 3052
E-mail: h.mielke@secondwww.chemistry.unimelb.edu.au

This study is designed to understand the interesting rheological behaviour of weak gel systems at a molecular level. Due to its regular chemical structure, the exocellular microbial polysaccharide from *Pseudomonas elodea*, gellan, is a simple model system for studying polysaccharide gelation and solution behaviour. The differing interpretations, of the large-scale molecular structure of the gel, stem from various models proposed for gellan gelation. AFM imaging offers an alternative method of investigation to physical chemical models of gel networks and precursors.

Tailoring Selective Surfaces for Metal Ion Uptake

M. Linh Tran, Ian R. Gentle and Lawrence R. Gahan

Department of Chemistry, The University of Queensland, Brisbane QLD
E-mail: l.tran@chemistry.uq.edu.au

The separation and concentration of metal ions under dynamic flow conditions is of interest from both pure and applied research perspectives. Chromatographic techniques may be able to separate metal ions, but do not offer real time analysis of the heterogeneous reactions between anchored receptors and metal ions. Quartz crystal microbalances (QCM) consist of alpha-quartz sandwiched between electrodes designed in a keyhole pattern. QCMs modified with receptor sites, responds to adsorption of target species (in solution), by changing the resonant frequency. Hence a frequency vs time profile can be used to follow the reaction.

This presentation provides results from preliminary studies conducted into tailoring selective surfaces on the gold electrode of a QCM, in order to uptake metal ions in solution. One strategy involves immobilising aminopolycarboxylate ligands onto micron sized silica beads and anchoring the beads to the surface of the gold electrode via a self-assembled mercaptosilane monolayer. Development and refinement of this procedure is under way with characterisation of the multilayer system being performed using techniques like XPS, microscopy and contact angle measurements. The surfaces are tested for their suitability using a flow cell set-up where various solutions are passed over the derivatised crystal to observe whether the systems do uptake metal ions reversibly and are stable. Metal binding experiments have shown the silica multilayer system binds a small amount of lead.

Phase Behaviour in Colloidal Dispersions

Simon Petris

Department of Mathematics and Statistics, University of Melbourne, Parkville VIC 3052
E-mail: s.petris@ms.unimelb.edu.au

The standard theory for the interaction between charged colloidal spheres was formulated almost 50 years ago by Derjaguin, Landau, Verwey, and Overbeek (DLVO). Anomalous observations of stable voids in dilute deionized colloidal latex dispersions suggest that the theory is not yet complete. Under the influence of the long-range double-layer repulsion, one would expect a homogeneous distribution of spherical latex particles. However, if such a dispersion is left to stand for long periods of time, one observes stable voids coexisting with surrounding regions of the latex particles distributed in a liquid-like structure. The observations will be described in detail, and some theoretical explanations will be discussed.

Stabilization of Cubic Phases

Gregory M. Nash & Gregory G. Warr

School of Chemistry F11, University of Sydney, Sydney NSW 2006
E-mail: g.nash@chem.usyd.edu.au

At sufficient concentrations, certain surfactants spontaneously aggregate to form cubic phases. There are two distinct types of cubic phases, discrete (micellar) and bicontinuous. These cubic phases are stable for a large temperature range. In this study, stabilization forces were determined using two techniques. Parallel plate oscillatory rheology, which yields insight into energy storage by the system, and osmotic stress coupled with small angle X-ray scattering (SAXS), which yields a relationship between potential and distance between surfaces inside the cubic phase. The results reveal the distinctive nature of the different types of cubic phases.

Semiconductor Nanobubbles and Coated Metal Nanoparticles

George Oldfield & Paul Mulvaney

Advanced Mineral Products Special Research Centre, School of Chemistry, The University of Melbourne, Parkville, VIC 3052
E-mail: g.oldfield@ugrad.unimelb.edu.au

Metal nanoparticles have attracted increasing attention recently for their novel physicochemical properties. In this study, 15nm diameter gold nanoparticles were synthesised using surface-catalysed reduction of Au^{3+} by citrate. SnO_2 was deposited on the surface of the particles by adjusting pH and applying heat, resulting in core-shell metal-semiconductor nanoparticles. Semiconducting quantum bubbles were synthesised by dissolving the gold core with cyanide. A variation of the technique was used to encapsulate dye molecules with SnO_2. The electronic and optical properties of the particles synthesised were explored.

Depletion Interactions in Charged, Binary Suspensions

Valeria Tohver[1], O. Sakurada[1], J.A. Lewis[1], J. Walz[2], A. Braem[3], & R.D. Tilton[3]

[1]University of Illinois, Champaign-Urbana, IL USA
[2]Yale University, New Haven, CT
[3]Carnegie Mellon University, Pittsburgh, PA
E-mail: v-tohver@students.uiuc.edu

The effect of colloidal forces on suspension stability plays an important role in ceramic processing of thick films and bulk parts. The presence of fine colloidal particles, nonadsorbed polymer, or dissolved salt can strongly influence suspension stability. We have investigated the influence of ZrO_2 depletant species (D=8nm) on the properties of colloidal SiO_2(D=500nm) suspensions. We observed dramatic changes in the initially weakly flocculated SiO_2 suspension behavior upon the addition of such species. Interestingly, we observed colloidal crystallization under pH conditions close to the isoelectric point of the silica. Rheology and optical microscopy were carried out to evaluate suspension stability. In addition, optical reflectivity, zeta potential, and ICP analysis of supernatant solutions were used to determine the extent (if any) of ZrO_2 adsorption on the primary colloid phase. Colloidal crystal formation was studied using sedimentation. Theoretical modelling of depletion interactions was carried out using the model of Walz and Sharma[1].

References:

1. Walz & Sharma, *J Coll Interface Sci* **1994**, 168, 485-496.

Polarised Attenuated Total Reflection Spectroscopy in Protein Adsorption Kinetic Studies

M. Luisa Jayme, Dave E. Dunstan, Michelle L. Gee

Department of Chemical Engineering, University of Melbourne, Parkville VIC 3052
E-mail: m.jayme@pgrad.unimelb.edu.au

Biopolymer adsorption – particularly that of protein systems - is an important phenomenon in a wide range of industries including the food, pharmaceutical and wastewater management industries. While numerous studies have been performed in order to elucidate the kinetics of adsorption for a number of protein systems, little attention has been paid to the kinetics of conformational reorganisation at the interface. The present study aims to relate the tertiary structure relationship to adsorption phenomena using chicken egg-white lysozyme.

Time resolved polarised Attenuated Total Reflection experiments provide in-situ measurement of both the biopolymer adsorption kinetics and the rate of conformational evolution at the interface. The technique and interpretation will be discussed specifically to the solid/liquid interface.

References:
1. Harrick, N.J.: *"Internal Reflection Spectroscopy"*, Interscience, NY, 1967
2. Neivandt, D.J., Gee, M.L., Tripp, C.P.: J. *Phys. Chem. B*, **102**, 5107 (1998)

Rheological Study of Kappa-Carrageenan and Locust Bean Gum System

Yu Chen

Department of Chemical Engineering, University of Melbourne, Parkville VIC 3052
E-mail: y.chen13@pgrad.unimelb.edu.au

The gelation and interaction of the kappa-carrageenan and locust bean gum binary system has been investigated. It is widely accepted that a synergy exists within these polysaccharides but the amount of synergy and the ratio at which this synergistic effect is an optimum has not been agreed upon. Rheological measurements such as compression and shear moduli tests were used to monitor the structural changes as the ratio of the two gums varied while maintaining the total polymer concentration constant. Rupture tests were also conducted during compression studies to determine optimal ratios. The effect of KCl concentration was also investigated. Various methods were tried in order to minimize the effects of slip caused by syneresis during shear measurements.

Removal of Aqueous Heavy Metals by Biosorption onto Fungi

Tamna C. Woolcock, Greg T. Lonergan & Russell J. Crawford

Centre for Applied Colloid and BioColloid Science, Swinburne University of Technology,
P.O. Box 218, Hawthorn 3122
E-mail: tamwool@yahoo.com

Heavy metals are found in the waste streams of many industrial processes, including those from tannery, alloy manufacture and electroplating industries. These heavy metals can have detrimental effects on both human health and the environment. Methods for the removal of these metals often involve precipitation by the addition of base. The disadvantages of such processes are the cost and introduction of high pH levels into waste streams.

Adsorption of aqueous heavy metals onto colloidal substrates has been shown to reduce the pH at which these metals can be removed from solution. Recently, biological substrates such as fungi and bacteria have been investigated, as potential adsorbent surfaces, however rigorous adsorption studies have not been performed. Biomass substrates have the advantage that they are renewable, and are available at low cost as by-products from the fermentation industry.

In the current study adsorption trials have been performed using Cr(III), Ni(II) and Zn(II). These metals have been adsorbed onto dead fungal biomass of the species *Rhizopus*, *Mucor*, *Agaricus bisporus*, *Pycnoporus cinnabarinus*, and *Perennaporia tephrophora* . These fungal types were selected since they provide substrates with a range of cell wall chitin levels, the degree of which has been empirically related to adsorption efficiency.

It has been found that whilst Ni(II) and Zn(II) are efficiently adsorbed onto the fungal substrates (in some cases lowering the pH of removal by up two pH units lower than that observed for direct precipitation), the presence of the fungi had little or no effect on the removal characteristics for Cr(III).

Reversible Wetting of Photo-Responsive Surfaces

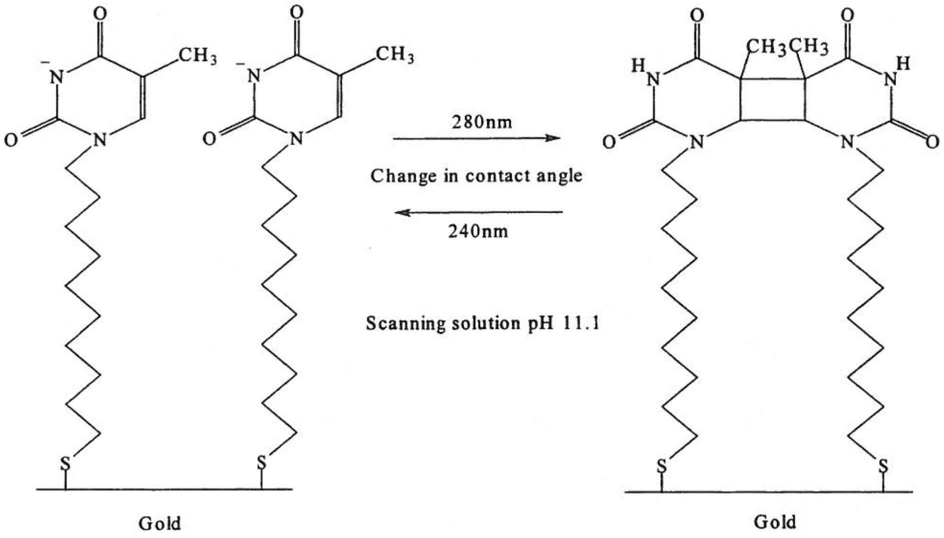
Peter Pullman and Scott Abbott

Ian Wark Research Institute, Univeristy Of South Australia, Mawson Lakes, SA 5095
E-mail: Peter.Pullman@unisa.edu.au

Surfaces coated with photo-responsive pyrimidine groups are to be prepared that undergo reversible wettability changes. The pyrimidine groups can be converted between monomeric and dimeric forms by irradiation with UV light at particular wavelengths. The two forms have different dipole moments and consequently different wettabilities, due to their different pKa's and inherent hydrophobicities. Pyrimidine groups are to be incorporated as ω-terminal groups in long chain alkylthiols and attached to gold surfaces as self assembled monolayers (SAM's).

Self assembled monolayers of thymine-terminated alkylthiols have produced static water contact angles of up to 26°. This system is to be improved by using a SAM in which two thymine groups are incorporated into each molecule. This will place thymine groups at an optimal distance for dimerisation by molecular design, and will avoid the need for close molecular packing on the surface.

Surfaces will also be prepared that enable the wettability change to occur over a more hydrophobic or hydrophilic range. This will be achieved by the use of mixed SAM's, incorporating both thymine-terminated alkylthiols, and alkylthiols terminated by either hydrophilic functionalities (such as hydroxyl or carboxylic acid groups) or hydrophobic functionalities (such as methyl or trifluoromethyl groups).



Thymine-terminated alkylthiol

MONOMER

Thymine-terminated alkylthiol

DIMER

Adsorption of Ampholytic Diblock Copolymers at Solid/Liquid Interfaces

Grant Webber, Simon Biggs, Erica Wanless

Department of Chemistry, University of Newcastle, Callaghan, N.S.W., Australia, 2308
E-mail: cpgw@paracelsus.newcastle.edu.au

The adsorption of an ampholytic diblock copolymer at the solid liquid interface has been studied using atomic force microscopy. The copolymer was poly(2-(dimethylamino)ethyl methacrylate-*block*-methyl methacrylate) (poly-(DMAEMA-*b*-MMA), see Figure 1, containing 70% DMAEMA and having a molecular weight of 42000. The adsorption of the copolymer, from a solution of 0.05% w/w copolymer, 0.01M added electrolyte (KNO_3) and pH 4, onto freshly cleaved muscovite mica was monitored over a twenty-four hour period. The kinetics of the copolymer adsorption were determined from the images obtained.

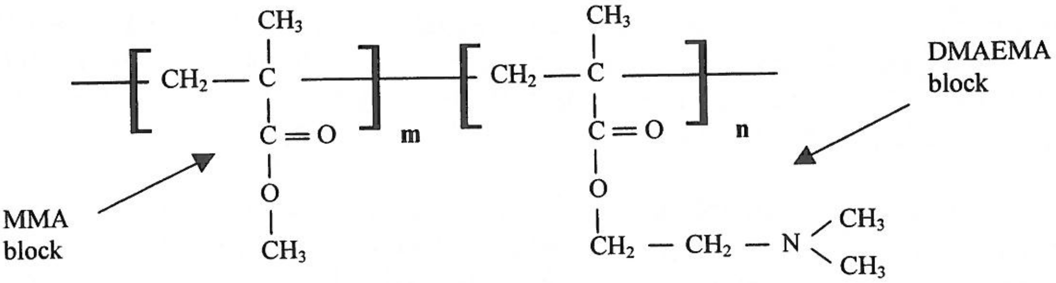


Figure 1

Flocculation and Dewatering of Bauxite Residues
Investigation of Paint Film Formation by Atomic Force Microscopy

Gordon Burns

School of Chemistry, University of Sydney, Sydney, New South Wales, 2006, Australia
E-mail: burns_g@chem.usyd.edu.au

The film formation of paint is investigated using atomic force microscopy. Paint films are comprised of pigment, binder, coalescing aid and additives. The effect of pigment and coalescing aid are examined. Coalescence and inter-diffusion of film formation are followed in simple latex binders, and the effect of coalescing aid on these processes investigated. Tapping mode atomic force microscopy enables high resolution imaging of these soft latex samples, with compositional as well as topographical mapping. Using compositional mapping, it is observed that Texanol promotes exudation of water sensitive material at the latex film surface during film formation. Examination of the extent of pigment wetting by polymer at the film surface is carried out using model paints of varying pigment volume concentration, and compositional mapping.

Polymer Adsorption onto the Different Surfaces of Kaolinite Clay

Matthew L. Taylor, Gayle E. Morris, Peter Self & Roger St. C. Smart.

Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA, 5095
E-mail: TAYML001@students.unisa.edu.au

In many minerals processing industries the flocculation and disposal of clay-based mining tailings is a major concern. It is therefore imperative that a good understanding into the operation of flocculants is achieved in order to optimise flocculation procedures.

Kaolinite ($Al_2Si_2O_5(OH)_4$) is the major component of many clay-based tailing systems. Kaolinite itself is a layered structure that has two very different, hydrophobic basal faces, one consisting of a siloxane surface with the other being a gibbsite surface. These basal faces of kaolinite are known to carry a small constant negative charge that is virtually independent of pH. The edge surface of kaolinite consists of both Si-OH and Al-OH groups that are pH dependent. These edge surfaces are estimated to comprise approximately 10% of the whole kaolinite surface and exhibit a hydrophilic character. Earlier work by Braggs (1993), proved that silane molecules only adsorb to edge surfaces and do not attach themselves to either of the basal surfaces. As a result, silane molecules block adsorption onto edge surfaces and expose a non-adsorbing surface to solution (Morris et al., 1999).

In this study the addition of polyacrylamide flocculants (commonly used in the minerals processing industry) onto the kaolinite surface was investigated using adsorption kinetics and equilibrium adsorption studies. The purpose of this study was to investigate the difference in the adsorbed amount of anionic polyacrylamide onto (1) an untreated kaolinite sample and (2) a silane treated sample, at pH 8.5. This study provides information regarding the location and amount of polymer adsorption onto the kaolinite surface.

References:

1. Braggs, B. R., The controlled modification and characterisation of the kaolinite surface. Ph. D. thesis, University of South Australia, 1993.
2. Morris, G. E., Fornasiero, D. and Ralston, J., Low molecular weight polyacrylamide adsorption by silane modified talc, *The Use of Polymers in Mineral Processing*, 3rd UBC-McGill Bi-annual International Symposium on Fundamentals of Mineral Processing, Quebec City, Canada, Aug. 1999.

The Effect of Citric Acid on the Adsorption of Cadmium to the Clay Mineral Illite

Kurt Lackovic

School of Management, Technology & Environment, PO Box 199, Bendigo, VIC 3552
E-mail: klac1@students.bendigo.latrobe.edu.au

During the past 50 years over 5000 tonnes of cadmium has been added to Australian soils as an impurity in superphosphate, and now represents a potential threat to human health in crops grown on affected land. This project investigates the adsorption of cadmium on illite, a 2:1 clay mineral common in cropping soils in Northern Victoria. The effect of citric acid on cadmium adsorption is studied because the roots of important crop species, such as wheat, are known to exude citrate ions which may affect the concentration of Cd(II) in the soil solution.

The illite sample chosen was obtained from CSIRO Division of Land and Water and has a high level of Fe(III) in the crystal lattice, probably replacing both Al(III) in the octohedral sheet and Si(IV) in the tetrahedral sheet.

Adsorption of cadmium and citric acid to illite has been studied as a function of both pH (adsorption edges) and concentration (adsorption isotherms). Cadmium adsorption in the presence of citric acid has also been investigated. Potentiometric titrations of illite, cadmium, citric acid, and combinations of the three were completed.

The results have been modelled using a constant capacitance surface complexation model assuming two differect sit types; permanent charge sites (X-)due to isomorphous substitution in the silica faces, and variable charge (SOH) sites on the edge of the crystals. While this model provided an adequate fit to most data, it is not as good as fits achieved with the 1:1 clay mineral kaolinite. We suspect that this is due to the substantial Fe(III) concentration in the crystal lattice which means that both Al-OH and Fe-OH groups are available for metal ion adsorption.

Experiments are currently underway using kaolinite and an iron oxide (goethite (alpha-FeOOH)) in an attempt to better understand the illite system.

Characterisation and Stabilisation of Lipid-DNA Complexes for Gene Therapy

Minh-Uyen Trinh

Ian Wark Research Institute, University of South Australia, The Levels Campus, Mawson Lakes SA 5095
E-mail: trimy002@students.unisa.edu.au

Gene therapy is an exciting new technology that involves the introduction of genetic material (DNA) into cell systems in order to treat human diseases. Viruses are currently the most widely used vectors for cell transfection, due to their high efficiency. However, this efficiency is coupled to a number of inherent problems, including the possibility of causing immunological responses in the body, the potential carcinogenicity of the viruses, as well as limited DNA-carrying capability (Hodgson, 1995). Due to these drawbacks, non-viral vectors, in particular lipids/liposomes are becoming increasingly popular as an alternative gene delivery system (Gao and Huang, 1995).

In this study, Tris conjugated cationic lipids were used as the vehicle for the transfection of DNA into cells. The aims of this project are to study the physicochemical properties of the complex formed between the lipid and DNA and to relate these properties to the transfection efficiency of these complexes into cells.

Dynamic light scattering measurements have shown that the size of these complexes are about 60-150 nm and is stable in the absence of NaCl. These sizes were confirmed using Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) techniques. In the presence of NaCl, the lipid-DNA complexes formed were found to aggregate. Increasing the lipid to DNA ratio resulted in a more stable complex in the presence of NaCl. Mechanisms of DNA-lipid interactions are proposed to explain the stability of the complex.

References:
Gao, X. and Huang, L. (1995) *Gene Therapy*, 2, 710-722
Hodgson, C.P. (1995) *Bio/Technol.*, 13, 222-225

The Colloid Science of Pasta Filata Cheese

Dorothy Attard[1], Peter Roupas[2] and Ian McKinnon[1]

[1]*Chemistry Dept., Monash University, Clayton, Victoria 3168, Australia*
[2]*Food Science Australia, Werribee, Victoria 3030, Australia*
E-mail: dorothy.attard@sci.monash.edu.au

Pasta filata cheeses (such as Mozzarella cheese) are distinguished by their fibrous structure, plasticity, melting and stretching properties. During the early stages of cheesemaking, the casein micelles are destabilised by the combined action of rennet and a lowering of pH. The 'micelles' are an open network of protein strands (caseins) held together by a mixture of hydrophobic interactions and interaction between the phosphoseryl groups of the proteins and nanocrystalline calcium phosphate (colloidal calcium phosphate, CCP). The micelles are *c.a.* 200nm in diameter. The reduction in electrosteric stabilisation that results from the hydrolysis of κ-casein by rennet and the reduction in the charge on the caseins as the pH approaches the isoelectric point together lead to the precipitation of casein micelles in the form of a gel, or 'curd'. The curd microstructure resembles an extended micelle. Pockets in the protein network encompass fat globules and pools of serum.

Upon stretching a dramatic transformation occurs resulting in the formation of fibrous protein strands oriented in the direction of stretch and containing emulsified fat and serum in the columns formed between the strands. This transformation, occurring during the stretching/plasticization treatment of the curd, is critically dependent on the levels of CCP and intact casein.

Curd pH is an important parameter in the cheesemaking process as it determines the extent of solubilisation of both calcium phosphate and casein and the extent of their removal from the system in the whey. The colloidal calcium phosphate gives a stiffness and rigidity to the network structure. Thus at high levels of CCP stretching does not occur. On the other hand, in the absence of CCP the casein network is unable to support itself. The degree of proteolysis of the caseins prior to stretching is also of importance through its effect on the network structure. The plasticizing treatment is normally performed in a cooker/stretcher and involves heating the curd at a pH 5.2 in brine at approximately 60°C, and stretching the molten mass along rotating augers; the latter also being performed in the presence of hot brine.

The object of this project is to gain a greater understanding of the plasticisation process. Of particular concern is the change in the interactions between the different phases present and the role of variables such as temperature, pH and CCP in the plasticisation reaction. It is hoped that the project will provide insight as to what properties (both chemical and physical) are imparted to the final cheese by the cooker/stretcher and of the how to control them.

References:

Kindstedt, P.S. (1993), Effect of Manufacturing Factors, Composition, and Proteolysis on the Functional Characteristics of Mozzarella Cheese, *Crit. Rev. Food Sci.*, **33**, 167-187.

Holt, C. (1992), Structure and Stability of Bovine Casein Micelles, *Adv. Prot. Chem.* **43**, 63-151.

Lawrence, R.C., Creamer, L.K. and Gilles, J. (1987), Texture Development During Cheese Ripening, *J. Dairy Sci.* **70**, 1748-1760.

Glass Formation in Microemulsions

Asaph Widmer-Cooper

School of Chemistry F11, University of Sydney, Sydney NSW 2006
E-mail: a.widmer@chem.usyd.edu.au

AOT (sodium dioctylsulfosuccinate)-isooctane microemulsion systems have been investigated by MDSC (Modulated Differential Scanning Calorimetry) over the temperature range 25°C to 120°C. Somewhat surprisingly perhaps, these systems were found to exhibit a glass-like transition. Furthermore, the transition temperature was found to be dependent on the concentration of AOT in the system over a 20 to 30 degree temperature range.

Swelling the micelles with glycerol or low weight percentages of water results in a single glass-like transition whose temperature is dependent upon the amount of glycerol or water present. The transition temperature decreases from that of the corresponding pure AOT-isooctane system, and in the case of glycerol approaches that for the glass transition of pure glycerol. On the other hand, for water the transition temperature reaches a minimum at about 2.5 water molecules per AOT that appears to be independent of the AOT concentration. If more water is added an exothermic peak is observed near 0°C, most likely due to water crystallising and the transition temperature increases back towards that of the corresponding pure AOT-isooctane system.

This work and further studies attempting to understand these observations is presented along with a hypothesis as to what is occurring.

Syneresis in Carrageenan Gels

Rob Salvatore

Advanced Mineral Products Special Research Centre, School of Chemistry, The University of Melbourne, Parkville, VIC 3052
E-mail: r.salvatore@pgrad.unimelb.edu.au

Syneresis in carrageenan gels as a function of polysaccharide concentration, potassium ion concentration and the addition of locust bean gum have been investigated. The amount of potassium bound by the gel as a function of the potassium ion concentration was determined by ICP analysis of the syneresis liquid from the gels. The kinetics of syneresis as a function of potassium ion concentration was also measured. The conductivity of carrageenan and locust bean gum mixtures through the gel point was measured as well as the dielectric response of these mixtures in solution and as a gel.

Novel Methods of Dewatering of Colloidal Suspensions

Daniel Lester

Advanced Mineral Products Special Research Centre, School of Chemistry, The University of Melbourne, Parkville, VIC 3052
E-mail: d.lester@chemeng.unimelb.edu.au

The chemical and in particular, mineral processing industries worldwide produce immense volumes of suspensions of fine particles as waste which are flocculated to form colloidal suspensions. Current industrial dewatering processes such as batch settling, continuous thickening and pressure filtration attempt to separate this waste into clear liquor for reuse and tractable solids for further processing. The rate and extent of separation can be optimized by sound design and operation, but are ultimately limited by the suspension dewatering properties. Such properties consist of the suspension permeability and compressive yield stress of the consolidating solid, which are generally considered fixed for a given material. However, application of external forces can modify the character of a dewatering process, altering the observed dewatering properties of the suspension. The change in suspension dewaterability generates potential to markedly improve separation efficiency, such that higher solids concentrations and lower process residence times can be achieved. Two different means of modifying the dewatering character are proposed; application of a DC electric field to the suspension, and vibration of the suspension. The influences are applied to a pressure filtration device and the changes in suspension permeability and compressive yield stress are measured. Dewatering processes can be then modelled using the filtration measurements, allowing the improvement in separation efficiency to be quantified.

Sonoluminescence from Ethylene Glycol-Water Mixtures

Melanie Bradley, Muthupandian Ashokkumar & Franz Grieser

Advanced Mineral Products Special Research Centre, School of Chemistry, The University of Melbourne, Parkville, VIC 3052
E-mail: m.bradley@student.unimelb.edu.au

When ultrasound passes through a liquid medium bubbles within the liquid expand and are compressed by the oscillating sound field. Under certain circumstances the bubbles undergo rapid collapse, which causes localized heating within the bubble producing high temperatures and in many cases emission of light, referred to as sonoluminescence (SL). The phenomenon is not well understood but evidence exists that interfacial effects at the bubble/solution boundary are important. This project examines the effect of surface active solutes - (C1-C8) aliphatic alcohol and ionic surfactants on the sonoluminescence observed in ethylene glycol-water mixtures. The presence of aliphatic alcohol in ethylene glycol caused a rise in the SL signal at low alcohol concentrations followed by a decrease in intensity at higher concentrations. Increasing the alcohol chain length and/or increasing the water/ethylene glycol solvent ratio promoted a quenching of the SL signal. The addition of surfactant caused an increase in the SL signal before a constant emission intensity was observed. These observations can be explained with respect to changes in the level of bubble coalescence induced by the partitioning of the solute at the bubble/solvent interface and the evaporation of the solute into the bubble core.

Adsorption of Oppositely Charged Polyelectrolyte and Surfactant onto α-Alumina Fibres

Ineke Muir

Advanced Mineral Products Special Research Centre, School of Chemistry, The University of Melbourne, Parkville, VIC 3052
E-mail: i.muir@student.unimelb.edu.au

The adsorption of oppositely charged polyelectrolyte and surfactant onto α-alumina fibres has been investigated. The adsorption was carried out at the point of zero charge of α-alumina. The polyelectrolyte used was poly(styrenesulfonate) (PSS), and the surfactant was cetyltrimethylammonium bromide (CTAB). In solution, they are negatively and positively charged respectively. The effect of the background electrolyte concentration was investigated using KBr. Force measurements were carried out on the Atomic Force Microscope. Adsorption was carried out using two different mechansims. The first was sequential addition, where PSS was adsorbed to α-alumina surfaces, and then CTAB was added to the system, and the second adsorption mechansim involved equilibration of PSS and CTAB together in solution, and the polyelectrolyte-surfactant solution was then adsorbed onto α-alumina fibres.

Growth of ZnO Films- a Several Variable Problem

Antonella J. Petrella, A. J. Hartmann & R. N. Lamb

School of Chemistry, University of New South Wales, Sydney NSW 2052
E-mail: antonella@student.unsw.edu.au

There have been numerous studies exploring growth methods of Zinc based II-VI thin films. Film growth methods can be generally grouped into two classes, these are the physical (eg sputtering) and chemical (eg chemical vapour deposition) methods. Whilst the physical methods are viable they also present severe limitations, for example resultant films are often highly stressed, depositing on rough surfaces is hindered due to shadowing effects and generally physical methods are high energy and inefficient.

Chemical methods for film growth have also been used extensively but have generally been complicated, involving highly reactive and toxic chemical precursors. A chemical method of increasing interest and which promises to provide simple and flexible growth procedures is single source chemical vapour deposition (SSCVD). This method offers a high level of control over resultant film structure, as many experimental parameters can be controlled.

Although SSCVD has been used for ZnO film growth for some time now what is significant is that the understanding of how factors such as substrate and precursor effect film growth has not been achieved.

This project aims to understand chemistry or more precisely decomposition, surface chemistry to such an extent that engineering film properties through manipulating chemistry can be done, with the added incentive that other films can be grown using the principles established.

The Origin of the Hydrophobic Interaction

Ana-Suncana Barisic

Department of Applied Mathematics, Research School of Physical Sciences and Engineering, ANU, Canberra ACT 0200
E-mail: asb110@rsphysse.anu.edu.au

Hydrophobic solutes of different sizes are studied with angle-averaged and the full molecular SPC/E models of water.

The radial distribution function (rdf) for solute-water and solute-solute interactions are calculated from different Monte Carlo simulations, performed using the effective angle- - averaged potential for water-water interaction and a hard-core solute-solute potential. The density distribution of water obtained from this approach, near a solute molecule is unphysical and therefore corrected using a hydrophobic field [1,2]. This result is found with a spherically symmetrical Hamiltonian model, where a potential of mean force for a solute-solute interaction is calculated.

Results are compared with those obtained by the "information theory"[3] model where the hydrophobic effect and the free energy of solvation of small solute particles can be accurately described. The fortuitous agreement occurs only as the "information theory" simultaneously neglects the angular dependence of the water rdf and changes between the bulk and solute-solvent interface (no hydrophobic field imposed). The angle dependent potential leads to the clathrate-like cage water formation in the vicinity of the solute. Consequently, the density is similar to that found in bulk. It is the preservation of the tetrahedral coordination of hydrogen bonding of water molecules that has the dominant role in the formation of the inhomogeneous structure of water and therefore it is difficult to ignore it. For larger solutes, clathrate structures are energetically unfavourable and the angle-averaged models are insufficient to describe short-range effects.

Molecular dynamics simulations have been performed to avoid limits of spherically symmetrical models. Now Lennard-Jones particles diluted in the water described by the SPC/E model, have been simulated to determine changes between the bulk water and solute-solvent interface as well as the solvation energy for a microscopic and mesoscopic solute size.

References:

1. G.Hummer & S.Garde , *Phys.Rev.Let.* Vol.80, 4193, (1998)
2. J.D.Weeks *et. al., Phys.Rev.Le.t* Vol.81, 4400, (1998)
3. G.Hummer *et. al., Proc. Natl. Acad. Sci.* USA, Vol.93, 8951 (1996)

Assessment of Surface Energy Heterogeneity. Principle and Applications

Laurent Michot

ENSQ –INPL- CNRS UMR 7569", Laboratoire "Environnement et Minéralurgie", BP 40
54501 VANDOEUVRE CEDEX, FRANCE.
E-mail: l.michot@chemistry.unimelb.edu.au

Real solid surfaces are now widely recognized as being energetically heterogeneous. Such heterogeneity can be due to local disorders, different crystallographic faces, surface roughness and impurities, as well as to the presence of various pores of different size and shape. Such features largely control adsorption at the solid/gas and solid/liquid interface in the sub-monolayer domain.

Gas adsorption experiments are well suited for probing surface heterogeneity, provided that a high accuracy can be obtained at very low pressures/coverages. In the past few years, we have developed an instrument and an analytical technique (the Derivative Isotherm Summation method) which allows the simulation of experimental derivative adsorption isotherms on heterogeneous surfaces as the sum of local theoretical derivative adsorption isotherms, resulting in a "mapping" of surface energies.

After a brief description of the technique, we will focus on the results obtained for various experimental systems. In the case of clay minerals, such an approach provides a reliable determination of the aspect ratio of the particles. Furthermore, the combined use of argon, a non-polar probe and nitrogen, a polar one, reveals the intrinsic complexity of the surface of such minerals and the importance of the nature and amount of surface cations. This provides essential information for a better understanding of the adsorption of more complex molecules. In the case of activated carbons, we have been able to show that such a technique can be more generally applied as a spectroscopic tool to reveal the adsorption mechanisms of simple organic micropollutants.

Direct Measurement of Colloidal & Polymeric Interactions Using Total Internal Reflection Microscopy

Michael Bevan

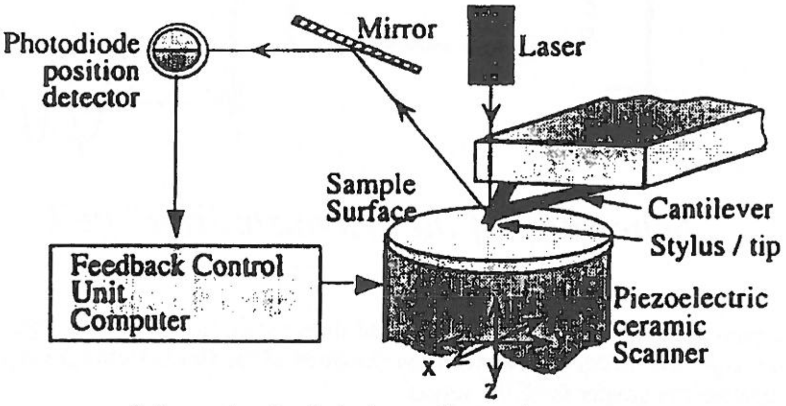
Advanced Mineral Products Research Center, School of Chemistry, University of Melbourne, Parkville, Victoria 3052 Australia
E-mail: m.bevan@chemeng.unimelb.edu.au

This talk will discuss the method of Total Internal Reflection Microscopy for direct measurement of the interaction of a single colloidal particle with a flat wall. The TIRM measurements presented will focus on the van der Waals, steric, and hydrodynamic interactions between a polystyrene particle and a polystyrene coated surface both with adsorbed polymer layers. This talk will discuss both the equilibrium and dynamic interactions, which can be measured with the TIRM technique. The force measurements will also be motivated by light scattering studies indicating interesting stability properties of sterically stabilized dispersions which have not been previously observed. Finally, TIRM will be compared to other surface force measurement techniques to indicate the novelty of these studies.

EXPERIMENTAL TECHNIQUES

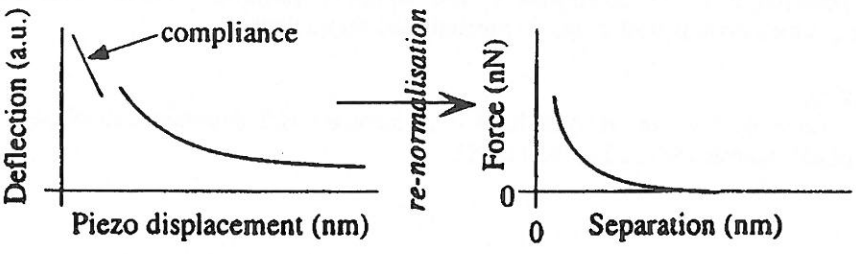
(ATOMIC) FORCE MICROSCOPY

The Force Microscope is one of a family of Scanned Probe Microscopes derived from the Scanning Tunnelling Microscope. They all share three attributes: a mechanism for translating a surface in three dimensions typically with a precision on the atomic scale, a probe which is sensitive to a particular surface phenomenon which decays as a function of distance normal to a surface, and a feedback mechanism which can couple the previous two elements. In the force microscope the translating mechanism is a piezoelectric ceramic, ad the probe is comprised of a sharp tip affixed to the free end of a cantilever. In its simplest operation as the sample is raster scanned under the tip which traces the contours of the surface causing the cantilever to be deflected. Thus the magnitude of the cantilever deflection is recorded as a function of sample position. Using feedback the piezo can be made to react to maintain the cantilever at a present deflection, and hence force. In this mode of operation the data collected is presented graphically as a topograph. Cantilever deflection is commonly determined by the displacement of a laser beam reflected off the free end of the cantilever (light-lever) technique.



Schematic of a light-lever force microscope

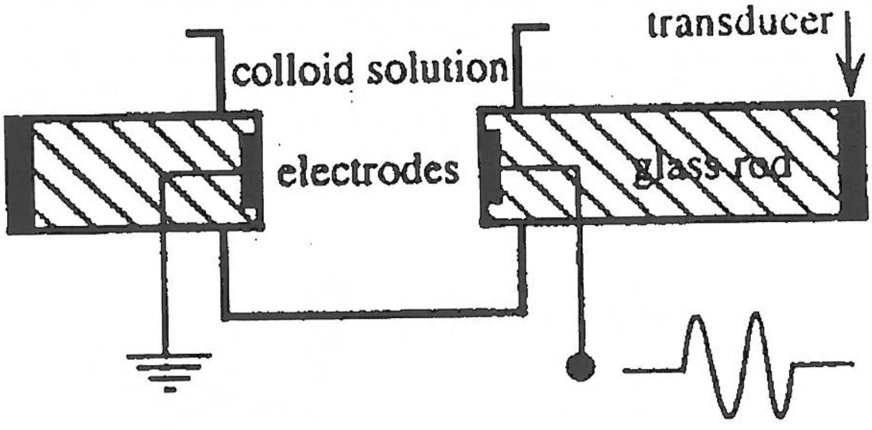
This scheme will operate in any non-viscous, optically transparent fluid. The tip may be replaced with other materials of different chemistry and geometry. Apart from providing information about surface topography and heterogeneity the scanning function can be disabled and the instrument be controlled such that only cantilever deflection versus normal displacement of the piezo is recorded. Curves of force versus relative surface separation can be obtained by normalising this deflection curve by the slope of the linear region found when the two surfaces are in 'contact' (compliance). Thus the interaction between two surfaces can be measured on colloidal length scales, {force O(pN - μN), distance O(Å-μm)}. Tip composition and geometry may be varied.



<u>Suggested reading:</u>
DiNardo, J., Nanoscale Characterisation of Surfaces and Interfaces, VCH, Weinheim, (1994).

ELECTROKINETIC SONIC AMPLITUDE EFFECT "ACOUSTOSIZER"

The application of an AC voltage across a colloidal dispersion causes the particles to vibrate at a velocity dependent upon their size, zeta potential and the applied frequency. At the high frequencies employed in the "AcoustoSizer", typically around MHz, the particles emit acoustic waves in response to the alternating voltage. By pulsing the voltage signal the acoustic response, or ESA of the particles can be recorded as a function of frequency. The ESA signal is a linear function of the applied voltage and hence a Fourier transform of the recorded acoustic response is required.



Schematic of the "AcoustoSizer" cell.

From the ESA spectrum the dynamic mobility is obtained from which the size and charge of the particles can be determined. The larger the difference between the densities of the fluid electrolyte and the colloid, or the larger the volume fraction the greater the ESA signal.

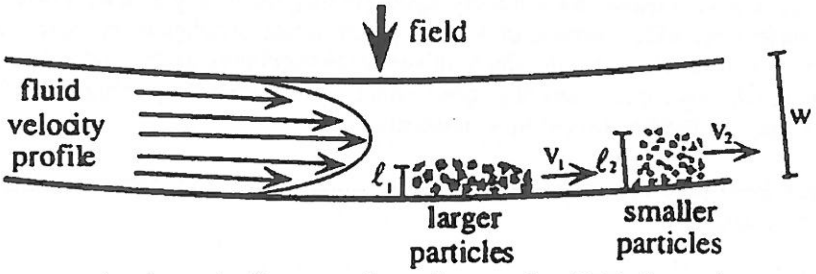
The dynamic mobility is a complex quantity equal in magnitude to the ratio of the particle velocity divided by the applied field. It is complex because there is a phase lag between driving frequency and the response of the particles to that field. As the applied field tends to zero the mobility becomes a real quantity, equal to the electrophoretic mobility defined for a static (DC) applied field. Field strengths are in the order of 100 Vm^{-1}, and at MHz frequencies typical particle displacements are in the order of 10^{-13} m. At low frequencies the inertia of the particle is not sufficient to cause a large enough phase lag to connect dynamic mobility with particle size, and only zeta potential is accessible. However, as the frequency increases the particle motion lags more and more behind the field and both size and zeta potential become available. At higher frequencies the ESA effect is too small to give a measurable signal. It is observed for many colloids systems that the equations governing the dynamic mobility simplify such that the size is determined solely by the argument and the zeta potential from the magnitude of this complex quantity. Unlike traditional electrokinetic measurements this technique is well suited to concentrated dispersions.

Suggested reading:

O'Brien, R.W., Cannon, D.W. and Rowlands, W.N., Electroacoustic determination of particle size and zeta potential, J. Colloid Interface Sci., 173, 406 (1995).

FIELD-FLOW FRACTIONATION

Field-flow fractionation is a set of high-resolution liquid chromatography-like elution methods used for sizing and separating various samples including humic substances, clays, bacteria, viruses and polymers. There are several FFF sub-techniques (eg. sedimentation, flow, thermal and SPLITT) which are specific for certain samples. The mechanism for separation involves only physical interactions. Particles are injected onto the channel without the field turned on (i.e. centrifugal, crossflow, thermal, gravitational). The particles are evenly distributed across the channel. Then a field is applied which compresses the solute zone into a narrow layer against one wall. When the liquid flow is initiated, the solute zone is carried downstream at a rate depending on the layer thickness, ℓ which can be related to the particle size.

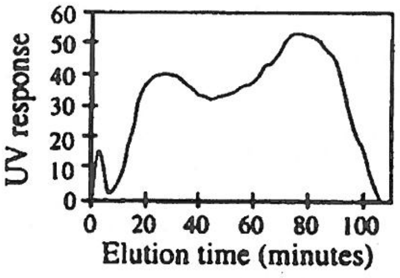


A schematic diagram of a sedimentation FFF channel.

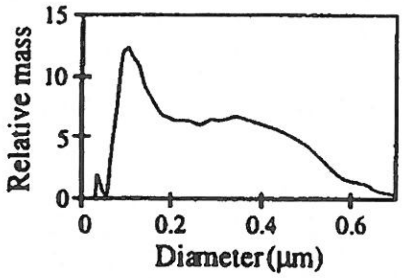
The data obtained is called a fractogram. The elution time can be converted to particle diameter using the equation;

$$d = \sqrt[3]{\frac{6kT}{\pi\omega^2 rw\Delta\rho\lambda}}$$

where, k is Boltzmann constants, T is the absolute temperature, w is the channel width, $\Delta\rho$ is the density difference between the particle and the carrier, ω is the field strength, λ is the retention parameter obtained directly from the measured retention time. Hence a particle size distribution can be calculated.



Typical Fractogram



Particle Size Distribution

Suggested reading:

Giddings, J.C., Field-flow fractionation: analysis of macromolecular, colloidal and particulate materials, Science, 260, 1456 (1993).

Summary provided by Jason van Berkel

FLOTATION

Flotation or froth flotation is a simple and inexpensive process used for the separation of particles (less than 500 microns) based on hydrophobicity differences of their surfaces. Only hydrophobic particles attach to gas bubbles (less than 2 mm) rising through the mineral pulp. At the top of the flotation cell, these gas bubbles break up allowing the floated particles to be recovered (Hallimond flotation tube). In froth flotation, the floated particles are trapped in the froth at the top of the flotation cell before being recovered; the froth constitutes an additional separation process.

To increase the mineral separation, a variety of reagents are added to the mineral pulp. Collectors are added to increase the surface hydrophobicity of valuable mineral particles and therefore increase their attachment to gas bubbles (only a few minerals are naturally hydrophobic, for example, talc, sulfur and molybdenite). Collectors are surfactants which consist of a head group which attaches to specific sites on the mineral surface and a hydrocarbon chain or tail which imparts hydrophobicity to the mineral surface. On the other hand, depressants such as inorganic ions or polymers are added to make the mineral surface more hydrophilic and, therefore, to depress the flotation of these minerals.

Flotation has also been used in the treatment of waste water, coal, clays, corn, proteins, dyes, fats, rubber, dyes, glass, plastics, etc.

Suggested reading
Matis, K.A. and Zouboulis, A.I, An Overview of the Process. Flotation Science and Engineering (Matis, K.A., Ed.), Marcel Dekker, New York, pp.1-43 (1995).
Fuerstenau, M.C., Miller, J.D. and Kuhn, M.C. in Chemistry of Flotation, AIME, New York (1985).

Summary provided by Daniel Fornasiero

LIGHT SCATTERING

Dynamic Light Scattering (DLS), also known as Photon Correlation Spectroscopy (PCS) uses the time dependence of the intensity of the scattered light to determine the translational diffusion coefficient of small particles. If a laser beam illuminates a suspension, and the scattered light is collected over a small solid angle, then the light will exhibit intensity fluctuations on the order of microseconds to milliseconds time scale. This is because the Brownian motion of the scatterers causes the phase of the light scattered from each particle to change with time, hence the total scattered intensity also fluctuates with time.

From the intensity fluctuations it is possible to determine the electric field auto-correlation function

$$\left|g^{(1)}(\tau)\right| = \exp(-\Gamma\tau)$$

Here $\Gamma = K^2 D_T$ is the decay constant, D_T is the diffusion coefficient and K is the magnitude of the scattering vector. For spheres, the Stokes-Einstein relationship applies and the diffusion coefficient can be related to the hydrodynamic radius by

$$D_T = \frac{k_B T}{6\pi\eta r}$$

Here k_B is the Boltzmann constant, T is the temperature, and η is the viscosity of the suspending liquid. This relationship is the basis for particle sizing by DLS.

Classical light scattering involves measurement of the total scattered intensity of light as a function of angle, concentration, or both. This is commonly summarised in a Zimm plot, which is described by the equation

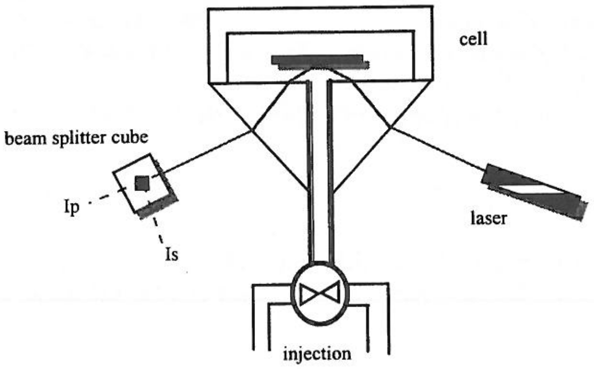
$$\frac{Hc}{R(\theta,c)} = \frac{1}{M_w}\left[1 + \frac{r_g{}^2 K^2}{3}\right] + 2A_2 c$$

Here c is the concentration, $R(\theta, c)$ is the excess Rayleigh ratio, K is the magnitude of the scattering vector, and H is an optical constant. Scattered light intensities are measured at several angles for each solution concentration and the pure solvent. It is then possible to determine the molecular weight, M_w, the radius of gyration, r_g, and the second virial coefficient, A_2, for the species under investigation.

Summary provided by Roland Keir

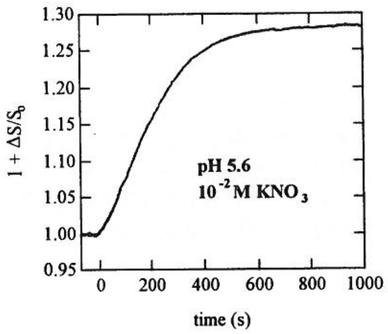
REFLECTOMETRY

This technique can be used to determine the kinetics of adsorption of polymers and nanoparticles at the solid-liquid interface. It is a simpler variant of ellipsometry and is readily combined with a stagnant point flow cell to measure adsorption under hydrodynamically well defined conditions.



Schematic of reflectometry in stagnant point flow

The surface of interest, usually a thin film (20-200nm thick) on a silicon wafer, is irradiated with a linearly polarised monochromatic and collimated beam (a He-Ne laser is often used). The refractive index difference between the film and wafer changes the polarisation of the incident beam. Passage of the reflected beam through a polarising beamsplitter cube allows detection of the intensity of the parallel and perpendicular polarised components. Adsorption of molecules or particles at the surface will change the refractive index immediately adjacent to the film and consequently, the ratio of the parallel/perpendicular components (S). It is the measured change in this ratio ($\Delta S/S_o$) with time that provides the desired kinetic information.



A typical reflectometer trace obtained for 90nm silica particles adsorbing on an aminosilane treated silicon wafer

Adsorption processes, involving polymers and particles, that occur on timescales of a minute or longer are readily monitored. To convert the raw optical data into adsorbed amount (calibration) an optical model, which treats the system as a series of flat, parallel layers of uniform refractive index is used. The method is not sensitive to the conformation of the adsorbed layers, unlike ellipsometry. However, its simplicity lends itself to kinetic studies in a range of liquids and particularly to sequential adsorption processes.

Suggested reading:

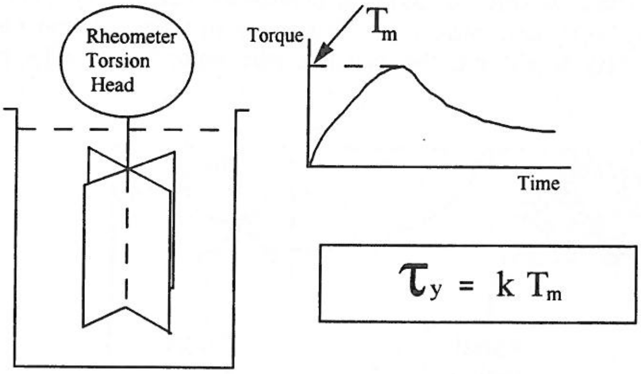
Dijt, J.C., Cohen Stuart, M.A., Hofman, J.E. and Fleer, G.J., Kinetics of polymer adsorption in stagnation point flow, *Colloids and Surfaces*, **51**, 141 (1990).

Summary provided by Rob Hayes

RHEOLOGY

Rheology is the study of material flow under application of deformation. In practice, rheology is concerned with the flow, transport and handling of complex fluids such as dispersions, emulsions, foams, polymer melts and polymer solutions. Many industrial processes, including minerals processing, waste disposal, food and pharmaceutical formulation and polymer processing are highly rheologically sensitive. Rheological properties are commonly measured using concentric cylinder rheometers, which may operate in either constant stress or constant rate modes. Constant stress devices induce a stress in the sample by way of a torque induction motor and precisely measure its deformation, often with an optical encoder. Constant rate devices shear the sample at predefined shear rates and measure the torque, hence stress, by way of a transducer. Both types of instruments can be used in static or dynamic modes to measure flow or viscoelasticity. The commercially available constant stress devices generally have the advantage of a wider range of measureable shear rates (10^{-6} to 10^{4} s^{-1}) and dynamic stresses or strains. Cone and plate is the prefered sample holding geometry, since homogeneous shear rates are experienced throughout the sample. However, suspensions are often analysed in cup and bob or plate and plate geometries for ease of handling and to avoid problems associated with particles in the gap between cone and plate.

In colloid and surface chemistry we are generally concerned with correlating rheological parameters with the colloidal micro-structure[1]. The yield value[2,3], which is defined as the maximum stress achievable in a sample prior to flow, is commonly used to quantify the structure in a colloidal network and can be thought of as the elastic limit of a system under shear. Yield stresses are obtainable from the application of a model to a flow curve, e.g. Bingham (extrapolated) or Casson. The agreement of these values with the true yield value τ_y is questionable and may be dependent on the range of shear rates analysed. The Vane technique is therefore the favoured method for yield value determination in highly concentrated dispersions.



$$\tau_y = k\ T_m$$

A bladed vane is slowly rotated at a constant shear rate (<< $1 s^{-1}$) in a beaker of the material of interest. The vane geometry is specifically utilised to minimise slippage, which can result in artefactually low stresses when smooth sample holding geometries are used. The torque on the vane is measured as a function of time, with the maximum torque assumed to correspond to the shear failure of the sample. The true yield stress can be calculated from the maximum torque and the dimensions of the vane[3].

Schematic of the Vane technique for yield value determination

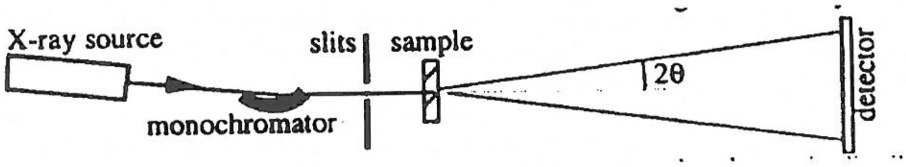
The viscoelastic characteristics of colloidal systems are also characterised by concentric cylinder rheometry, through measurement of the response to application of a sinusoidal stress or strain. G', the storage or elastic modulus and G", the loss or viscous modulus, are determined from the stress-strain inter-relationship and the phase angle (δ) between them: $G''/G' = \tan\delta$. For non-destructive oscillatory measurements a material should be deformed within its linear viscoelastic region, typically <0.1% strain for aggregated suspensions. A material's viscoelastic response to frequency is generally characterised and this can then be related to colloidal interactions within the system[1].

1. Tadros, Th.F., Adv. Coll. Interface. Sci. **68**, 97 (1997)
2. Cheng, D. C-H, Rheol. Acta. **25**, 542 (1986)
3. Nguyen, Q. D., and Boger, D.V., J. Rheol. **27**, 321 (1985)

Summary provided by Clive Prestidge

SMALL ANGLE X-RAY SCATTERING

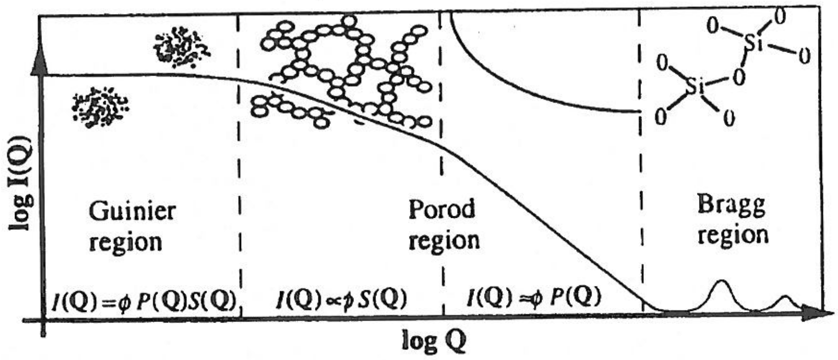
Small angle X-ray scattering allows the physical characteristics - dimensions, surface roughness and spatial arrangement - of particles (∅10 - 1000Å) in solution to be studied. In practice a collimated beam of monochromatic X-rays is passed through the sample and the intensity of scattering measured as a function of scattering angle 2θ (usually <2°).



The scattering of those X-rays arises from their interaction with the electronic distribution of the scattering material, the extent of scattering is dependent on the scattering length density, p_x, of the material given by;

$$\rho_x = \frac{n\rho N_A b_x}{MW}$$

where n is the number of electrons in the molecular unit of the scatterer, p is the physical density of the scatterer, N_A is the Avogadro's number, b_x is the scattering length per electron and MW is the molecular weight of the scatterer. The intensity of the scattering signal is proportional to the square of the contrast, (p_1-p_2), where p_1 and p_2 are the scattering length densities of the particles and the surrounding medium respectively. The intensity of small angle scattering, I(Q), is given by the general equation; $I(Q) = \phi P(Q)S(Q)$; ϕ is the number density of particles in solution and Q is momentum transfer, $Q = (4\pi/\lambda)\sin\theta$. The form factor P(Q) which contains the $(p_1\text{-}p_2)^2$, term, reflects the distribution of scattering material in the scattering particle and the structure factor. S(Q) is related to the spatial distribution of the scattering particles in the solvent.



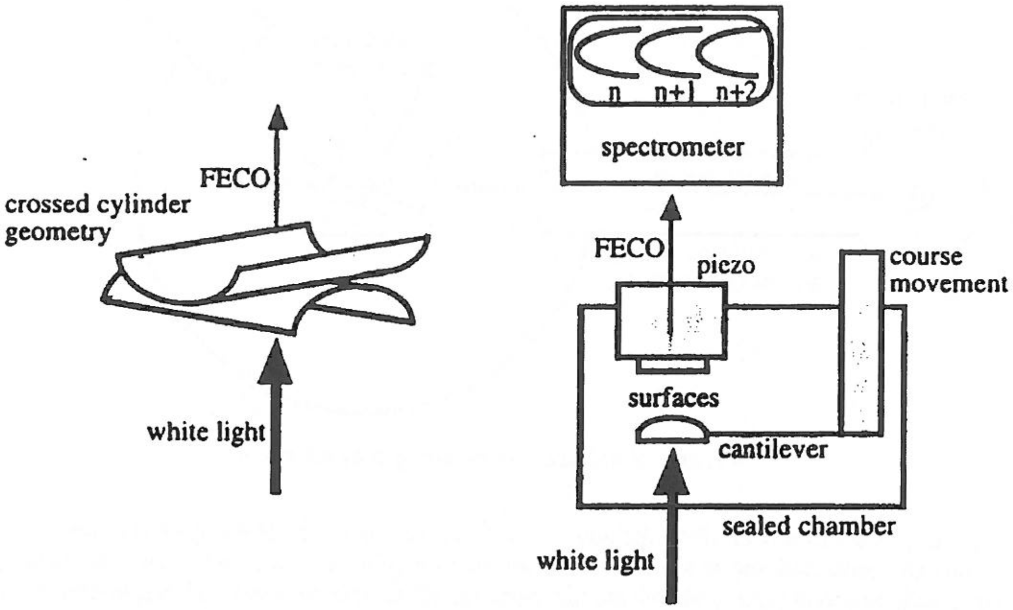
At a large scattering angle, information on the atomic scale is obtained with Bragg diffraction. On the low-Q side of the Bragg region information regarding the surface texture of the primary scattering particles is obtained. At slightly lower Q again information regarding the physical density of scattering material within the aggregate is accessible. In the lowest Q-region depicted here, the Guinier region, the overall dimension and shape of the aggregates can be determined.

<u>Suggested reading:</u>
Glatter, O. and Kratky, O. (eds), Small angle X-ray scattering, Academic Press, Sydney (1982).

Summary provided by Julieanne Dougherty

SURFACE FORCE APPARATUS

The Surface Force Apparatus has been the main-stay technique in the measurement of surface force for close to 30 years. Typically it is comprised of two partially silvered, thin (O(μm)) mica crystals, one surface supported on a piezoelectric ceramic for fine movement control, and the other on a cantilever. When white light is passed through the two opposing silvered mica surfaces the optical cavity formed transmits light of discrete wavelengths (FECO, Fringes of Equal Chromatic Order). These wavelengths are known for a given separation of the mica surfaces and refractive index of the intervening medium. By analysing the transmitted light in a spectrometer the surface separation may be determined directly (cf. force microscopy).



Schematic of SFA with detail of partially silvered mica surfaces (left).

In the absence of any interactions between the surfaces the separation between the two surfaces reduces at the same rate as the piezo is displaced. However, when a force acts between the two surfaces, the cantilever deflects and the separation changes by a sum of the piezo displacement and the spring deflection. As the surface separation is directly measured the deflection of the spring is taken as the difference between the measured separation and the separation expected when no force is present for a given piezo displacement. Hooke's law then gives the spring restoring force, which is equal and opposite to the measured surface force. {force O(0.1μN-mN), distance O (Å-μm)}.

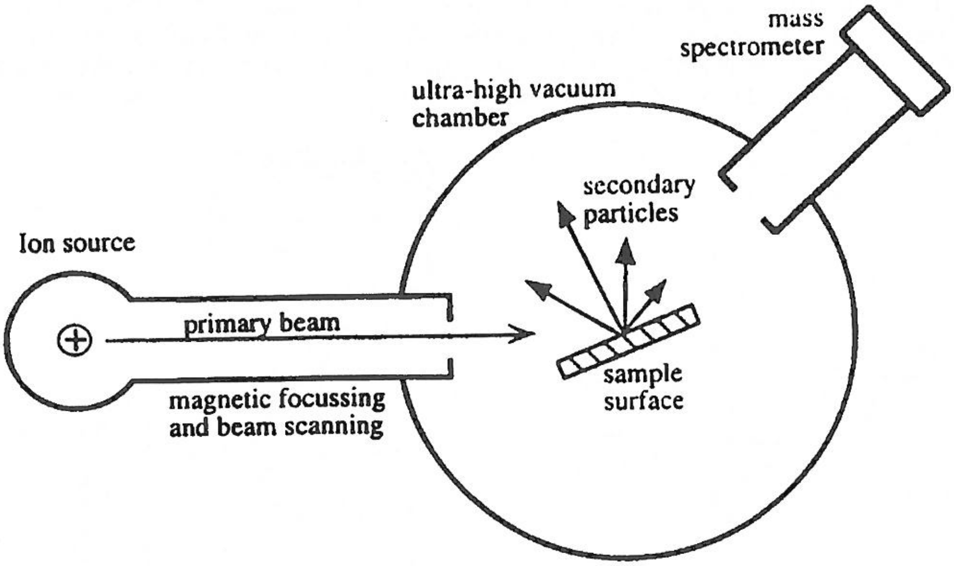
The crossed cylinder geometry approximates well as a sphere, with a radius equal to the geometric mean curvature of the two cylinders, interacting with a plane. Surfaces are restricted to those that can easily form transparent, thin smooth films, e.g. silica, sapphire, mica. Alternatively the interferometer may be formed between one reflective and one partially transmitting surface, e.g. mercury and mica.

Suggested reading:

Israelachvili, J.N., Intermolecular and Surface Forces, 2nd Edition, Academic Press, San Diego (1992).

SECONDARY ION MASS SPECTROSCOPY

SIMS is defined as the bombardment of a sample surface with a primary ion beam followed by mass spectrometry of the emitted secondary ions.



A (very) simplified schematic of a SIMS setup.

Primary beam species useful in SIMS include Cs^+, O^{2+}, O, Ar^+, and Ga^+ at energies between 1 and 30 keV. Primary ions are implanted and mix with sample atoms to depths of 1 to 10 nm. The bombarding primary ion beam produces monatomic and polyatomic particles of sample material and resputtered primary ions, along with electrons and photons. The secondary particles carry negative, positive, and neutral charges and they have kinetic energies that range from zero to several hundred eV. The SIMS primary ion beam can be focussed to less than 1 micron in diameter. Scanning where the primary ion beam strikes the sample surface provides for microanalysis, and the measurement of the lateral distribution of elements on a microscopic scale.

During SIMS analysis, the sample surface is slowly sputtered away. Continuous analysis while sputtering produces information as a function of depth, called a depth profile. Sputter rates in typical SIMS experiments vary between 0.5 and 5 nm/s. Sputter rates depend on primary beam intensity, sample material, and crystal orientation.

When the sputtering rate is extremely slow, the entire analysis can be performed while consuming less than a tenth of an atomic monolayer. This slow sputtering mode is called static SIMS in contrast to dynamic SIMS used for depth profiles.

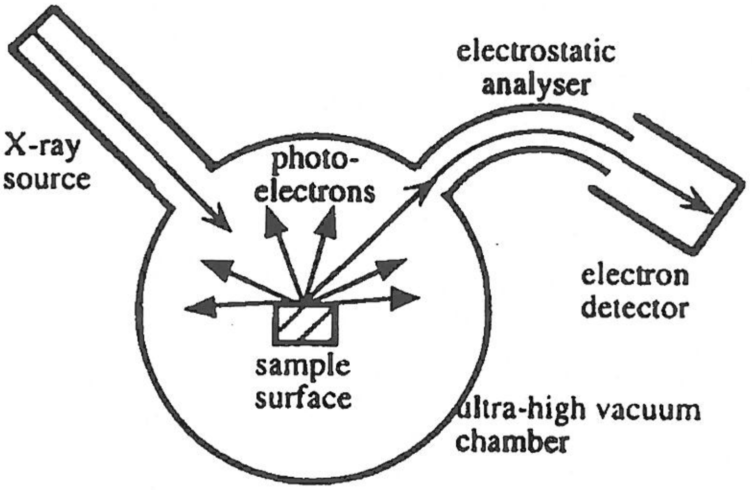
Mass spectroscopy not only provides isotopic discrimination, but both negative and positive species can also be analysed.

<u>Suggested reading:</u>

Benninghoven, A., Rüdenauer, F.G. and Werner, H.W., Secondary Ion Mass Spectrometry; Basic Concepts, Instrumental Aspects, Applications and Trends. Wiley, New York, (1987).

X-RAY PHOTOELECTRON SPECTROSCOPY

XPS, also called ESCA (Electron Spectroscopy for Chemical Analysis), exploits the photoelectric effect to obtain information about the chemical composition and structure of a surface. The technique uses soft X-rays to eject electrons from core levels within the atoms. The energies of these core levels (binding energies) are characteristic of a particular element and its chemical environment.



Schematic of XPS setup

The kinetic energy of the emitted photoelectron, KE, is determined during the experiment, hυ is the energy of the incident photon, hence the binding energy, BE, for the emitted photoelectron can be calculated.

$$KE = h\nu - BE$$

The energy of the photoelectrons emitted from an atom is also determined to some extent by the charge residing on the atom as a result of chemical bonding. Thus, a relationship between electronegativity and binding energy has been shown for many elemental systems, and a theoretical understanding of "chemical shifts" has become well-developed. From a practical point of view, it is usually possible to distinguish elemental oxidation states and sometimes other structural effects.

The kinetic energies of the photoelectrons leaving the sample are so low that, in practice, only those from the top 1-5 nm of the surface escape and arrive at the spectrometer, making it an extremely surface sensitive technique. Most elements (except hydrogen and helium) have practical detection limits of 0.02-0.2% a/a. This corresponds to 1-10% of a monolayer. Energy spectra are reported as binding energy against intensity. With the use of sensitivity factors, peak intensities can provide quantitative elemental surface compositions.

Suggested reading:

Brundle, C.R. and Baker, A.D. (Ed.), Electron Spectroscopy: Theory, Techniques, and Applications, Vols. 1 and 2, Academic Press, London (1977).

PRESENTER INDEX

Proudly hosted by

The UNIVERSITY
of NEWCASTLE
AUSTRALIA