

25th Australian Colloid & Surface Science Student Conference



**Program
and
Abstracts**

**Beechworth,
Victoria, Australia
6-10 February, 2006**

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"What is the purity of the CaCl_2 "?
"is Gibbsite everywhere"?

Welcome

Welcome to the 25th Australian Colloid and Surface Science Student Conference.

The Australian Colloid and Surface Science Student Conferences have, since 1967, provided postgraduate students of colloid and surface science with the opportunity to present and discuss their research in an informal, supportive and friendly atmosphere. The conferences have grown from rather humble beginnings when Bob Hunter and Tom Healy, the founding fathers of Australian colloid science, would meet informally with their research groups to discuss and debate (rather animatedly folklore has it!) their research findings. Today, postgraduate students, academics and research staff from Universities, nationally funded research organisations such as CSIRO and ANSTO as well as industry across Australia and increasingly the UK and Europe attend the Australian student conference series. Despite the increase in the number of conference participants, in excess of 130 for this current conference, the spirit of these early conferences remains today.

The Particulate Fluids Processing Centre at the University of Melbourne and La Trobe University, Bendigo have the honour of co-hosting the 25th Australian Colloid and Surface Science Student Conference (25ACSSSC).

We thank you for your participation in this conference. We are also grateful for the level of interest and support shown for this conference by our range of sponsors.

We hope you enjoy your time here at La Trobe at Beechworth and that you take away with you many fond memories.

Kate Drummond
Devi Sunartio

Michael Angove
Tabitha Cesnak

Muthupandian Ashokkumar
Francoise Gelb

Previous Conferences

Year	Location	Total No Attendees
1967	Melbourne	unknown
1968	Sydney	unknown
1970	Melbourne	14
1972	Sydney	unknown
1973	Melbourne/Blackwood	30
1974	Sydney/Woy Woy	39
1976	Canberra	33
1977	Melbourne/Blackwood	34
1978	Yarrawood	unknown
1980	Kioloa	50
1982	Mt. Eliza	75
1983	Yarrawood	51
1985	Roseworthy	49
1987	Kioloa	55
1988	Albury	107
1990	Camden	unknown
1991	Roseworthy	118
1993	Deakin Uni	144
1995	Fairy Meadow	185
1996	Murramarang	118
1998	Hahndorf	141
1999	Morpeth	143
2001	Bendigo	110
2002	Lake Hume	114
2004	Sunset Cove	116
2006	Beechworth	135

Conference Participants

AUSTRALIAN NATIONAL UNIVERSITY

Christine Henry
Shaun Howard

BRAGG INSTITUTE, ANSTO

Jamie Schulz

CSIRO MOLECULAR & HEALTH TECHNOLOGIES

Calum Drummond
Cara Doherty
Nelly Gong
Tamara Greaves
Peter Harbour
Patrick Hartley
Ferry Lie
Thomas Kaasgaard
Florian Rovere
Asoka Weerawardena

CURTIN UNIVERSITY OF TECHNOLOGY

Shandelle Bosenberg

DAIRY INGREDIENTS GROUP OF AUSTRALIA

Bogdan Zisu

LA TROBE UNIVERSITY

Mike Angove
Bruce Johnson
Eben Quill
David Piper
Tristan van Emmerik
John Wells

MONASH UNIVERSITY

Ben Boyd
Jayani Chandrapala
Charlie Dong
Alex Harris
Mandeep Jeswan Singh
Ian Larson
Ian McKinnon
Bridget Murphy
Sofia Øiseth

MSACT, UK

Richard Buscall

SWINBURNE UNIVERSITY OF TECHNOLOGY

Russell Crawford
Ian Harding
Jacqui McRae

SWISS FEDERAL INSTITUTE OF TECHNOLOGY

ZURICH, SWITZERLAND

Monika Limacher

UNIVERSITY OF BRISTOL, UK

Michael O'Sullivan

UNIVERSITY OF COLOGNE, GERMANY

Regina Schwering

UNIVERSITY OF DELAWARE, USA

Stanley Sandler

UNIVERSITY OF LEEDS, UK

David Harbottle

UNIVERSITY OF MELBOURNE

Muthupandian Ashokkumar

Joannelle Bacus
Sasha Boskovic
Derek Chan

Thanh Tam Chau

Lucy Clasohm

Sam Cook

Christina Cortez

Ray Dagastine

Will Ducker

Daniel Fisher

Jonathan Foong

George Franks

Yuanhua He

Tom Healy

Chris Honig

Fuzhi Huang

Rógerio Manica

Anat Kiviti-Manor

Judy Lee

Greg Martin

Clayton McKee

Scott McLean

William McMaster

Wade Mosse

Anna Mularski

Shashi Parcha

Sean Peters

Andrew Rapson

Gwynneth Rice

John Sader

Hemadri Saha

Colin Scholes

Anthony Stickland

Lindsay Studer

Devi Sunartio

Thu-Hang Ta

Elvira Tjipto

Shane Usher

David Verrelli

Rachael Wall

Xingdong Wang

Richard Watson

Grant Webber

Heng Pho Yap

Meifang Zhou

Jasmina Zukan

UNIVERSITY OF NEWCASTLE

Paul Fitzgerald

Yang Gan
Marc Hampton
Tim Hunter
Emelyn Smith
Ben Tremain
Erica Wanless
Ying Zhou

UNIVERSITY OF OTAGO, NZ

Aidan Young

UNIVERSITY OF SHEFFIELD, UK

Damian Dupin

UNIVERSITY OF SOUTH AUSTRALIA

Jonas Addai-Mensah
Maria Ayucar Rubio
Heramb Bal
Jarred Clasohm
John Denman
Anil Gautam
Carlos Gontijo
Gary Hanly
Shuhua He
Roger Horn
Ivan Kempson
Chris Macdonald-Bradley
Angus McFarlane
Melanie McGuire

Peter Majewski
Tatu Miettinen
Gayle Morris
Dennis Palms
Sun-Young Park
Luke Parkinson
Anuttam Patra
Clive Prestidge
John Ralston
Evgueni Resnianski
Santanu Ray
Rossen Sedev
Illiana Sedeva
Mariyka Semchyshyn
Jingfang Zhou

UNIVERSITY OF SOUTHERN DENMARK

Esben Thormann

UNIVERSITY OF SYDNEY

Rob Atkin
Annabelle Blom
Sophie Bobillier
Bob Hunter
Jeannette McAlpine
Jain Nirmesh
Kathryn Topp
Greg Warr
Hui Zhang

Sponsors

The 25th Australian Colloid and Surface Student Conference is generously supported by the following sponsors. The Conference Organising Committee sincerely thanks our sponsors.

We would like to acknowledge The Royal Australian Chemical Institute for financial aid.



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Australian Mineral Science Research Institute

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A joint venture of CSIRO &
the Victorian Government



**Dairy
Ingredients
Group of
Australia**

Program

	6/2/06	7/2/06	8/2/06	9/2/06	10/2/06
07:00		Breakfast	Breakfast	Breakfast	Breakfast
Chair		Gayle Morris	Calum Drummond	John Sader	
9:00		Lindsay Studer	Damien Dupin	Sun-Young Park	GO HOME!
9:20		Tristan Van Emmerik	David Harbottle	Heng Pho Yap	
9:40		Jingfang Zhou	Angus McFarlane	Emelyn Smith	
10:00		Scott McLean	Jacqui McRae	Elvira Tjipto	
10:20	Registration	Morning Tea	Morning Tea	Morning Tea	
Chair		Ian Larson	Erica Wanless	Greg Warr	
11:00		Sasha Boskovic	Gwynneth Rice	Richard Watson	
11:20		John Denman	Anuttam Patra	Heramb Bal	
11:40		Gary Hanly	Regina Schwering	Jarred Clasohm	
12:00		Rogério Manica	Christina Cortez	Jonathan Foong	
12:30	Lunch	Lunch	Lunch	Lunch	
Chair		Russel Crawford		Patrick Hartley	
2:00	Registration - cont	Shashikanth Parcha		Melanie McGuire	
2:20		Evgueni Resnianski		Tatu Miettinen	
2:40	Plenary Speaker	Colin Scholes		Alexander Harris	
3:00		Devi Sunartio		Kathryn Topp	
3:20		Afternoon Tea	Staff-Student Cricket Game	Afternoon Tea	
Chair	Mike Angove	Muthupandian Ashokkumar			
3:40	Clayton McKee				
4:00	Carlos Gontijo	David Verrelli			
4:20	Shuhua He	Ying Zhou			
4:40	Michael O'Sullivan	Joannelle Bacus			
5:00		Tam Chau			
5:20	Free Time	Free Time	Free Time	Free Time	
6:00	Happy Hour	Happy Hour	Happy Hour	Happy Hour	
7:00	BBQ	Dinner	Dinner	Conference Dinner	
		Quiz Night	Talent Night		

Tuesday 7/2/06

11:00-12:20pm
Chair: Ian Larson

ORAL # 3

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Gary Hanly, Rossen Sedev, Daniel Fornasiero and John Ralston
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Tuesday 7/2/06

12:30-2:00pm

LUNCH

2:00-3:20pm

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Tuesday 7/2/06

3:20-4:00pm

AFTERNOON TEA

4:00-5:20pm

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6:00-7:00pm

HAPPY HOUR

7:00pm-late

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Thursday 9/2/06

4:00-6:00pm

WINE TASTING

7:00pm-late

CONFERENCE DINNER

Friday 10/2/06

7:00-9:00am

BREAKFAST

10:00am

**BUS DEPARTS
LEAVE FOR HOME**

Conference Awards

Healy-Hunter Award



Established in 1998, this award honours the founders of the conference: Bob Hunter (University of Sydney) and Tom Healy (The University of Melbourne). The most outstanding oral presentation will be awarded the Healy-Hunter Award. The award consists of a medal and a travel grant (\$1500). The award is voted by staff attending the conference.

Best Poster Prize

Awarded to the student with the most outstanding poster presented at the conference. The award is a prize of \$300 cash and is voted by the staff attending the conference.

Most Probing Question Award

Students are encouraged to ask questions of each presenter and the most probing query is awarded this specially designed trophy. Just occasionally a supervisor asks a more probing question... The winner is decided by a carefully chosen panel of judges.

Most Memorable Moment Award

This non-scientific award is another specially designed trophy made for the most outstandingly memorable contribution to the conference in any arena! To be eligible, the event is nominated and a winner decided by a carefully chosen panel of judges. In addition to the award the prize includes – embarrassment and notoriety!

Abstract Plenary Lecture

Chemical Weapons: Their Construction and Destruction

Stanley Sandler*

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716, USA

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A chemical weapon consists of the agent (nerve agents such as sarin and VX, or a blister agent such as mustard sulfur) and explosive charges for agent dispersal. During the two World Wars and thereafter, Germany, the Soviet Union, the United States and other countries developed large stockpiles of chemical weapons. Germany has since destroyed all of its weapons and the US some of its weapons by incineration. However, because of strong public resistance to incineration, other technologies will have to be used for the remaining stockpiles. The speaker has been involved in evaluating possible alternatives to incineration for the US Army and the US Congress. These technologies include chemical neutralisation, supercritical water oxidation, biological oxidation, plasma arcs, electrochemical oxidation, and other methods. This talk will start with a description of what chemical weapons are, where they are located in the US and Russia, the engineering, political and social issues involved in their destruction, and a unique method of public involvement in the decision-making process.

* Stanley I. Sandler is the H. B. du Pont Chair of Chemical Engineering at the University of Delaware, and a frequent visitor to the Department of Chemical and Biomolecular Engineering at the University of Melbourne. He is editor of the AIChE Journal, the author of about 350 papers, and several books including the widely used "Chemical and Engineering Thermodynamics" published by Wiley. The 4th edition of this book entitled "Chemical, Biochemical and Engineering Thermodynamics" has just been published. He is a member of the U.S. National Academy of Engineering, and has received numerous awards from the American Institute of Chemical Engineers, the American Chemical Society, the American Society for Engineering Education, and other groups. He has been a visiting professor at universities in England, Australia, Argentina and the US.

Abstracts

Oral Presentations

The Refractive Index of Thin Aqueous Films between Hydrophobic Surfaces Studied using Evanescent Wave Atomic Force Microscopy

Clayton McKee^{1,2} and William Ducker²

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We have studied the refractive index of a thin aqueous film between microscopic hydrophobic surfaces using Evanescent Wave Atomic Force Microscopy (EW-AFM). An evanescent wave, generated at a solid-liquid interface, is scattered by AFM tips or glass particles attached to AFM cantilevers. The scattering of this wave is used to determine the refractive index as a function of separation between these surfaces. Measurements were performed on surfaces that were rendered hydrophobic with octadecyltrichlorosilane, which produces solid-water contact angles in excess of 90°. For AFM tips, the average refractive index in the thin film was always equal to that of water when the film was thicker than about 100 nm. At smaller separations, the refractive index was always greater than or equal to water. This is inconsistent with the formation of air or vapour films, and consistent with a small amount of organic material between the surfaces. For colloidal spheres ($R \sim 10 \mu\text{m}$), we were not able to detect changes in the refractive index of the thin film between the sphere and plate.

H-H Award
Score

Coarse Particle Flotation

Carlos Gontijo, John Ralston and Daniel Fornasiero
Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia

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Coarse particles are often not recovered during the flotation process. Inertial forces play a dominant role for coarse particle flotation. The flotation behaviour of coarse quartz particles was studied under well-defined conditions. A bubble pick-up experiment confirmed the theory on the upper particle size of floatability of Schulze. To fit the experimental data the bubble capillary pressure force had to be neglected, indicating that it does not affect the bubble-particle aggregate stability. Flotation under quiescent and turbulent conditions was performed in a Hallimond tube and in a Rushton turbine cell, respectively, to explore the flotation limits. Particle contact angle threshold values, below which the particles could not be floated, were identified for the particle size range 50-1000 μm , under different hydrodynamic conditions. Bubble-particle interactions in a flotation cell occur in a dynamic situation. The bubble-particle relative velocities have to be considered. Gravitational and interfacial forces limit the flotation of coarse particles. Equations to calculate the particle centrifugal acceleration were developed. The hydrodynamic force acting on a particle sliding on the bubble surface was incorporated in the calculation of the bubble-particle aggregate stability. The maximum centrifugal acceleration occurs at the bubble equator and limits the maximum floatable particle size, by affecting the bubble-particle aggregate stability. The bubble size plays an important role in determining the critical contact angle. At potential flow, the bigger the bubble, the smaller is the particle centrifugal acceleration and the critical contact angle, leading to higher recoveries and rate constants. At Stokes flow, which is the condition for small bubbles ($d_b = 0.2 \text{ mm}$) the maximum floatable particle size is larger, due to the smaller centrifugal acceleration, which leads to smaller critical contact angles. Detachment ultimately controls the maximum floatable particle size, defining a gravitational limit for flotation, but the critical contact angle also determines another limit for flotation, controlled by interfacial forces. At low and intermediate contact angles, particles larger than the critical particle size cannot attach to the bubble, although the presumably formed aggregate would be stable up to the gravitational limit. Flotation recovery and rate constant depends mainly on the particle contact angle, size, and bubble size. This information shall be incorporated into the flotation models.

H-H Award
Score

Characterisation of Thioglycolic Acid Behaviour in the Flotation Separation of Chalcopyrite from Pyrite

Shuhua He, Daniel Fornasiero and William Skinner
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It was found that thioglycolic acid (TGA) added during grinding could increase the separation of chalcopyrite from pyrite at pH 9.0 by selectively depressing the flotation of pyrite. However, when TGA was added in the conditioning stage pyrite depression was only observed in the presence of citric acid (CA). Surface analysis by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy (ToF SIMS) and infrared spectroscopy has indicated that TGA is not present on the pyrite surface and therefore is not directly responsible for pyrite depression. XPS and ToF SIMS also indicate that much less copper and xanthate species are found on the pyrite surface after the addition of TGA and CA. Furthermore, other experiments have shown that both TGA and CA act as complexants by reacting with copper and iron hydroxide precipitates to form soluble complexes at pH 9.0. On addition of xanthate, a yellow precipitate of Cu(I)-xanthate was only formed with the soluble copper-CA complex but not with the soluble copper-TGA complex, indicating that the latter complex is more stable than the former. It is concluded that both CA and TGA may decrease the amount of copper species on pyrite (mainly copper hydroxide in alkaline pH condition) and therefore reduce xanthate adsorption. CA may only be necessary to stop TGA being consumed by the surface ferric hydroxide. During grinding the amount of surface ferric hydroxide is less than during conditioning, and TGA alone is then able to complex and remove copper hydroxide or prevent its adsorption on pyrite.

H-H Award
Score

PDMS Core/Silica Shell Particles

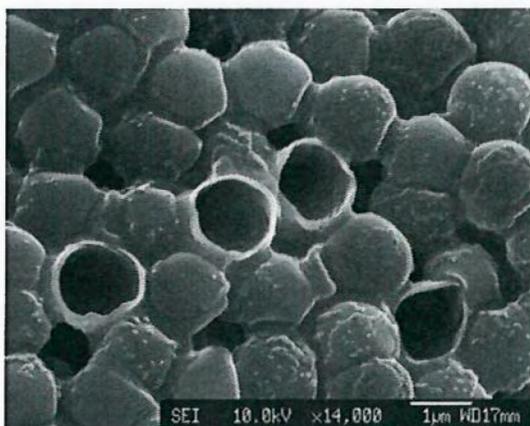
Michael O'Sullivan,¹ Jonathan Phipps² and Brian Vincent¹
¹School of Chemistry, University of Bristol, United Kingdom
²Schlumberger Cambridge Research, Cambridge, United Kingdom

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The encapsulation of one material by another, to form core-shell particles, has many applications: principally the containment, protection, and distribution of an active material. A focus of this project is the development of core-shell systems with shells of tuneable thickness.

Polydimethylsiloxane (PDMS) droplets coated with silica are being developed as a model core-shell system. PDMS is used because it may be simply produced as monodispersed droplets, in low concentrations, from the base catalysed hydrolysis and condensation of dimethyldiethoxysilane (DMDES) in water. Incorporation of a cross-linking material methyltriethoxysilane (MTES) during PDMS synthesis allows the production of a microgel if a more rigid core material is required. Organic materials may then be absorbed into the PDMS phase. Silica shells are subsequently formed from the condensation of tetraethoxysilane (TEOS) and residual DMDES; again in a basic aqueous environment. Manipulation of the shell-growth conditions allows for a degree of control over shell thickness.

These particles are intended for quantitative studies involving mechanical disruption of the shell material and may find practical use in pressure release systems.



H-H Award
Score

New Approaches to the Optimisation of Wastewater Dewatering and Processing

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The dewatering of wastewater treatment plant (WWTP) sludge is a critical step in the treatment process, as it significantly reduces sludge volumes to be disposed of (i.e. sent to landfill or incineration). Up to 50% of WWTP operating costs are associated with dewatering.

While increasingly stringent legislation continues to raise discharge standards, (resulting in increased quantities of sludge), disposal options are becoming increasingly limited. As a result, industry is keen to optimise dewatering operations to limit sludge volumes. However, there are currently no mathematical tools available to industry for describing or optimising sludge behaviour in dewatering equipment.

Previous research at the University of Melbourne has seen the development of mathematical models able to predict the behaviour of solid-liquid suspensions in common dewatering equipment. However, these models require a mathematical description of dewaterability.

The dewaterability of solid-liquid suspensions can be characterised with the theory developed by Buscall and White.¹ This theory describes dewaterability using two experimentally determined parameters: the *Hindered Settling Function*, $R(\phi)$, indicative of the rate of dewatering, and the *Compressive Yield Stress*, $P_c(\phi)$, a measure of the compressibility of the suspension. Both parameters are functions of the solids volume fraction, ϕ .

The dewatering parameters are determined via pressure filtration (high ϕ region) and batch settling (low ϕ region) tests and are routinely conducted for mineral suspensions. Early work on biological sludges (*biosludges*) has shown that accurate data in the intermediate ϕ region (between batch settling and pressure filtration data) is critically important to accurately characterise the dewaterability of *biosludges*. As the previous testing regime did not collect data in this region, a new test has been implemented – the Centrifugal Batch Settling Test. The addition of this test to the standard methods for dewaterability characterisation has resulted in a modified *Biosludge Characterisation Protocol* specific to *biosludges*.

In future work, the *Protocol* will be used to characterise different WWTP sludge types and the effect of additives upon dewaterability. Once completely characterised, the behaviour of these sludges in dewatering equipment can be predicted. This will give the wastewater industry a powerful new and unique tool to optimise dewatering operations.

1. R Buscall and L R White, Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases 83(3): 873-91 (1987).

H-H Award
Score

Sorption of Phosphate to Clay Minerals

Tristan Van Emmerik¹, Dan Sandström², Oleg Antzutkin², Bruce Johnson¹, Michael Angove¹ and John Wells¹

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Phosphorus is an essential nutrient for plant growth and development. Soil is a major source of phosphorus for plants, with additional phosphorus, in the form of fertilisers, often added to soils in large quantities. Whilst phosphorus is essential for plant growth, run-off into water bodies (rivers, lakes, etc.) can cause very significant damage in the form of eutrophication and algal blooms. Sorption of phosphate by clay minerals and (hydr)oxides is of interest not only because it plays a critical role in the availability of phosphorus for plant and animal uptake but also in the potential for phosphorus to leach into waterways.

Previous work on the sorption of phosphate to both whole soils and sediments¹, and to clay minerals and (hydr)oxides² have mainly focused on using macroscopic and spectroscopic (e.g. FTIR) techniques to study sorption mechanisms. In this work novel solid-state NMR techniques have been used to investigate the nature of the sorbed phosphate species on the common soil minerals montmorillonite and gibbsite.

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H-H Award
Score

Preparation and Colloidal Stability of Photoresponsive Thymine Functionalised Gold Nanoparticles

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Photochromatic thymine molecules have been used to coat small gold nanoparticles with diameters of around 2 nm and 7 nm, by using *in situ* and ligand replacement two phase transfer methods. The structure and morphology of these gold particles have been characterised by UV-Vis, FTIR and TEM. Thymine derivatives with long hydrocarbon chains have been grafted onto gold particle surfaces through the thiol group, leaving the thymine units outside under selected preparation conditions. The particles can form transparent and stable dispersions in highly polar organic solvents such as DMF and DMSO, as well as in aqueous solution with high pH values, due to the deprotonation of hydrogen attached to the thymine at position N2. The gold surface plasmon band for particles of 2 nm becomes broad and blue shifts compared with that obtained with the 7 nm particles. The colloidal stability of nano-gold suspensions in aqueous solution have been studied as a function of pH and salt concentration, using zeta potential determination as one guide to stability. pH controlled particle dispersibility can be achieved. Zeta potential has been determined using the phase analysis light scattering (PALS) technique. The values of zeta potential are very small, which means the electrostatic force is very weak. NaCl, KCl and CsCl show different effects on nano-gold stability. The results indicate that not only steric forces, caused by the long hydrocarbon chains tethered on nanoparticle surfaces, but also hydration forces play an important role on colloidal stability of these composite gold nanoparticles.

H-H Award
Score



Surface Interactions Between Silica-Adsorbed Poly(2-vinylpyridine)-Poly(ethylene oxide): The Effects of Di-Block Micellisation

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The adsorption of poly(2-vinylpyridine)-poly(ethylene oxide) (P2VP-PEO) at the silica-solution interface as a function of pH has been investigated using the Atomic Force Microscope (AFM) and ultra-violet/visible Attenuated Total Reflection (ATR) spectroscopy. When P2VP-PEO is initially adsorbed above the pK_a of the P2VP block, P2VP-PEO adsorbs from solution as micelles that exist as either partially collapsed- or as hemi-micelles at the silica surface, with an equilibrium adsorbed amount attained after approximately 20 hours. Below the pK_a of P2VP the P2VP-PEO adsorbs as individual polymer molecules, forming a compact layer with little extension into solution. When P2VP-PEO initially adsorb as unimers, any driving force to self-assembly of the now charge-neutral polymer (i.e. above the pK_a of P2VP) is kinetically hindered. This occurs because the molecules already adsorbed strongly hinder any surface reorientation of the molecules, such that the layer maybe undergoes a slow surface restructuring towards self-assembly and equilibrium. As the pH is increased further, the adsorbed amount reaches equilibrium, and the adsorbed P2VP-PEO molecules continue to "unravel" from the surface, extending away from it, towards eventual complete surface self-assembly.

H-H Award
Score

Characterisation of a Hierarchically Porous Silica-Organic Functional Hybrid

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Since their discovery in 1992, the M41S family of mesoporous molecular sieves has sparked enormous interest in materials templated by surfactant micellar systems and in mesoporous materials in general (mesopores: 2 – 50 nm pores). The interest has been driven by the potential of these materials in applications such as catalysis and biomolecule separation and immobilisation. More recently, a desire for larger pore materials has resulted in the growing use of amphiphilic block copolymers over surfactants as templates for mesoporous molecular sieves. Mesoporous silica materials templated from amphiphilic block copolymers containing poly(ethylene oxide), either by true liquid crystal templating or those templated via cooperative processes, however, have been shown recently to be hierarchically templated. The supramolecular template contributes to the mesopores, which can be characterised using standard techniques, while the hydrated poly(ethylene oxide) in the amphiphilic block copolymer gives rise to much smaller micropores (micropores: less than 2 nm pores) located within the pore walls, the size of which has been relatively difficult to characterise. For the application of these materials for biomolecule separation and immobilisation, the formation of organic functional hybrid materials constitutes a key step; however, the functionalisation also provides an added level of complexity to these materials that already possess a hierarchically porous structure.

In this study we provide a detailed characterisation of such a silica material that has been templated from an amphiphilic block copolymer (containing poly(ethylene oxide))/mesitylene microemulsion and functionalised via a reaction with (3-aminopropyl)triethoxysilane (APTES) to impart amino functionality. The chemical nature of the attached silane was determined using ²⁹Si magic angle spinning nuclear magnetic resonance (MAS NMR) and thermogravimetric analysis (TGA). ²⁹Si MAS NMR showed multiple overlapping peaks associated with various chemical environments of the attached silane, while TGA revealed a significant amount of adsorbed water, consistent with a polymerised layer being deposited on the surface of the pores. The porous environment was characterised via nitrogen sorption and positron annihilation lifetime spectroscopy (PALS). Nitrogen sorption comparison plots with a non-microporous amorphous silica reference material revealed that the non-functionalised silica had significant microporosity. For the APTES functionalised silica, the BET surface area was seen to have reduced from 570 to 288 m²/g, while the pore size only reduced from 41 to 38 nm. Analysis via comparison plots with similarly functionalised non-microporous amorphous silica and characterisation via PALS, indicated that the micropores were blocked and the microporosity present was now a closed microporosity associated with the APTES polymer layer formed within the mesopores. The use of these combined techniques is a powerful approach for characterisation of the porosity and chemistry of hierarchically porous silica-organic functional hybrid materials.

H-H Award
Score

Surface Analytical Investigations of Forensic Trace Evidence

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Forensic science is a broad field that combines many different sciences including criminalistics, in which trace evidence analysis is an important aspect. Trace evidence is defined as "physical evidence that results from the transfer of small quantities of material" and often includes small samples of paint, glass, hair and fibres. This study aimed to investigate a number of types of trace evidence using surface sensitive techniques as a way to better characterise the materials and discriminate between samples.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is an analytical technique suited to forensic analyses due to its high spatial resolution, part-per-million detection range and non-destructive mode of operation. This makes it a good candidate for forensic glass analysis, where the current method of refractive index (RI) analysis may not be sufficiently discriminating enough, due to the narrow range of RI values produced by manufacturers. Homogeneity within a piece of float glass was examined, as well as investigations into the surface properties of the glass. Distinct surfaces are produced during manufacture due to different processes influencing the chemistry of the "float" and "non-float" surfaces. Of particular interest is the penetration of tin into the underside, or "float" surface, and the mechanism by which this occurs. This study also involved nanoSIMS analysis in an attempt to gain an understanding of the tin profile present.

The compositional analysis of ink and pencil evidence relating to "questioned documents" is also of interest to the forensic scientist. Ink examinations may involve determining whether two or more entries were written with the same pen or if entries have been altered, as well as dating of the ink entry. While previous work had utilised ToF-SIMS to characterise the organic components of ballpoint pen inks, current work looks at the inorganic metal ions as a basis of characterisation and discrimination. Similarly, ToF-SIMS was used to distinguish between grades and manufacturers of pencils on the basis of the varying ratios of graphite, clays and waxes present.

H-H Award
Score

Wettability of Silanated Titanium Dioxide Surfaces

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When metal oxide surfaces react with water, ionisable hydroxide groups form on the surface. These ionisable groups are the primary origin of the surface charge. The influence of surface charge on the properties of metal oxide surfaces, particularly the contact angle and equilibrium liquid film thickness were investigated.

The surface of titanium dioxide was investigated with different surface coverages of an organosilane, namely octadecyltrihydrosilane. Surface charge was controlled by changing both the pH and the ionic strength of the background electrolyte. At a complete surface coverage of octadecyltrihydrosilane there is no effect of a changing pH on the contact angle. However with a decrease to partially covered surfaces, an effect was found. The maximum contact angle occurs at approximately pH 4.8, which corresponds to the point of zero charge of titanium dioxide. It was found that as the pH of the solution is changed, either above or below the point of zero charge, the contact angle decreases. This decrease can be related to the change in number of remaining ionisable hydroxide groups on the surface. At low surface coverage and high ionic strength, the difference in contact angle from pH_{pzc} to 5 units above can be as much as 20°.

The effect of surface charge on the thickness of an aqueous thin film was also investigated with a Derjaguin-Schuledko thin film balance. A transparent glass slide coated with titanium dioxide was studied at various pH and salt concentrations. The equilibrium thickness of the thin liquid film was investigated. The pH of the solution had a significant effect on thickness with an increase in pH causing an increase in thickness, with very thin films observed at low pH values. The ionic strength also had a strong influence on the thickness on the film, with the higher ionic strength films becoming thinner. Surface hydrophobicity resulted in unstable films, with change in pH and ionic strength having little notable effect.

H-H Award
Score

Modelling Hydrodynamic Interactions between a Mica Surface and a Mercury Drop

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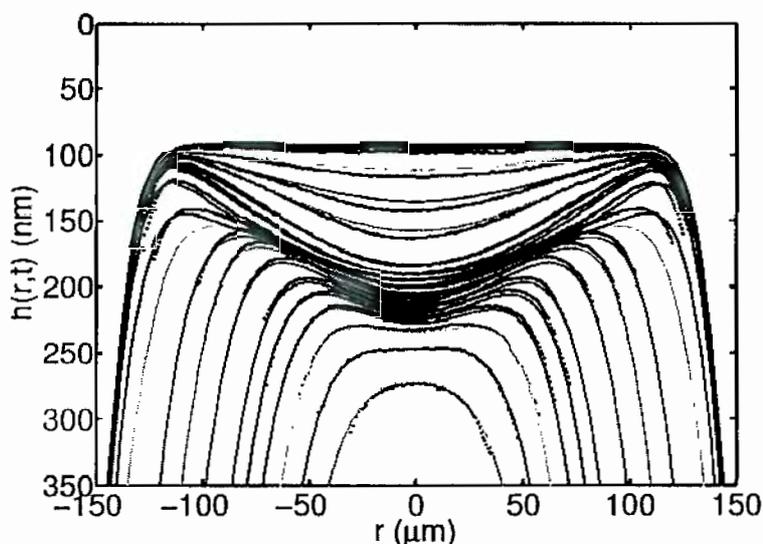
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A quantitative understanding of the role of deformation during the interaction of colloidal or nano particles has important implications in a wide range of applications. In mineral processing, bubble deformation is key to understanding capture efficiency in flotation collection. In emulsion systems, interactions involving deformable constituent components, and in bio-adhesion deformation of cellular components can affect the strength of interaction. The Surface Force Apparatus (SFA) has been used successfully to measure the interaction between deformable drops and a solid surface.

A detailed experiment, in which a flat mica surface was driven towards a mercury drop, was performed by Connor and Horn.¹ Using video imaging they were able to obtain the time evolution of the profile of the mercury drop. Due to the relatively large size of the drops (radius about 2 mm) and velocity (about 23 $\mu\text{m/s}$), the results show the presence of a classical dimple in the mercury drop due to hydrodynamic pressure. The evolution of this dimple depends on surface potential, which can be varied to provide strong repulsion to strong attraction. A new experiment performed by Clasohm et al² in which a drop already close to the mica surface is abruptly pushed towards it, showed the presence of a completely new phenomenon, which they called 'wimple'.

This work developed a mathematical model previously used to study deformation of much smaller drops to predict the time evolution of the dimple and the wimple including the main variables of the experiments. A feature of the model is the use of a new boundary condition, obtained by matched asymptotic expansions, to incorporate the weak deformation at the drop scale into the thin film scale. Numerical solutions show good agreement between theory and experiments for most of the tested cases. An example is shown in the figure, in which there is repulsion between the mercury and mica. The black dots represent the experimental evolution of the mercury surface with time and the lines the developed theory for those times.

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2. Clasohm et al., Langmuir 21: 8243-8249 (2005).



H-H Award
Score

Imaging the Different Types of Cells by AFM in the Contact Mode and the Generation of Elasticity Contour Map

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Each cell type in the animal body performs a characteristic function. For example the tissue cells, muscle cells, bone cells etc. During a disease condition each type of cell exhibits abnormal structural and functional properties. The former is directly related to the elasticity of an individual cell. The overall mechanical properties of a cell are dependant on the dynamic role of individual cytoskeleton elements. One can effectively probe the local structural and mechanical stability properties of the cell through direct interaction between the cell surface and the cantilever tip using Atomic Force Microscopy (AFM). Images of live cells (*in vitro*) are obtained in contact mode, then approach and retract cycles (force curves) are taken across the cell surface in uniformly spaced grid pattern. Localised elastic properties can be determined with the use of an appropriate indentation model from the force curves. Results for two systems, 3T3 fibroblasts and N2A neuronal cells are presented.

H-H Award
Score

Measurement of Fluid Velocity and Turbulence in Rushton Turbine Cells

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In flotation, the rate of recovery of particles depends on several variables including the particle and bubble size, particle hydrophobicity (contact angle), bubble/fluid velocity and turbulence dissipation energy inside the flotation cell.¹ The value of these variables can all be measured with different levels of success (eg., measurement of bubble size using a bubble size analyser and particle hydrophobicity using the equilibrium capillary pressure technique.¹ For the measurement of fluid velocity and turbulence in flotation cells, several methods can be used such as those based on optical (eg. Laser Doppler Velocimeter), electrochemical (eg. constant temperature (Hot-Wire) and constant current anemometry) or pressure detection. All these methods have some limitations, particularly in the presence of particles.^{2,3,4}

In this study, a pressure probe has been used for the measurements of fluid velocity and turbulence in Rushton turbine cells. It was found that, in the absence of gas bubbles and particles, this probe gave similar values of fluid velocity than the Laser Doppler Velocimeter (LDV) in 2.25, 10 and 50 L Rushton turbine cells, in a large range of agitation speeds and at various locations inside the cell. The turbulent dissipation energies were calculated from pressure fluctuations and preliminary results in the 2.25 L Rushton turbine cell indicate that the values obtained from the pressure probe are in good agreement with those obtained by LDV.

The other advantage of the pressure probe is that it can also measure fluid velocity and turbulence in the presence of particles at high weight percent solids (the values of gas flow rate and weight % solids are those used in flotation experiments). It was found that fluid velocity decreases with increasing gas flow rate but increases with increasing weight percent solids. The size of the particles presented in the pulp has no or little effect on fluid velocity. Turbulent dissipation energy, measured near the cell wall, decreased with an increase in weight percent solids.

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2. A A Gunkel and M W Weber, *American Institution of Chemical Engineering Journal* 21(5): 931-949 (1975).
3. D A Deglon, C T O'connor and A B Pandit, *Chemical Engineering Science* 53(1): 59-70 (1998).
4. A Ramond and P Millan, *Experiments in Fluids* 28: 58-63 (2000).

H-H Award
Score

Conformational Studies of Oligo-Nucleotide Adsorption to Silica through Evanescent Wave induced Absorbance and Fluorescence Spectroscopy

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The effect phys-adsorption has on the conformational helices of oligo-nucleotides is poorly understood. In particular, little is known about how hydrogen bonding and electrostatic interactions at surfaces can affect these highly ordered structures. Thus, understanding conformational variation upon adsorption will greatly improve DNA technologies.

This study aims to investigate the conformational change within a short oligo-nucleotide (46 base pairs) upon adsorption to hydrophilic silica. To ensure surface selectivity, the interfacial specific evanescent wave, a product of total internal reflection (TIR), is utilised to undertake both Attenuated Total Reflection (ATR) spectroscopy and Evanescent Wave induced Förster Resonance Energy Transfer (EW-FRET) studies. The variable penetration depth capability of the evanescent wave allows ATR studies to provide detailed information on the centre of mass of the adsorbed oligo-nucleotides from the silica/water interface. Energy transfer studies may be used as a 'molecular ruler' of chain conformation when the donor and acceptor pairs are strategically placed along the molecular chain given that the efficiency of transfer between the pair is strongly spatially dependent. Thus, these evanescent wave based spectroscopic techniques provide detailed conformational information on adsorbed oligo-nucleotides.

H-H Award
Score

Sonochemical Hydroxylation of Food Chemicals

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High-intensity ultrasound is being increasingly employed in the food industry in an attempt to improve process efficiency. Some examples that have attracted considerable interest include extraction of various food compounds, homogenisation of milk, emulsification and modification of food properties. While most of these processes utilise the physical effects of ultrasonic-induced cavitation, the chemical effects brought about by the primary radicals produced upon cavitation are also important factors that must be considered. So far, these have been largely overlooked in food processing. Sonication of aqueous solutions results in the generation of primary radicals, H[•] and [•]OH. During the ultrasonic processing/extraction, the food compounds that are present in the solutions might react with these radicals to produce new compounds. This may or may not be desirable, depending on the particular application. Our previous reported results have shown that the addition of suitable radical scavengers helps to minimise these radical attacks in cases where they are undesirable (e.g adverse flavour development). This presentation will focus on the hydroxylation of phenolic compounds undertaken as a model system. The mechanism is being investigated on selected phenolic products, representative of food systems, with the ultimate aim to achieve desirable functional properties.

H-H Award
Score

Drinking Water Sludge: The Influence of Coagulant Dose and Coagulation pH

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The production of potable water is conventionally carried out by coagulation with a hydrolysing metal salt such as aluminium sulfate ("alum") or ferric chloride ("ferric"). This process is effective at removing turbidity, colour, and micro-organisms, but also results in a waste by-product as the coagulant precipitates into particles that aggregate to form flocs. Settling of these flocs results in a sludge that can be thickened, centrifuged or filtered prior to ultimate disposal. These dewatering procedures reduce the volume of the waste stream, with both environmental and financial benefits.

Separation of the solid aggregates from the water is influenced by numerous factors — including density differences between the solid and liquid, and structural configuration — depending upon the dewatering mechanism employed. However, from an operational perspective, it is useful to gain an understanding of how such practical parameters as coagulant dose and coagulation pH affect dewatering performance, or "dewaterability".

A phenomenological theory developed by Landman, White and others has been adopted to model various dewatering unit operations. The dewaterability is characterised in terms of an equilibrium term, the compressive yield stress (p_y), and a kinetic term, the hindered settling function (R), which both depend on the solids volume fraction (ϕ).

Characterisation of alum sludges generated both in the laboratory and in industrial plants shows that the compressive yield stress increases as the coagulant dose is increased, until a point where the precipitated coagulant completely dominates behaviour. The hindered settling function was also more favourable at the lowest coagulant doses. In terms of coagulation pH, values around 6 yielded the most dewaterable sludges, with handleability deteriorating moving away from this pH in either direction.

A similar analysis was undertaken for ferric sludges. In this case the solids density was found to vary by a factor of about 2, depending upon the proportions of ferric (oxy)hydroxide and natural turbidity and colour elements in the resultant sludge. This alters the analysis because of the necessary conversion from mass fractions obtained experimentally to volume fractions used in the theory. Ferric sludges were found to be less strongly influenced by either coagulant dose or coagulation pH, tending to have 'intermediate' dewaterability compared to the alum sludges under all conditions studied, except for the effect of solids density.

It is believed that the dominant influences on dewatering behaviour are solids density and floc structure. The latter is akin to a 'bulk density'. It is expected that stronger, more compact structures will result from slower formation dynamics, such as at low coagulant doses.

H-H Award
Score

Aggregation Mechanism Induced by Cationic Polymers in Relation to Aggregation Conditions

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Aggregate properties (such as size distribution and structure) are important parameters governing the rate and performance of solid-liquid separation processes. In this study, silica particles (90 nm) are used as the colloid to be removed from the water. A series of cationic polymers ($MW = 3.01 \times 10^5$, 1.09×10^5 and 1.26×10^5 g/mol) with different charge densities (10, 40 and 100%) are used as the flocculants. Aggregates induced by each flocculant were produced by manipulating aggregation conditions, such as polymer dosage, solid concentration, background electrolyte concentration and shearing. The size and structure of such aggregates were determined using the static light scattering technique. The insight gained from aggregate properties aided our understanding in the mechanism of aggregation induced by three different charged polymers.

It is widely accepted that polymers with higher molecular weight but lower charge density favour bridging aggregation, producing large and loose aggregates while polymer with lower molecular weight but higher charge density favor electrostatic patch aggregation.

This study has found that 10% and 40% charged cationic polymers at their optimal dosages produce large but loose aggregates while 100% charged one induce small but dense aggregates. Bridging aggregation induced by 10% and 40% cationic polymers at their optimal dosages can readily be affected by solids concentration. The increased solids result in larger but looser aggregates. Electrostatic patch aggregation induced by 100% charged polymer is not influenced by the solids concentration. The addition of background electrolyte aids in bridging aggregation induced by 10% and 40% charged cationic polymers at their optimal dosages while is detrimental to electrostatic patch aggregation induced by 100% charged polymer. It is also found that the effect of shearing on mass fractal dimension is dependent on polymer charge density.

H-H Award
Score

A Study of the Film Drainage Between Solid Silica and an Approaching Oil Droplet Using Imaging Ellipsometry

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The stability of emulsions is of interest in various products and processes for a diverse range of industries. A high degree of emulsion stability enhances shelf life and quality for numerous consumer products. On the other hand, various industrial processes require emulsion instability in specific stages of the process to effect coalescence of droplets and efficient phase separation. The need for varying degrees of stability makes control of emulsion systems highly desirable.

Emulsion stability is highly dependent upon the coalescence of dispersed droplets, a process involving the drainage of a thin film of the continuous phase between adjacent droplets. Several factors contribute to the rate of film drainage and vary from system to system. Thus, understanding the mechanisms of film drainage and how such a process can be affected is the first step in effectively controlling the degree of stability within an emulsion.

Imaging ellipsometry, an optical technique, is used to measure the thin film formed between a solid silica surface and an oil droplet in an aqueous phase. Time-resolved measurements show the drainage profiles and changes in thickness of the thin aqueous film between silica and the droplet. Examining the rates of drainage in this dynamic process allows for the study of factors influencing drainage, as well as the effect of additives.

A comparison of film drainage in different systems as well as the effect of mass transfer between the dispersed and continuous phases is the focus of this study. Previous studies have demonstrated that the transfer of solute from one phase to another can either promote or retard film drainage depending on whether mass transfer occurs into or out of the thin film. Current studies are aimed at observing these effects on the evolution and drainage of the film.

H-H Award
Score

The Static and Hydrodynamic Interaction Forces Between Pluronic® Stabilised Oil Droplets Using AFM

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Emulsion systems are of great interest in many areas such as food technology, petroleum science, solvent extraction, chemical manufacturing and cosmetics. The desired stability of colloidal systems may vary from industry to industry. In some industries such as solvent extraction, oil recovery and membrane separations, fast controlled coalescence is highly preferred to increase the efficiency of the industrial processes. In other industries such as food industry and cosmetics, highly stable emulsion systems are required to prolong the product's life and quality. Understanding the interfacial forces is crucial in controlling the stability in these colloidal systems and it is also the focus of this work.

Pluronics®, commercial (PEO-PPO-PEO) tri-block co-polymers, are commonly used in a wide range of industrial applications such as emulsifying, stabilising and thickening agent. Also, they are intensively used in medical and pharmaceutical industries such as drug delivery due to their low toxicity and price. Despite their broad applications, quantitative measurements of the behaviour of adsorbed Pluronics® layers at the oil-water interface and their effect on the nanometre scale interactions is quite limited although this information is crucial in controlling emulsion stability. In this work, we have employed a recently developed method using atomic force microscopy (AFM) to study the static and hydrodynamic interactions between oil droplets in aqueous solution stabilised by a series of Pluronic co-polymers. The selected Pluronics have the same PPO molecular weight. The effects of changing the PEO molecular weight on static forces and brush size as well as changes in drainage behaviour will be discussed.

H-H Award
Score

Effect of Synthesis Parameters on the Particle Size and Swelling Behaviour of pH-Responsive Microgels

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Increasing attention is being paid to the synthesis and applications of new stimulus-responsive microgels. One of the most well documented microgel systems is based on poly (N-isopropylacrylamide) [PNIPAM], which is a thermo-responsive water-soluble polymer with a lower critical solution temperature (LCST) of approximately 32 °C. A number of applications have been suggested for such 'smart' microgels, including viscosity modifiers, delivery vehicles, biosensors, particulate emulsifiers. Over the past decade or so, several classes of pH-responsive microgels have been reported. These include (i) methacrylic acid-based alkali-swelling latexes; (ii) N-isopropylacrylamide-based copolymer microgels containing either acidic or basic comonomers; (iii) acid-swelling latexes based on basic monomers such as 4-vinylpyridine (4VP), 2-vinylpyridine (2VP) or tertiary amine methacrylates such as 2-(diethylamino)ethyl methacrylate (DEA) or 2-(diisopropylamino)ethyl methacrylate (DPA).

The present study is focused on poly(2-vinylpyridine)-based microgels. This system was first reported by Loxley and Vincent, who described the synthesis of near-monodisperse, charge-stabilised P2VP latexes at relatively low solids. In contrast, in this work we show that the use of a suitable reactive polymeric stabiliser allows the convenient synthesis of sterically-stabilised P2VP latexes at much higher solids at neutral pH. These latexes acquire microgel character at low pH due to protonation of the pyridine residues.

Moreover, judicious adjustment of the synthesis parameters enables the mean particle diameter of these P2VP latexes to be varied over a surprisingly wide range, with narrow size distributions being obtained in each case.

A series of sterically-stabilised, lightly cross-linked, pH-responsive poly(2-vinylpyridine)-based microgels has been synthesised at 10 % solids by emulsion polymerisation using a well-defined monomethoxy-capped poly(ethylene glycol) monomethacrylate macromonomer as a reactive polymeric stabiliser. Varying the concentration of this stabiliser, together with that of the cationic co-surfactant and the cationic initiator, allows the mean particle diameter of the P2VP latexes to be controlled over a surprisingly wide range (370 to 970 nm). In each case narrow size distributions are obtained, as judged by disk photosedimentometry and scanning electron microscopy. The critical pH for the latex-to-microgel swelling transition of these P2VP particles is around pH 4.1. Preliminary studies of the kinetics of swelling of these sterically-stabilised (and related charge-stabilised) pH-responsive latexes using stopped-flow techniques indicated significant discrepancies with previously published data. Finally, we note that this flexible new synthetic protocol should allow us to evaluate whether the Tanaka equation, originally derived for macroscopic gels, is also valid for microgels.

H-H Award
Score

Applying the Quartz Crystal Microbalance Technique to Determine the Stability of Colloidal Suspensions

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Colloidal suspension behaviour is strongly influenced by the particle – particle interaction forces operative in the system. In aqueous systems, suspension stability can be easily altered either by the addition of electrolyte or by changes in the pH. Such changes result in changes to either the net surface charge of the particles or the thickness of the diffuse electrical double layer around the particles. If the charge or the double layer is sufficiently reduced, the ubiquitous attractive van der Waals interaction forces can dominate and the dispersion is destabilised.

QCM-D is used to determine the stability of particle suspensions in different solution conditions. Mono-dispersed silica suspensions were prepared for investigation, at various pH and KNO₃ electrolyte concentrations. The conditions used here were chosen on the basis of measurements of the particle zeta potentials as a function of pH at various salt concentrations. This study shows that by varying the suspension stability, the frequency shift of the resonating crystal, recorded as the energy input into the QCM cell is increased, is significantly greater for an unstable silica suspension compared to a stable suspension.

H-H Award
Score

Flocculant Adsorption Kinetics and the Dewatering Behaviour of Clay Dispersions

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Polymer mediated flocculation is central to efficient water recovery and impoundment volume reduction of mineral tailings waste, particularly where clay minerals comprise a significant proportion. In this study, the adsorption kinetics of four high molecular weight polymeric flocculants onto clay substrates under orthokinetic conditions have been investigated. For both kaolinite and smectite surfaces the adsorption rate decreased in the sequence polyacrylamide homopolymer (PAM N) - polyacrylamide polyacrylate copolymer (PAM A) - polyethylene oxide (PEO) - polyacrylamide 2-acrylamido 2-methylpropane sulfonate copolymer (PAM S). After flocculation under laminar flow conditions, optimum subsidence rates for both clay types decreased according to flocculant type in the order PAM S - PEO - PAM A - PAM N, implying slower adsorption rate facilitated improved floc character. Calculation of first order rate constants for the adsorption of PAM A and PAM S onto kaolinite at 25 °C and 50 °C implied an activation energy of 44 kJ·g⁻¹ polymer. The settling rate, corrected for viscosity, of kaolinite dispersions flocculated with PAM S increased with increased temperature, in contrast to the diminished performance of PAM A and PEO. An attempt is made to rationalise flocculation and settling performance with flocculant adsorption kinetics and the physico-chemical flocculant characteristics.

H-H Award
Score

Processes Involved in the Separation of Plant Compounds for Drug Discovery

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Secondary metabolites produced by higher plants as a chemical defence system are an incredible source of novel compounds with pharmaceutical potential. Although they have been the basis for many beneficial drugs such as aspirin and digitalis, interest in natural products for drug discovery waned with the influx of synthetic pharmaceutical compounds. This was due to the inherent difficulty in separating and isolating plant compounds and the comparative ease and speed of obtaining synthetic medicines. However, as secondary metabolites are products of millions of years of evolution, they comprise a molecular diversity and biological functionality that cannot be matched by combinatorial chemistry.¹

Separation of plant compounds is the rate-determining step of drug discovery, making this process less efficient than synthesis. Crude plant extracts are made by exposing the plant samples to various solvents, including chloroform, ethanol, methanol, and water. The crude extracts, containing a plethora of compounds are separated by repeated, HPLC-piloted, chromatography. Separated fractions of the crude extract are tested for activity against the target organism, and fractions containing the desired activity are further separated with chromatography until the active compound has been isolated.

With the exception of alkaloids, which are separated by differences in pH, natural products are separated by differences in polarity. Non-polar terpenes, for example, are separated most efficiently on a polar silica stationary phase, while polar flavonoids are separated with a non-polar stationary phase. Examples of non-polar stationary phase media include C18, whereby the active sites of silica gel are replaced with long-chain hydrocarbons, and hydrophobic resins, such as XAD-16.

Where compounds exhibit similar polarities, other media with different principles of separation can be used for the stationary phase. Sephadex LH20 gel is commonly used for the further separation of active fractions of the crude extract. This porous media separates compounds based on molecular size rather than polarity, where larger compounds elute first. Smaller compounds will enter the different-sized pores, winding their way through the media. The smallest compounds will be able to enter all of the pores and will therefore elute last. Sephadex LH20 gel is a useful media for separating chlorophyll from other, non-polar compounds of leaf extracts.

The use of different media is necessary to be able to separate compounds for drug discovery. Improvements in this area will speed up the conversion of crude plant extracts into pharmaceutical lead compounds, and make this great resource a more accessible tool in the fight against disease.

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H-H Award
Score

Dairy Nanofiltration Fouling

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Skim milk ultrafiltration (UF) permeate is currently an underutilised by-product of protein concentrate production within the dairy industry. However, high concentrations of potentially valuable lactose and calcium within this permeate make their recovery both economical and environmentally beneficial. Nanofiltration (NF) is therefore being investigated to separate these components from unwanted monovalent salts in skim UF permeate. A major problem faced by industry during membrane filtration however is the fouling phenomenon, which can significantly reduce efficiency. Therefore, the main focus of this study is to understand and characterise the membrane fouling behaviour during this filtration. This will help to optimise operation and reduce downtime and costs associated with cleaning.

Constant concentration NF experiments using dairy UF permeate and a flat-sheet polyamide membrane have been performed for varying temperatures from 10-50 °C and feed pH from 5 to 9. Specific attention has been paid to the role of calcium within the fouling process. It was observed that the operating temperature and feed pH have a significant influence on flux decline during NF. In particular, decreasing feed pH was shown to dramatically alleviate flux decline attributed to precipitation of calcium salts. Temperature had little effect on fouling at low pH levels, but a greater influence as feed pH increased. Contrary to expectations, increasing the temperature at high pH was shown to decrease the total resistance due to fouling.

The fouling mechanism during filtration was investigated by plotting t/V vs. V , which relates filtration time (t) with total volume of permeate passed (V). These plots have indicated that the mechanism of membrane fouling at these temperature and pH conditions is one of pore blockage, followed by cake formation. This cake layer has been visualised in cross-sectional field emission scanning electron microscopy (FESEM) images of the clean and fouled membrane, following filtration at 50 °C and pH 6.9 (Figures 1 and 2).

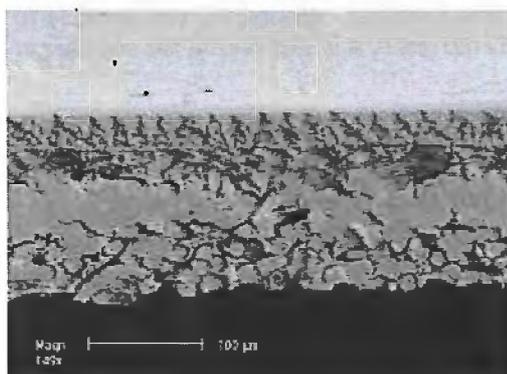


Figure 1. FESEM cross-section image of clean NF membrane

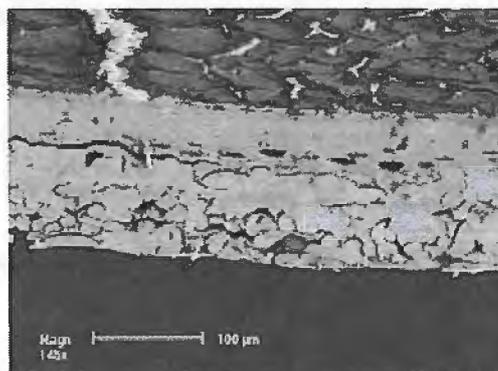


Figure 2. FESEM cross-section image of fouled membrane after filtration at 50°C, pH 6.9

H-H Award
Score

Design of Photoresponsive Surfaces

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The light-sensitive behaviours of pyrimidine molecules (bases present in nucleic acids) were exploited to design reversible, photoresponsive surfaces. These molecules dimerise on exposing to UV radiation of wavelength 280 nm; the reverse reaction occurs when the dimer is irradiated with light of wavelength 240 nm. This whole process is reproducible over a number of cycles. Long alkyl chains terminated with methyl (non-polar) and thiol (polar) groups were attached to the pyrimidine molecules. The prepared molecules (from respective ethanolic solutions) were used to dip-coat quartz surfaces. The thiol terminated molecules were grafted on to a flat gold surface as a self-assembled monolayer (SAM). Reactions on the surface were carried out using high intensity UV radiation of particular wavelengths. Static water contact angles were compared with surface changes (monitored using UV & FTIR spectroscopy) during the progress of the reaction. In a similar way, the reaction rate of the pyrimidine attached to the surface was measured and related to reaction mechanism, rate determining step, quantum yield, etc. Moreover, the three components of the total system, i.e., i) pyrimidine groups, ii) chain length and iii) metal surfaces were varied to find their individual effect on surface wettability changes and to optimise the conditions for the reactions involved.

H-H Award
Score

Adsorbed Polymerised Surfactant Mixtures on Solid Substrates

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Adsorbed surfactant micelles have been demonstrated to form a variety of aggregate shapes and regular surface patterns on solid substrates. Using polymerisable surfactants ("surfmers"), these adsorbed structures are polymerised in the interface under UV light or thermal conditions. Then the adsorbed polymer films are investigated with the help of soft-contact AFM imaging.

Trying to preserve the surfactant-templated nanostructure we polymerise surfmers mixed with conventional surfactants, then dissolve/wash out monomer surfactants to leave the polymerised "skeleton" structure. We studied mixed solutions of the polymerisable cationic surfactant methacrylate dodecyldimethylammonium bromide (MEDDAB) and different non-polymerisable surfactants such as the cationic surfactant dodecyltrimethylammonium bromide (DTAB) and the technical nonionic surfactant polyoxyethylene 23 lauryl ether (12A23) at varying compositions on solid surfaces such as mica and graphite before and after polymerisation to find out the influence of polymerisation on the adsorbed structure.

H-H Award
Score

Biofunctionalisation of Core/Shell Particles for Cell Targeting

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Recently, a great deal of research interest has focused on using nano- and microparticles in areas such as biolabelling, medicine, and in gene or drug delivery.¹ The particles under investigation are based on core/shell particles formed by the layer-by-layer (LbL) self assembly technique.² These particles have a decomposable core, allowing the production of hollow capsules with high loading capabilities. The surface of these particles can be easily modified and functionalised with specific biomolecules (eg. antibodies, targeting ligands) for targeted delivery to a particular site or cell type. Targeting provides a high local concentration of the therapeutic on the target site and reduces unwanted toxic effects in surrounding cells. Various nano- and microparticles have been conjugated to a wide range of targeting biomolecules, but there is currently limited work using LbL particles.

Fluorescent, polystyrene core-polyelectrolyte shell particles and capsules were biofunctionalised by physical adsorption of a cell-specific targeting protein, the A33 antibody (Ab).³ This antibody binds to the A33 antigen which is present in almost all colorectal cancer cells.⁴ The LbL build-up of polyelectrolyte on the particles was monitored using microelectrophoresis and showed reversal of charge after each deposition step and upon protein adsorption. The presence of protein on particles was determined using fluorescence methods and quantification of the adsorbed protein was carried out using Q-sense (based on quartz crystal microbalance) and MicroBCA™ protein assay. Flow cytometry was employed to investigate the binding of the functionalised, fluorescently-labelled particles/capsules to various human colorectal cancer cell lines. It was found that the A33 Ab-coated particles bound selectively to cells expressing the A33 antigen as demonstrated by a competitive binding assay.

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H-H Award
Score

Controlled-Release of Allyl Isothiocyanate from Locally-Ordered Mesoporous Materials

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The locally-ordered mesoporous material MCM-41 offers a relatively well-defined hexagonally organised pore structure with a modifiable surface chemistry. As such, this and similar materials offer themselves as a convenient reservoir for organic guest molecules and their controlled release. Several recent studies exploit the release property of MCM-41 as a potential drug carrier. The present study explores the effect of selected local-order, template-directing molecule concentrations on the pore size development and controlled release rates from synthesised MCM-41-type porous materials.

Allyl isothiocyanate (AITC), an extract from wasabi and horseradish, was selected as a model molecule for drug delivery system development. It exhibits strong antibiotic properties displaying antimicrobial effects against *Escherichia coli*, *Salmonella typhi*, *Pseudomonas aeruginosa*, *Vibrio parahaemolyticus* and other bacteria, and inhibits the growth of *Staphylococcus aureus*, *E-coli*, *Proteus vulgaris*, *Pseudomonas fragi*, and *P. aeruginosa*. Since AITC presents a relatively high vapour pressure at 298 K, we suggest that it can deliver these antimicrobial properties more effectively if it is adsorbed and "released" in a controlled manner from the pore structure within MCM-41.

Mesoporous silica MCM-41 was produced by the well-established hydrothermal synthesis of tetraethoxysilane (TEOS) modified by *n*-hexadecyltrimethylammonium bromide (C₁₆TABr), aqueous ammonia (32 wt.%), and absolute ethanol (EtOH), using the ratio of molar composition as: 1 TEOS:0.3 C₁₆TMABr:11 NH₃:144 H₂O:58 EtOH. We explored variations in these ratios as well as ageing conditions and silica source on the final pore structure. The effects of these variations were characterised via nitrogen gas adsorption and X-ray diffraction. We adsorbed AITC into the porous MCM-41 from ethanol or supercritical carbon dioxide solvent systems with the release rate being monitored via GC and GC-MS analyses.

The MCM-41 pore size distribution and structure affect the amount of adsorbed AITC and hence pore structure, pore size, pore volume, and specific surface area influence the desorption or release rate. Different templates and silica sources have been shown to influence Ibuprofen controlled-release rates. However, in this study, differences in the pore volume and specific surface area using MCM-41 silicas synthesised by different ratios of template and silica source do not adversely affect the AITC release rate. Sample loading via direct vapor adsorption is compared with loading via supercritical carbon dioxide, with the former leading to a "maximum" amount adsorbed. We demonstrate how AITC volatility may be exploited for controlled release purposes where release at 298 K is considerably greater than at 273 K.

H-H Award
Score

Colloid Surface Engineering via Deposition of Multilayered Thin Films from Polyelectrolyte Blend Solutions

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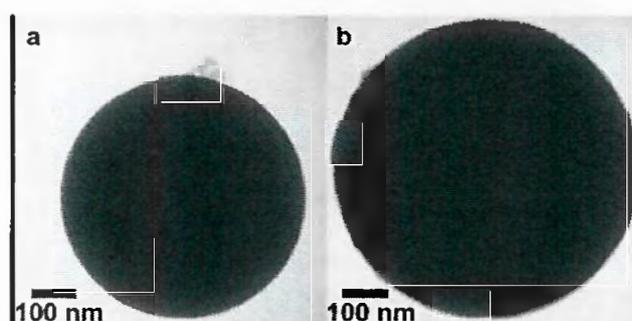
Weak polyelectrolytes (PE) have been attracting increasing interest as an assembly component in the construction of multilayer thin films. Weak PEs are charged polymers in which the extent of ionisation depends on the pH of the surrounding solution. When used in the assembly of multilayer thin films, weak PEs give rise to interesting properties and films that are responsive to assembly and post-treatment conditions.

Colloidal stability is the major issue that needs to be addressed when using weak PEs in the construction of multilayers on a colloidal substrate. Herein, we demonstrate that PE blending can be used to improve colloidal stability, while obtaining thick multilayers.

Poly(allylamine hydrochloride) (PAH) was used in the assembly of multilayer thin films on colloidal polystyrene particles at pH 7.5 and also at pH 3.5 with a blend of weak and strong polyanions [poly(acrylic acid) (PAA) and poly(styrene sulfonate) (PSS) respectively] – the blend solutions consisted of different compositions (10% to 97% PAA) and ionic strengths (0 and 0.5 M NaCl).

Alternation of the ζ -potential after the assembly of each layer suggested the formation of a multilayer film on the particle surface. Transmission and scanning electron microscopy confirmed that smooth and homogenous coating was achieved with a blend composition of up to 90% PAA. Colloidal stability was vastly improved when compared to particles assembled without adding a strong PE. Thicker multilayers were also achieved when compared to particles assembled with only strong PE coatings.

The results demonstrate that multilayers assembled from blended solutions can be used to control the surface properties, colloidal stability and the shell thickness of core-shell particles. The control of these parameters may have important applications in the fields of controlled delivery, photonics, catalysis and separations.



TEM images of (a) a 600 nm diameter PS particle and (b) a 600 nm diameter PS particle coated with 20 layers from blend (PAA/PSS) and PAH adsorption solutions of pH 3.5 and 7.5, respectively. The PAA/PSS blend composition used was 25:75 wt % containing 0.5 M NaCl. The PAH solutions contained 0.5 M NaCl.

H-H Award
Score

Adsorption of pH-responsive Diblock Copolymer Micelles to Silica

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The adsorption behaviour of diblock copolymers has become of significant interest in recent years due to the possibilities for using these copolymers as nanomaterial building blocks. However, there is only reasonably limited qualitative literature pertaining to the adsorption of diblock copolymer micelles. Here we present a study into the adsorption behaviour of the pH-responsive diblock copolymer poly(2-(dimethylamino)ethyl methacrylate)-*block*-poly(2-(diethylamino)ethyl methacrylate) at the silica/aqueous solution interface. This polybasic copolymer has only subtle differences in hydrophobicity between the two blocks, where in an alkaline solution where the charge is reduced it forms core-shell cationic micelles above a certain copolymer concentration (critical micelle concentration, cmc), whereas it exists as unimers in acidic solution. As a result, adsorption behaviour of PDMA-PDEA on silica is strongly dependent on both the copolymer concentration and the solution pH. In our investigation we studied several copolymer samples with a comparison between two block ratios, and also samples with selective quaternisation of the PDMA block to investigate the effect of charge.

Predominantly we have investigated adsorption from micellar solutions using Optical Reflectometry (OR) measuring adsorbed amounts and adsorption kinetics. We have teamed this information with data from Quartz Crystal Microbalance (QCM-D) to gain an understanding of the layer structure and solvency in order to build a strong understanding of these systems. AFM images were also taken to visualise the adsorbed micelle layers.

H-H Award
Score

Tailoring the Interfaces Between Thermotropic Liquid Crystals and Aqueous Phases via Layer-by-Layer Assembly

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Molecules that form liquid crystals (mesogens) possess mobilities characteristic of liquids but still retain some degree of orientational and/or positional order. This ordering is highly sensitive to interfacial interactions, and the orientations established at the interfaces can propagate up to 100 μm into the bulk of the liquid crystal. Because liquid crystals can amplify interfacial phenomena to the visible scale, they are very attractive candidates for chemical and biological sensing. Recent studies have shown that the ordering transitions in liquid crystals near interfaces can be coupled to the adsorption and/or organisation of surfactants, lipids and proteins.

Our collaboration centres on using the layer-by-layer (LbL) technique to deposit polyelectrolyte multilayer (PEM) films at interfaces between liquid crystals and aqueous phases. This approach can be used to prepare chemically tailored interfaces since the technique is applicable to a wide variety of materials such as polymers, proteins, biomolecules, nanoparticles etc.

We have previously shown that it is possible to prepare PEM films on an approximately planar interface between the nematic liquid crystal 4'-pentyl-4-cyanobiphenyl (5CB), (hosted in a gold grid), and an aqueous phase (water). The PEM films preserved the planar anchoring of 5CB in water and can mediate the interactions of solutes with liquid crystals. Film growth was followed with fluorescence microscopy using fluorescently-labelled poly(allylamine hydrochloride) (PAH) and the orientation of liquid crystal was observed with polarised microscopy.

One advantage of the LbL method is that it is also applicable to colloids. We have recently found that 5CB can be emulsified with water to form small droplets and when 5CB is emulsified with a charged lipid or poly(styrene sulfonate) (PSS), a charged interface is formed on which PEM films can be assembled. This is an important development because the liquid crystal emulsion has a much higher mobility and surface area than when the liquid crystal is hosted in a grid. These improvements offer potential advantages for sensing applications. The growth of PEM films on liquid crystal emulsions was studied with microelectrophoresis and confocal microscopy.

H-H Award
Score

Shear Impacts upon Luminescent Rod-coil Block Copolymers

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The next generation of optoelectronic devices are expected to be made from either small molecules or polymeric systems. Polymeric systems allow use of the widely known and simple production techniques spin coating and jet printing. These processes offer significant processing advantages for polymeric system over small molecule systems. Large scale manufacturing desires simple already understood techniques to limit the required research and development. However both of these processes are high shear processes. This study of shear impacts on rod-coil luminescent polymers will aid in understanding these impacts.

A group of proposed systems utilise polymers combining balanced hole and electron transporting groups to optimise optoelectronic device performance. The combination of these donor and acceptor groups in a single polymer allows a stable and predictable light emission to be produced also incorporating the processing benefits of polymer solutions.

The polymer system studied contains a single rod in the backbone of the polymer being a derivitised anthracene (chromophore). The coils are an oxadiazole side chain upon an aliphatic backbone. The oxadiazole groups efficiently transfer their energy to the anthracene chromophore.¹ The energy transfer between the oxadiazole units and the anthracene chromophore is not able to pass along the backbone of the polymer to the chromophore as is the case in conjugated polymers. The energy transfer between the donor oxadiazole groups and the acceptor chromophore is by resonance energy transfer.

The efficiency of resonance energy transfer between molecules is controlled by the distances between the donor and acceptor units and the overlap in their spectra. This is described by the Förster equation below.² Where R_0 is the Förster distance, r is the distance between the donor and acceptor, $k_T(r)$ is the rate of energy transfer and τ_D is the donor lifetime when no energy transfer occurs.

$$k_T(r) = \frac{1}{\tau_D} \left(\frac{R_0}{r} \right)^6$$

With the oxadiazole chain segments behaving as a random coil polymer the characterisation of the distances between the donor and acceptor parts of the polymer will remain relatively constant. The application of shear to this molecule in solution is expected to alter the polymer chain conformation. The alteration in the conformation is expected to result in changes in the average distance between the donor and acceptor. The spectral properties of the donor and acceptor will not be altered by the applied shear. Any changes seen in the resulting fluorescence response will be due to the altered conformation.

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H-H Award
Score

Influence of High Molecular Weight Polyacrylamide on Surface Chemistry, Particle Interactions and Dewatering Behaviour of Gibbsite Dispersions

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The dewatering of mineral dispersions presents a substantial problem to the mineral and mining industries. Colloidal sized particles are difficult to dewater as they do not settle under gravity. Devising an effective dewatering process will have many benefits that include: compact consolidation, which will reduce space requirements for storage of both valuable minerals and tailings, enhanced water recovery, cost reduction on recovery of entrapped useful chemicals, and reduction in operating costs. Gibbsite forms a large part of valuable and waste mineral tailings. It is very important to investigate the dewatering behaviour of gibbsite for improvement, as the new knowledge gained will be useful to other hydrophilic minerals such as iron oxide, silica and titanium dioxide. There is a very urgent need to reduce the water content of gibbsite concentrates in the minerals and chemicals industry (ceramic, pharmaceutical, paper, Bayer process etc). The Bayer process (alumina production) involves filtration of alumina hydrate, where a slurry of alumina hydrate is pumped and filtered through the filters. In this operation the pumping cost involved for filtration is very high, making the operating cost very high. High molecular weight polymers can be employed to obtain a thickened slurry of gibbsite, reducing operating costs significantly.

The flocculation performance of polymers is commonly evaluated by measuring the settling rates of flocs, the percentage of flocs (consolidation) settled and the strength of flocs (yield stress). In this study, the influence of high molecular weight Na-acrylate (carboxyl substituted) polyacrylamide copolymer (PAM A, molecular weight 7.5×10^6 , 25 mol % anionically charged) and S-acrylate (carboxyl substituted) polyacrylamide copolymer (PAM S, molecular weight 7.5×10^6 , anionically charged) and non-ionic polyacrylamide homopolymer (PAM N, molecular weight 9×10^6) on the surface chemistry, particle interactions and dewatering behaviour of gibbsite dispersions has been investigated at three pH values (7.5, 10, 12.5), where particles are positively charged, close to the iso electric point (iep) and negatively charged respectively. Anionic PAM was found to be more effective in flocculating gibbsite dispersions at higher pH. High settling rates were obtained at pH 12.5, the settling rate at the other two pHs showing nearly similar values. Anionic PAM has a significant effect on the surface chemistry than its counterpart non-ionic showing different behaviour at different pH values. Expanded form of polymer exists due to repulsion between negatively charged gibbsite particles and polymer responsible for producing large flocs showing high settling rate. Anionic PAM was found to have a significant effect on the rheology and consolidation of gibbsite dispersions, showing high yield stress at pH 12.5. At same flocculating conditions non-ionic PAM showed a low settling rate and yield stress. It can be concluded from this study that high suspension pH and anionic polymer affects flocculation positively for aqueous gibbsite dispersions, showing high settling rate and high yield stress. The results noticeably indicate that the anionic polymer is more effective at higher or basic pH than at acidic or neutral conditions.

H-H Award
Score

Investigating Slip Boundary Conditions with Squeeze Film Measurements in the SFA and AFM

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According to the no-slip boundary condition of hydrodynamics, the flow velocity of a liquid at a solid-liquid interface is equal to the velocity of the solid. The general acceptance of the validity of the no-slip theory for Newtonian liquids is based on experimental observations, rather than on any fundamental theory. In recent years, with the improvement of fine-scale experimental techniques, questions have been raised about the universality of this boundary condition, and whether in some situations the velocity-matching condition should be applied not at the interface but some distance to the solid side of it. This would correspond to the liquid slipping over the solid surface, and the distance between the interface and the (virtual) position of the velocity match defines the 'slip length', which is used to characterise the amount of slip. A better understanding of hydrodynamic boundary conditions is important to the study of liquid flow in confined spaces.

The flow of simple liquids in a confined geometry has been studied by means of *squeeze film* experiments, using the surface force apparatus (SFA), and more recently using the colloid-probe atomic force microscope (AFM). These experiments consist of a thin liquid film confined between two solid surfaces that can be driven up and down relative to one another in a direction normal to both surfaces. In the current project, we investigate and compare the two aforementioned techniques for studying the boundary conditions in the squeeze film geometry, both from an experimental viewpoint and by examining the data analysis and interpretation methods employed.

H-H Award
Score

Yielding of Concentrated Nanoparticle Suspensions

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The apparent yield stress of concentrated coagulated particulate systems has been widely investigated and found to be related to the strength of inter-particle interactions. The most common method for measuring the apparent yield stress is the vane technique. However, this technique gives a single point value and fails to fully describe the deformation of a material. Alternatively, dynamic mechanical analysis can be used to probe the changes and failure in the structure of the material throughout the deformation process. Lissajous graphs were found to be insensitive to small changes during deformation, while Fourier Transform Rheology is able to detect small changes throughout the deformation process. From preliminary results, it is hypothesised that the yield strain can be related to the interparticle separation between a pair of particles. Models are currently being developed to relate the yield strain to particle size, the Hamaker constant and the zeta potential. This method of analysis is useful for investigating the effect of additives such as surfactants, which change the rheological properties of the coagulated particulate suspension. Dispersant style surfactants have been investigated as well as molecules that give rise to phenomena such as hydrophobic forces.

H-H Award
Score

The Dewaterability of Iron Oxide Dispersions and the Mechanisms of Polymer Adsorption

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The dewatering of colloiddally stable iron oxide and other mineral dispersions presents a substantial problem to the mining and minerals processing industry. Although recent advances in technology have improved the efficiency of thickeners, current dewatering methods still only produce thickened mineral waste dispersions of low to moderate solid content of approximately 25 to 60 wt%. Iron oxide represents typical, hydrophilic mineral oxides that form a large part of both valuable and waste mineral dispersions that must be dewatered routinely during hydrometallurgical mineral processing operations. Due to the hydrophilic nature of iron oxide, colloiddally stable dispersions have proven to be significantly difficult to dewater to a high solid loading.

The influence of two high molecular weight polyacrylamides (anionic polyacrylamide, PAM A and non-ionic polyacrylamide, PAM N) on the interfacial chemistry, rheology and dewaterability of a colloidal iron oxide dispersion has been investigated at three pH values (6, 8.5 and 11), where the particles are at the isoelectric point (iep = 8.5) and either side of the iep. PAM A was found to adsorb with a lower affinity than PAM N at all pH values tested; however, the former had a more significant effect on the particle zeta potential and the shear yield stress. Higher settling rates (up to 100 m/h) were achieved with PAM A at pH values at and below the iep, with flocculant dosage below 100 g polymer/t solid. Settling rates with PAM N at similar concentrations, however, only produced settling rates in the range of 5-10 m/h. Pulp pH and higher flocculant dosage (up to 500 g/t solid) had no noticeable effect on the extent of the pulp consolidation (~35 wt%). Significantly, shear of pre-sedimented dispersions was found to increase the consolidation by up to 15 wt% to around 50 wt%. Polymer structure type was found to have a significant effect on the rheology of the dispersion, with PAM A-flocculated dewatering leading to a higher yield stress than dewatering with PAM N.

The mechanisms of polyacrylamide adsorption onto iron oxide particles were investigated via DRIFT spectroscopy at the three pH values. At pH values above and below the isoelectric point for the anionic polymer, bidentate chelation was the main adsorption mechanism, along with hydrogen bonding. At the iep, bidentate bridging was observed to be the mode of adsorption along with hydrogen bonding. For the non-ionic polymer, in all cases hydrogen bonding through the carbonyl group was the main mode of adsorption. The adsorption of both polymers conformed to the Freundlich model suggesting that the adsorbed polymer amount increases with polymer concentration rather than approaching monolayer coverage. Spectroscopic evidence was found to suggest hydrolysis of non-ionic polyacrylamide at pH 11 occurred, which led to similar behaviour by both polymers at high pH.

H-H Award
Score

Fine Particle Flotation

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Fine particle flotation is becoming increasingly important, since the demand for minerals is increasing while the extent of available sources of ore is decreasing. The recovery of valuable mineral particles by flotation is most successful in the size range from 20-100 μm in particle diameter. The recovery rate for fine particles drops drastically, due to their lower momentum in collisions with bubbles, resulting in significant losses of valuable minerals in tailings. At the same time, selectivity also becomes an issue for effective separations.

The main goal of this study is to investigate the intrinsic mechanism(s) of fine particle flotation so that a high flotation rate of fine particles with appreciable selectivity can be achieved, without adversely affecting the flotation rate of intermediate and coarse particles. In general, there are three methods for increasing the flotation rate of fine particles, i.e., decreasing bubble size, selectively aggregating particles and increasing the turbulence intensity. In this study, these methods have been employed with particles between 0.5 and 5 μm in diameter in a modified Hallimond flotation tube and a Rushton turbine flotation cell.

Flotation experiments with single bubbles and bubble swarms in a modified Hallimond flotation tube showed that there is an optimum bubble size (OBS) for fine particle flotation. Existence of the OBS is attributed to the transition of flow regime from Potential flow to Stokes flow as the bubble size decreases, which basically affects the particle-bubble collision efficiency. It has been observed that there exists a critical contact angle, above which the hydrophobised particles start to float. The effect of salt concentration for fine particle flotation has also been examined in combination with surface hydrophobicity. Depending on the surface chemistry of particles the salt effect could be significant or critical. From experiments with the Rushton turbine flotation cell, turbulent conditions seem to play a strong role for fine particle flotation, or fine particle selective "aggregating flotation". These results will be discussed based on the hetero-coagulation, coupled to classical kinetic coagulation and flotation theories.

H-H Award
Score

Development of an Atomic Force Microscope for High Speed, In Situ Electrochemical Imaging

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Atomic Force Microscopy (AFM) has become a popular method for high resolution imaging of surfaces since its initial invention 20 years ago. Originally it was designed as a simple mechanical force-measuring tool by scanning a tip on a surface. The concept has since been extended to sense other types of interactions such as electrostatic and magnetic forces. Different methods of imaging have also been developed such as tapping mode, where the tip is oscillated at its resonance frequency and the probe amplitude is used to map the surface. This working mode is popular for imaging sensitive and soft surfaces such as biomolecular systems and living cells because the force applied to a sample is significantly reduced.

While imaging in air is fairly straight forward, many interesting and important processes occur in a liquid environment. Most commercial AFMs are equipped with liquid cells, which are only suitable for aqueous solutions and require high levels of caution and skill to use. When using tapping mode in these liquid cells, typically the entire cell is oscillated rather than just the cantilever, which often results in undesired effects. Attempts to couple these liquid cells with other techniques to create a combined instrument have mostly failed due to the complexity of the system.

We are developing an AFM that is capable of high speed imaging in a range of environments, in particular in fluids such as water, organic solvents and ionic liquids. This AFM can be coupled with electrochemistry to enable *in situ* AFM of the dynamic processes that occur on an electrode surface during voltammetric, potentiometric and amperometric control. Means to decouple the liquid cell resonations from the cantilever oscillations have also been investigated.

H-H Award
Score

Colourful Oligomeric Surfactants by an Unusual Route

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Oligomeric surfactants consist of two or more ordinary surfactant units, the hydrophilic heads of which are linked by spacer units. They are known to display interesting and unusual self-assembly and rheological properties. Since their synthesis can be a lengthy and difficult process, we have investigated polymerisation techniques as a way of producing a range of oligomeric surfactants.

Conventional polymerisation techniques can be difficult to control, particularly when only extremely short oligomers are desired. In addition, the analysis of the resulting multiply charged and surface-active species has inherent problems. Here we present a simple system that addresses both of these problems using the alkylpyridinium surfactant family.

Chain growth during polymerisation takes place by nucleophilic attack, with two mechanisms being implicated, one of which is a variant of the Michael reaction. The reaction occurs under mildly basic conditions, requires no deoxygenation and is easily quenched by lowering the reaction pH. By varying parameters such as concentration and reaction time, the size of the oligomers can be controlled.

A set of pyridinium surfactant oligomers has been produced using this reaction, and possess interesting surface-active properties. A subset of the surfactants also display pH-dependent chromophoric properties, which are attributed to the formation of an intramolecular charge-transfer complex under basic conditions.

H-H Award
Score

Abstracts

Poster Presentations

Electrokinetic Mobility of Metal Oxides

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The electrokinetic mobility of titanium dioxide (TiO_2) and indium tin oxide were measured with a Rank Brothers microelectrophoresis apparatus as a function of solution pH and electrolyte concentration, and for different surface hydrophobicities. The particle size of the sample was less than 10 microns. The surface hydrophobicity of the samples was modified by adsorption of octadecyltrihydrosilane (OTHS) in cyclohexane. Silanation of metal oxide removes ionisable surface groups and should therefore decrease their electrokinetic mobility. However, Laskowski and Kitchener¹ found that silanation of a silica surface with trimethylchlorosilane did not result in a significant reduction in the zeta potential of silica.

The zeta potential of the TiO_2 samples will be used to interpret the results of contact angles of these samples as a function of surface hydrophobicity, solution pH and electrolyte concentration.

Tin doped indium oxide (In_2O_3) is a transparent conducting material with applications to photovoltaic cells, gas sensing and also to touch screen LCD displays. However, the film must contain a high density of charge carriers to conduct, but generally higher charge density, leads to lower transparency². Therefore a balance between these two factors must be obtained. Little information on the surface charge of such conducting metal oxides is available in the literature.

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2. J Stotter, Y Show, S Shihua and G Swain, *Chemical Materials* 17: 4880-4888 (2005).

Poster 1
Score

Self-Assembly of Non-Ionic Surfactants in Room-Temperature Ionic Liquids

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Ionic liquids are low-melting salts with negligible vapour pressure. As a result, they have been extensively studied for applications in synthesis, catalysis and separation techniques as environmentally-friendly alternatives to traditional solvents. Comparatively little attention has been placed on their physical properties, in particular their ability to support surfactant self-assembly. To date, ethylammonium nitrate (EAN) is the only ionic liquid in which unambiguous evidence of self-assembly of conventional surfactant molecules has been shown. It is believed that its capacity to form an extensive network of hydrogen-bonds similar to that in water is a crucial contributor to its success in supporting surfactant self-assembly.

In this work, three ionic liquids with a molecular architecture derived from EAN were prepared: propylammonium nitrate (PAN), ethylammonium hydrogensulfate (EAHS) and propylammonium hydrogensulfate (PAHS) – the latter two being previously unreported. The self-assembly behaviour of polyoxyethylene alkyl ether non-ionic surfactants, C_nE_m, where $n = 16$ or 18 and $3 \leq m \leq 8$, was explored in these three ionic liquids using polarising optical microscopy to observe lyotropic liquid crystal phases. The mesophases observed in PAN followed similar trends to the ones previously observed in EAN and water. EAHS and PAHS also supported self-assembly, favouring almost exclusively the formation of lamellar phases.

Poster 2
Score

Mineral Equilibria in Skim Milk during Changes in Composition of Skim Milk and its Effect on Aggregation in Forming Cheese Curd

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The equilibria governing the partition of mineral salts between the colloidal and aqueous phases of skim milk which are separable by ultra centrifugation are dependent on the physico-chemical characteristics of the aqueous phase including pH and mineral composition. The ability of milk to form a gel and the properties of the gel when milk is treated with rennet are influenced by the partitioning of mineral salts (particularly calcium and inorganic phosphate) and caseins between the colloidal and aqueous phases of milk. Thus this partitioning of salts between these phases is of major importance to the manufacture of cheese.

The aim of the project is to observe the changes in calcium and phosphate partitioning in aqueous and colloidal phases of skim milk and micellar charge by the addition of salts and varying pH and also to observe its consequences on renneting of casein micelles. The partitioning of calcium and phosphate ions between the serum and the colloidal phases of skim milk, casein micellar size, zeta potential of casein micelles and the consequences on the renneting process were analysed at fixed pH (6.65 ± 0.05) and varying pH by the addition of salts. In this work, the non-pelleted components are regarded as the serum components and the pelleted components as the colloidal components. Changes in the amount are taken to indicate the transfer of constituents between the two phases.

The addition of salts and varying pH resulted in a change in the mineral equilibria. Upon salt addition no significant changes in the effective diameter of casein micelles were observed. This was in agreement with the newest accepted model for casein micelles, where ions have freedom of movement in and out of the micelles without affecting the structure.

Zeta potential is a very important particle property as inter-particle forces, stability of the suspension and the adhesion of particles can be determined by it. Most of the work found in literature has used buffer solutions as the diluant. In contrast, the corresponding supernatant obtained was used in this study, which makes the task more complex.

The ability of casein micelles to preserve their integrity on renneting was determined by the aggregation time which varied with the shifts in mineral equilibria. However, no direct relationship between the charge of the casein micelles and the aggregation time was observed with the addition of phosphate or lowering pH. On addition of calcium, the zeta potential slightly decreased, which is an indication of a structural change on the surface of the micelle. Even though the aggregation times decreased with the addition of calcium, no direct correlation between the charge of casein micelles and the aggregation times was observed.

The quality of the resulting gels treated with rennet can be improved by changing the composition of milk in an appropriate way. Hence this study broadens the knowledge of mineral equilibria which might be advantageous in the cheese manufacturing.

Poster 3
Score

Selective Recovery of Zinc from Hot Dip Galvanising Effluent Streams by Membrane-Based Solvent Extraction

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The hot dip galvanising industry produces large volumes of an acidic effluent that is high in zinc (Zn^{2+}), iron (Fe^{2+}), and chloride (Cl^-) ions. The current method for disposal of the spent pickle acid is to precipitate a worthless, environmentally harmful mixture of iron and zinc hydroxides which must then be disposed of to landfill. This method is not sustainable as there are large associated transport costs, a large amount of water is wasted and there is an unnecessary risk to the community due to transportation via public roads. The recovery of relatively pure zinc (II) chloride or iron (II) chloride from the spent pickling acid therefore offers important benefits in terms of economics, safety and the environment.

Membrane-based solvent extraction has been identified as a potentially suitable method for the selective recovery of zinc over iron (II). In this project preliminary zinc equilibrium data has been collected for two industrial extractants, Tri-butyl Phosphate (TBP) and Hostarex A226 (diisotridecylamine), by performing bench-scale shake tests. Both solvents extract zinc in the form of anionic chlorocomplexes. The data obtained will be used in the design and optimisation of a novel membrane-based solvent extraction process.

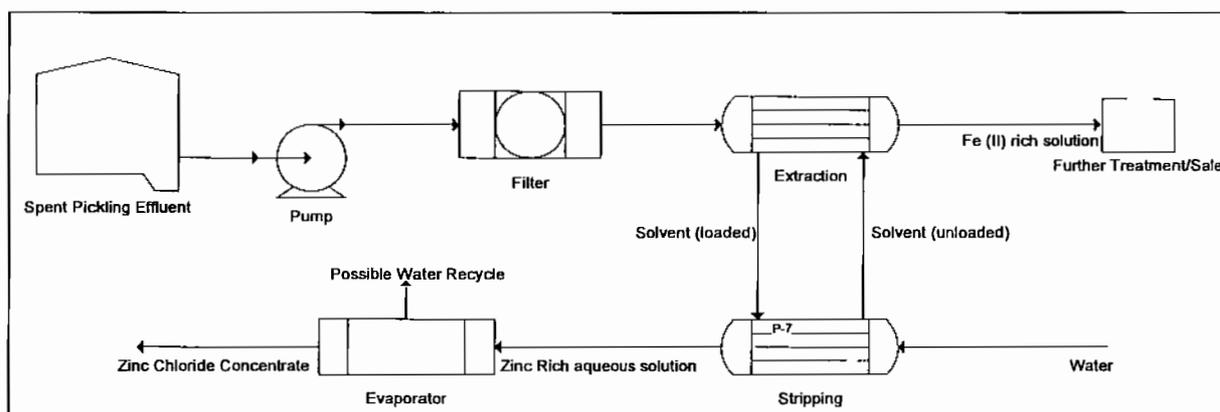


Figure 1 Schematic for potential batch treatment of galvanising pickling effluent using Hollow Fiber Membrane Contactors (HFMC)

Poster 4
Score

Mesoporous Lithium Iron Phosphate as an Electrode Material for High Powered Energy Storage Devices

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Demand for batteries with high power and high energy density has increased significantly over the last few decades due to the increased popularity of portable electronic devices such as lap tops and mobile phones. Lithium ion batteries have fast become the dominant rechargeable portable battery since their introduction commercially in the early 1990's. It is highly desirable to further improve upon the electrochemical properties of these batteries, which is potentially achievable through the design of nanostructured electrodes which enable fast lithium transport.

Nanostructured electrode materials are designed to increase the interfacial surface area between the electrode and the electrolyte. This allows for efficient ion transport, improving the rate capability of the battery. Recent developments of nanostructured electrode materials have moved beyond using nanoparticles and are now incorporating three dimensional nanostructures through the use of structure directing templates. Synthesis of periodic mesoporous materials involves the self-assembly of supramolecular arrays. Ionic or block copolymer surfactants form micellar aggregates which provide a framework for the inorganic precursors. Once the organic template is removed, an ordered mesoporous inorganic material is obtained with high surface area.

Lithium ion batteries are made up of a carbon anode and a metal oxide cathode which provides the source of lithium ions. Lithium cobalt oxide is currently the most common cathode material for commercial lithium ion batteries, however there are problems associated with this material including its high cost, environmental impact and toxicity. Lithium iron phosphate, LiFePO_4 is promising as an alternative cathode material for the lithium ion batteries due to its sound electrochemical properties, low cost and low toxicity.

The aim for this project is to synthesise ordered mesoporous LiFePO_4 particles using amphiphilic surfactants as structure directing organic templates. These nanostructured particles are to be tested as cathode materials for lithium ion batteries to show enhanced electrochemical properties.

Preliminary efforts to synthesise LiFePO_4 using a triblock copolymer, F127, as the surfactant have proven difficult. It has been found that the porosity and nature of the synthesised material is dependent on many parameters including pH, humidity, solvent, drying profiles and calcination temperatures. Surface areas of up to $60 \text{ m}^2/\text{g}$ have been obtained, however further optimisation will be required.

Poster 5
Score



The Complex Rheological Characteristics of Nickel Laterite Slurries

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Nickel is a highly sought after metal that is widely used in chemical industry, the construction industry and for consumer products. Approximately 60% of the world's current nickel resources are in nickel laterite ore bodies. Nickel laterite deposits are formed as a result of tropical weathering which breaks down the sulphide ore to a more stable oxide. Due to the stability of these oxide ores, extreme temperature, pressure and pH conditions are required to concentrate and process the nickel in readiness for smelting. The capital cost of processing equipment that operates under such extreme conditions is considerable. Consequently, minimising the volume of slurry to be processed (increasing the solids concentration) and hence reducing the size of the required processing equipment is very important.

Relatively little is understood about the unusual flow characteristics of nickel laterite slurries other than that they are more difficult to process than the more commonly mined nickel sulphide. A number of studies have already been undertaken looking at nickel laterite rheology at medium to high solids concentrations. The general conclusions have been that nickel laterite samples can exhibit shear history dependence, thixotropy and settling characteristics on a timescale relevant to the measurements. As solids concentrations increase, consistent and meaningful rheological characterisation of these very complex feed slurries becomes very difficult.

The aim of this project is to find the reasons for this unusual behavior as well as industrially relevant ways of characterising it using various rheological, particle sizing and mineral composition techniques. The range of samples investigated covers those with relatively simple flow behaviour and those with complex flow behaviour. By looking at the physical and chemical characteristics, of these various nickel laterite samples from around the world, it is hoped that the specific factors that affect the complex flow behaviour can be identified.

Poster 6
Score

Use of Functionalised Alkanethiol Monolayers to Study the Wetting of Heterogeneous Surfaces

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Many industrial processes such as micro fluidics, coal recovery, high speed coating, electronic display technologies, oil recovery, lubrication, and plant protection involve controlled wetting. The interaction between a liquid and a solid surface at the molecular level is the key to understanding wetting phenomena.

The wetting of a surface is influenced by heterogeneity both physical and chemical as well as by the type of functional groups exposed to the contacting liquid. The work of adhesion, W_{sl} of a liquid to a solid is given by

$$W_{sl} = \gamma_{lv} (1 + \cos \theta)$$

The surface free energy γ_i of a phase i is the consequence of all the electromagnetic interactions whether Lifshitz-van der Waals (non polar) interactions or polar (acid base) interactions:

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB}$$

The van Oss Chaudhary and Goodman model allows one to determine the work of adhesion of two interacting surfaces, which is given by

$$W_{ad} = 2 \left((\gamma_s^{LW} \gamma_l^{LW})^{1/2} + (\gamma_s^+ \gamma_l^-)^{1/2} + (\gamma_s^- \gamma_l^+)^{1/2} \right)$$

For an apolar liquid on a solid surface

$$W_{ad} = (\gamma_s^{LW} \gamma_l^{LW})^{1/2}$$

This work here describes the use of model smooth surfaces to investigate static and dynamic wetting. Mixed monolayers of alkanethiol molecules with different tail groups on a nano-scale substrate will be produced by self assembly processes. These surfaces will be characterised using AFM, ToF-SIMS, XPS, FTIR and the contact angle measurement will be done using sessile drop and Wilhelmy balance techniques. This study of mixed alkanethiolate SAMs on smooth gold surfaces is used to investigate how the surface composition (with different functional groups) affect static and dynamic wetting. The goal is to predict dynamic wetting behaviour knowing the strength of interactions between the liquid and the solid, combined as the liquid properties.

Poster 7
Score

The Phase Behaviour of Isoprenoid Branched Urea Based Surfactants

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Urea based surfactants are a class of amphiphiles containing urea as a headgroup and a hydrophobic tail. Urea is a small organic molecule consisting of a carbonyl group and two amine groups. The carbonyl group in the urea moiety functions as a hydrogen bond acceptor that is able to accept both of the neighbouring nitrogen donors to form a bifurcated hydrogen bond. This strong urea hydrogen bonding interaction plays a dominant role in the physico-chemical properties of urea based surfactants. Previous studies on linear chain urea based surfactants showed that they were not capable of forming liquid crystalline phases. Instead, three other phases formed in the linear alkyl chain urea surfactant water mixtures; namely a crystalline solid, a dilute aqueous solution of the neat surfactant and an isotropic liquid. However, recent studies illustrate that the impact of the urea intermolecular interactions can be reduced by introducing a long chain with either an unsaturation or a terpenoid hydrophobe. This promotes the formation of liquid crystalline phases. In this work, the physicochemical properties of urea surfactants with terpenoid chains were further investigated.

The thermotropic behaviour of 3,7-dimethyloctyl urea, 3,7,11-trimethyl-dodecyl urea and 3,7,11,15-tetramethyl-hexadecyl urea, was determined using Differential Scanning Calorimetry (DSC). The binary surfactant-water phase behaviour of these three surfactants was also characterised. Unlike 3,7-dimethyloctyl urea, dodecyl urea with three methyl branches behaved similarly to the hexadecyl urea with four methyl branches. Both formed an inverse hexagonal phase, and this phase was stable in excess water and present at both room and physiological temperature. Colloidal dispersions of these inverse liquid crystalline phases have potential in drug delivery applications through the encapsulation of small molecular therapeutic agents.

Poster 8
Score

An AFM Study of Nanobubbles on Graphite: The Effect of Alcohol, Salt and Gas

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Previous experimental results have indicated the existence of a long range interfacial force between hydrophobic surfaces which is not included in the classical theories of colloid science. The mechanism of the hydrophobic force is at yet unknown, but different theories have been proposed to explain the existence of the force. One of these theories, the nanobubble theory, is the most popular at the present time. The force is thought to arise from the bridging interaction of nano-sized bubbles on the hydrophobic surfaces. A number of experimental results agree with the existence of nanobubbles (e.g. variable range of the force, influence of gas and images of nanobubbles), but despite this there is still controversy over nanobubbles. The main problem with the theory is the stability of the bubbles. For bubbles of this size the Young-Laplace equation predicts very high internal gas pressures, therefore the bubbles should dissolve within milliseconds.

The aim of this study is to examine the influence of different experimental parameters (alcohol, salt and gas) on nanobubbles. Presently, tapping mode AFM images have been taken of nanobubbles on a graphite surface in water/alcohol mixtures. It was found that the size of the nanobubbles increased as the concentration of water increased. The type of alcohol used was also found to influence the size of the bubbles. Further experiments will be carried out with different amounts of gas and salt. By changing the amount of gas in the liquid phase it can be proved that the artefacts on the surface are indeed gas bubbles. As the size of larger bubbles is influenced by the type and concentration of salt, it is expected that the presence of salt will also influence the size of the nanobubbles. A manipulation of these different parameters will give a greater insight into the stability of these bubbles and why the Young-Laplace equation does not extend to bubbles of nanometre scale.

From a better understanding of the hydrophobic force this work will help in a number of applications such as froth flotation, colloid destabilisation, emulsion flocculation, rheology control and biotechnology involving hydrophobic surfaces.

**Poster 9
Score**

Sonochemical Synthesis of Pt / Ru Composite Nanoparticles

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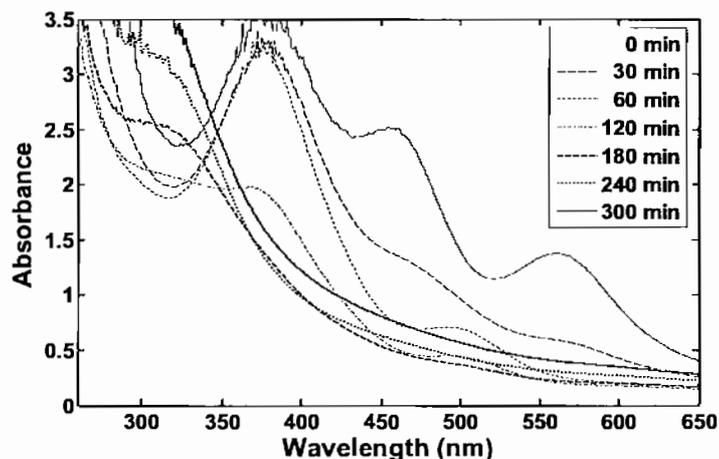
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It is well known that the catalytic performance of direct methanol fuel cells (DMFC) strongly depends on the size of the precious metal catalyst particles. Composite Pt-Ru catalyst particles have attracted a considerable amount of attention in recent years as the ruthenium helps to protect the platinum catalyst from CO poisoning. Conventional preparation techniques often do not provide adequate and effective control of particle size and usually involve undesirable stabilisers for fuel cell application. It is well known that ultrasonic irradiation of aqueous noble metal solutions results in nanometre sized metal colloids.

In our study, Pt-Ru composite nanoparticles were synthesised by ultrasound induced reduction of aqueous solutions of K_2PtCl_4 and $RuCl_3$ using a 213 kHz ultrasonicator. As shown in the figure below, after 5 hours of sonication, the absorbance bands arising from Pt(II) and Ru(III) disappear and the composite Pt-Ru nanoparticles are formed. The reduction of Ru(III) in the composite system is accelerated dramatically, compared with the reduction of Ru(III) by itself with the sonication time decreasing from 12 hours to 5 hours. It has been concluded that Pt nanoparticles which are formed first play an important role in catalysing the formation of Ru nanoparticles. TEM images of the Pt and Ru particles in the composite colloid indicate typical diameters less than 10nm.

This is the first time that nanosized bimetallic Pt and Ru composite particles have been prepared by sonochemical reduction. The results of this study are potentially important in enhancing the DMFC performance.



The absorption spectrum of a solution of 1 mM K_2PtCl_4 , 1 mM $RuCl_3$ in 200 mM propan-1-ol 8 mM SDS and 0.1 M $HClO_4$ solution as a function of sonication time. The solution was saturated with argon gas.

Poster 10
Score

Nanorheology: A Quantitative Atomic Force Microscopy Technique to Dynamically Study Properties of Small-Volume Materials

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The atomic force microscope (AFM) has previously been applied to the measurement of surface forces (including adhesion and friction) and to the static investigation of material properties. By the use of a dynamic technique, one can measure material properties with sensitivities several orders of magnitude greater than their static counterparts. We use a modified AFM that allows dynamic and static measurements to be made simultaneously. The dynamic information is obtained from the system response to an applied sinusoidal oscillation. We describe here the calibration of the instrumental response to oscillation, which enables us to extract quantitative data. Typically this technique has been used to study the dynamic behaviour of highly confined liquids. In particular, we can probe the existence of hydrodynamic slip at the solid-liquid interface with considerable sensitivity. Examples of this technique will be illustrated by some recent experimental results.

**Poster 11
Score**

Oscillatory Mode Evanescent Wave Atomic Force Microscopy for Localised Refractive Index Measurements

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Optical components have been integrated into an Atomic Force Microscope (AFM) to facilitate the measurement of the local refractive index of a sample near a surface. An evanescent wave is generated under total internal reflectance at the surface of a prism, and the AFM tip is then used to scatter the wave. Our spatial resolution in refractive index normal to the interface is comparable to the spatial resolution in force in a conventional AFM. We use an oscillatory mode (similar to tapping mode in AFM measurements) to significantly improve signal-to-noise.

Poster 12
Score

Phase Separation in Mixed Monolayers: A Model System for the Development of Novel Membranes

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Membrane technology will play a crucial role in the development of microscale medical technology such as lab-on-a-chip devices. These new applications require fabrication of functionalised membranes on molecular level. This study explores Langmuir-Blodgett technology as a means to construct mixed organosilane monolayers as a model for ultrathin, robust, functionalised membranes. A number of chemical variables were investigated in addition to external forces such as surface pressure, temperature, and the application of electric fields. Molecular chain length, temperature, and surface pressure were found to have the greatest influence on the morphology of phase-separated organosilane monolayers. Novel interpretations were offered for the effects of temperature and surface pressure. We concluded that organosilanes were capable of creating robust monolayer films with excellent mechanical stability, however, their use as membrane materials is limited due to rapid uncontrolled polymerisation.

Poster 13
Score

Al-Containing Porous Titanium Dioxide Networks: Template/Sol-Gel Synthesis and Photocatalytic Activity

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As a wide band-gap and non-toxic semiconductor, titanium dioxide has been studied widely in the past in a range of scientific and industrial fields, especially for photocatalytic applications¹. The photocatalytic activity of titanium dioxide depends on various parameters, such as the surface area, the addition of dopants and their concentration, the surface acidity and the surface sorption properties. Doping with a second metal ion or mixing with a second metal oxide will result in changes to the surface area, surface properties and the band-gap of TiO₂^{2,3}, hence greatly affecting its photoactive behaviour. Recently alumina/titania or Al-doped titania systems have been employed for a range of applications.^{4,5} However, relatively few studies have detailed the influence of the addition of alumina on the photocatalytic behaviour of the Al/Ti samples.

In this study the aim is to determine the most effective Al/Ti ratio for photocatalytic activity when using a mixed precursor sol-gel synthesis route. Here agarose gels have been used as template allowing designed pore structure and pore size of the final metal oxide networks. By infiltrating mixed alumina and titania precursor solutions into the agarose gel and then conducting hydrolysis and condensation reactions, porous networks of Al-containing titania are achieved. The amount of aluminum added to the titania system was studied from 0 - 10 wt. % (where wt. % corresponds to the Al₂O₃ x 100/Al₂O₃+TiO₂ expected from the initial precursor concentrations). The morphology of the samples, the crystallisation characteristics and surface properties (as a function of both wt. % and heating temperature) are studied along with the photocatalytic activity of the samples, measured by the degradation of methylene blue.

It is found that doping with Al to 4 wt. % decreased the size of anatase crystal for samples heated to 450 °C, with a corresponding increase in the surface area of prepared materials. However, at aluminum quantities greater than 4 wt. % the anatase crystal size remained relatively constant, while the surface area continued to increase. For the samples with aluminum quantities greater than 4 wt. %, α-Al₂O₃ was observed when samples were heated up to 780 °C. Hence it is concluded that the maximum Al-doping using this preparation method was 4 wt. %; for increased quantities of Al, amorphous Al₂O₃ was formed in the sample. The presence of the amorphous Al₂O₃ hindered the anatase-rutile transformation when the sample was heated to higher temperatures. For the photodegradation of methylene blue, the 4 wt. % sample (450 °C) was most active, with an efficiency nearly 4 times that of the non-doped sample.

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Poster 14
Score

Surface Tension of the Air-Water Interface in the Presence of Nanoparticles, Cationic and Anionic Surfactants; an Indication to Foam Stability

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There has been increasing attention in recent years, to the use of nanosized particles as stabilisers in emulsions and foams. Work pointedly looking at particles as foam stabilisers has been accelerated due to successes in using particles to stabilise emulsions. However, areas such as flotation have indirectly considered the role of particles in stabilising foams and froths for many years. In both foams and emulsions, particles of intermediate hydrophobicity (say contact angles of around 90°) increase stability by accumulating at the phase interface and forming a steric barrier. In foams, additional stability can be created from dispersed particles inhibiting inter-film liquid drainage between bubbles. Another possible mechanism for stability, and one of interest here, is the role of particles in effecting the surface tension of foams and emulsions stabilised by traditional surfactants.

There is evidence in the literature that nanoparticles can synergise with surfactants of opposite charge, leading to significant decreases to the air-water surface tension in foams, compared to surfactant alone. This study clarifies and further categorises this behaviour, from surface tension measurements of the air-water interface. Hydrophilic nanosilica (15-100nm), cationic dodecyltrimethylammonium bromide (DTAB) and anionic sodium dodecyl sulfate (SDS) surfactants are added to the aqueous solution either separately or in combination. Particles of varying size are used; giving an indication of the effect of changing particle surface area and volume fraction in surfactant-particle mixtures, and, if time permits, further effects of salt addition to the resultant surface tension will be measured. From these results, theories describing the mechanisms of the observed synergistic behaviour are considered. Also, results are highlighted in terms of indications to general foam stability. The findings have important consequences for research into the use of nanosilica as a foam stabiliser, but also lead to insight into the behaviour of fine particles in general froth flotation.

Poster 15
Score

Thickener Dewatering Optimisation in the Minerals Industry

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An important requirement in the chemical, wastewater and mineral industries is the ability to separate a suspension into its respective solid and liquid constituents. This separation often occurs in thickeners. In the thickener, a dilute particulate suspension settles under gravity, creating a compact bed and at the same time producing clarified liquid.

A raking mechanism is used in thickeners and serves two purposes. The first is to transport material to the discharge point, and the second is to improve dewatering in the sediment. The raking mechanism introduces a shear force which plays an important role in the thickening process and affects dewatering properties.

Shear in a feed well for example, increases the collision rate between particles and helps disperse the flocculant. However, relatively little is known about how shear forces affect dewatering when applied to aggregates post flocculation, i.e. as they dewater. Some studies show that high shear rates can be detrimental, leading to structural deterioration of the polymer flocculated network. On the other hand, several studies show that vast improvement in dewatering behaviour is achievable by gently stirring the sediment.

The aim of this study is to quantify the relationship between shear force and the dewatering process for a range of floc formation conditions and flocculant types. Initial work has been conducted on the formation of a range of flocs, all made with calcite, but with very different settling and shear stability attributes. To date, settling tests have been used as the main screening mechanism. Fluidisation and shearing of the flocs to establish the dynamics of the floc re-arrangement process is the next stage in this study. This will involve shear tests on suspensions across a range of concentrations as a function of time. The study combines transient settling and fluidisation tests in the presence of a shear field, using a pipe reactor to generate flocs and a fluidisation cell incorporating a couette shear module.

Poster 16
Score

Assembly of Nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ via Sol-Gel Templating

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Lithium titanate, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, has unique features that make it very attractive as a potential negative electrode in lithium ion batteries. It has a flat operating voltage during charge-discharge cycles, and negligible capacity fading. The flat operating voltage is believed to be the result of two phase lithium intercalation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - $\text{Li}_7\text{Ti}_5\text{O}_{12}$. Its negligible capacity fading is associated to the fact that the dimension of the material is almost constant during the electrochemical reaction, thus $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is called a 'zero strain' insertion material.

Research has shown that the charging capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be improved by at least 30% by it having nanocrystalline morphology¹. An ordered mesoporous structure is expected to provide an increased surface area for the electrode-electrolyte interface, as well as a smooth passage for the lithium ions to intercalate from one electrode to another in a rocking chair battery.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ is normally synthesised via solid state reaction, which requires the precursors to be heated up to a high temperature (>1000°C) for a long time (16-24 h). An alternative is to use a sol-gel synthesis method, which is renowned for being inexpensive, simple and requiring relatively low temperatures. Sol-gel techniques also provide good control over the morphology and stoichiometry of the final products. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesised by sol-gel methods is normally obtained after heating at 500-800°C for 2-4 hours^{2,3}

The aim of this study is to build an ordered mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ structure using a sol-gel method. Surfactant will be used as a template to control the morphology. In order to maintain the structure, optimisation of several parameters in sol-gel synthesis will be required. The key parameters include hydrolysis and condensation rate, aging, drying and calcination.

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Poster 17
Score

Physical Roughness and Dynamic Wetting

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The wettability of a surface by a liquid dominates the dynamic behaviour of droplets formed on that surface. Understanding and predicting the wettability of liquids on surfaces is therefore of great technological importance to many industrial processes as well as the prospective development of engineered surfaces capable of performing nano-scale liquid manipulation.

Wetting is where a liquid moves across a solid surface entirely, covering it and displacing a vapour phase that had previously been in contact with the solid. The 'three-phase contact line' is where the boundary between the liquid and vapour comes into contact with the solid surface and a 'contact angle' is formed between this boundary and the solid surface.

The static and dynamic behaviour of the three-phase line and the contact angle formed is influenced both by the physical and chemical forces between the phases and also other mechanical forces on the system, such as vibration of the solid substrate.

Hysteresis of the contact angle may be observed in the transition from one dynamic state of liquid motion to another. For example, a contact angle greater than in the static equilibrium state can occur in the transition from the static to dynamic wetting conditions. This happens while the three-phase contact line remains stationary and appears 'pinned' on the solid surface prior to the liquid-vapour front being forced to advance.

This hysteresis is considered to reflect an underlying heterogeneity of the surface roughness and/or chemistry. We demonstrate the behaviour of the dynamic contact line in the presence of defined physical roughness and homogeneous surface chemistry. This research therefore addresses how physical roughness alone influences dynamic contact angle and contact line behaviour, and focuses on the level and nature of that roughness where it influences dynamic wetting.

We prepare [locally] uniform and non-uniform surfaces, graduated and ungraduated across the samples by using differing sizes and shapes of particles, and by other means to prepare samples that can then be coated to control for surface species. New experimental techniques for the purpose of addressing these issues are described in the poster, in addition to established experimental techniques such as the Wilhelmy plate and moving rod apparatus used for dynamic contact angle studies.

Poster 18
Score

Physico-Chemical Studies of Milk Proteins during Powder Rehydration

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Bovine milk is a familiar yet extremely complex food, consisting of over 100 000 different molecular species. It contains an oil-in-water emulsion of fat globules and a colloidal system of protein associations (casein 'micelles') suspended in an aqueous solution containing lactose, soluble proteins, minerals and vitamins. It can be processed in a multitude of ways to produce the great variety of available dairy products. Among the most important products is the range of dehydrated milk powders, produced by water removal in a process known as spray-drying. The removal of water confers extended shelf-life and facilitates economical transportation. These powders are used in a multitude of food applications and represent a substantial portion of Australia's dairy exports.

Despite the importance of these powders, little has been learnt about the mechanisms and kinetics of establishing equilibrium upon rehydration in water. Of particular interest are the calcium-laden casein micelles which represent 80% of the protein in milk. This important polydisperse system of sub-micron-sized particles appears difficult to correctly reestablish in milk reconstituted from powder. Preliminary results suggest that the casein micelles aggregate during the dehydration process and do not return to their original state upon rehydration.

This project has employed dynamic light scattering to monitor changes in the particle size distributions of the casein micelles, and turbidity measurements to follow the kinetics of the disaggregation process. These techniques have allowed us to investigate the effects of dilution and shear on the rehydration process, giving new insights into the behaviour of the casein micelle system. The project has been funded by the Dairy Ingredients Group of Australia (DIGA) to develop increased understanding of milk powder rehydration which can be used to direct process improvements for producing better powders.

Poster 19
Score

Template/Sol-Gel Synthesis of Aluminium, Gallium, and Indium Oxide-Modified Titanium Dioxide Structured Materials

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Titanium dioxide is a semiconducting, wide energy band gap metal oxide, which is extensively employed in the synthesis of photocatalytic materials. As such, titanium dioxide finds many photocatalytic applications, including the degradation of organic pollutants, and the photoelectrolysis of water to produce hydrogen. Titanium dioxide is also suitable for use in dye-sensitised solar cells (DSSC).

Doping titanium dioxide with a second metal is known to affect the photoactive properties of titanium dioxide. It is also possible to regulate the crystal phase transitions, increase the solar spectrum range of the material, and change surface area and surface properties by doping.

The aim of this study is to dope (0.0-9.1 mol %) the titanium dioxide matrix with selected Group III metals – aluminium, gallium or indium. Templating and sol-gel synthesis are used to achieve this. A titanium dioxide precursor is infiltrated into the pores of 3 wt. % agarose gel which, following hydrolysis and condensation reactions, forms amorphous titanium dioxide. Calcination of the amorphous titanium dioxide/gel structure removes the organic template, leaving a porous and crystalline titanium dioxide. A Group III metal is introduced either by mixing into the titanium dioxide precursor, or by dissolving into the hydrolysis solution. Overall, it is expected that the doping will increase the photocatalytic and photovoltaic efficiency of titanium dioxide-based materials.

Characterisation of the synthesised materials is by thermogravimetric and differential thermal analysis, nitrogen gas sorption for specific surface area, x-ray diffraction to determine crystallisation properties and scanning electron microscopy. Results suggest that increasing the concentration of aluminium in the titanium dioxide matrix increases the material's surface area, and also increases the temperature at which crystallisation occurs.

Poster 20
Score

Evanescent Wave AFM Measurements of Forces in Polymer Solutions

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The ability of functional polymer layers to modify surfaces has potential applications in colloid stability, antifouling coatings, enzyme immobilisation, and a range of other areas. Most polymers developed for control of surface properties rely on steric forces to produce a strictly repulsive force between surfaces of interest.

To gauge the potential effectiveness of such layers, surface forces are commonly measured using an atomic force microscope (AFM). A significant problem with this is the inability of traditional AFM techniques to determine true separation between surfaces in the presence of an adsorbed polymer layer. In response to this problem, an Evanescent Wave AFM (EW-AFM) was developed, which uses evanescent wave scattering from an AFM cantilever tip, to determine the actual separation between the tip and a surface while normal force measurements are taken. Studies with EW-AFM using polymer films showed significant enhancements over traditional AFM.

Current work using EW-AFM concerns polybetaines, a class of polymers under study as antifouling coatings for biomedical applications. Their zwitterionic sidechains cause polybetaines to be insoluble in pure water, but they become soluble due to chain expansion in the presence of salt. The unusual behaviour of polybetaines may aid the formation of an appropriately dense polymer layer to prevent protein adsorption and biofouling.

**Poster 21
Score**

Measurement of Lactose Crystallinity Using Raman Spectroscopy

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Knowledge of the crystallographic form of actives and excipients in solid dose forms is a necessity for the pharmaceutical industry. The ability of a compound to crystallise into two or more chemically identical, yet functionally or behaviourally different polymorphic arrangements or into an amorphous form can greatly affect formulation, stability, and efficacy. Dry powder inhaler (DPIs) formulations for pulmonary delivery of therapeutics drugs generally consist of micronised drug (1-5 μm) and an inert coarse carrier particle (50-200 μm) which aids the flow and dispersion of the highly cohesive drug particles. The carrier commonly used is α -lactose monohydrate. The micronisation process used to control the carrier size is known to induce the formation of amorphous regions on the carrier surface. The amorphous state is a thermodynamically unstable state with a higher energy level than the crystalline forms, leading to problems regarding stability, hygroscopicity and drug delivery consistency.

The objective of this study was to demonstrate the potential of Raman spectroscopy (RS) as a valid method for determining the crystallinity of lactose powders. Crystalline α -lactose monohydrate and amorphous lactose were prepared by precipitation and lyophilisation respectively. The anomeric forms were confirmed using differential scanning calorimetry (DSC) at a rate of $10^\circ\text{C}/\text{min}$ and heated to 250°C . The Raman spectra and depolarisation ratios (ρ) of the crystalline and amorphous samples were obtained using a Raman microscope with a 782 nm diode laser coupled to an optical microscope. Measurements were taken using a grating scan over the region $50\text{-}1500\text{ cm}^{-1}$. Depolarisation ratios were determined using polarisation filters and comparing peak heights.

Samples confirmed by DSC displayed visually different Raman spectra; α -lactose monohydrate displayed clearly defined peaks over the entire fingerprint region whilst amorphous lactose displayed wider peaks and an overall decrease in peak intensities. At the prominent Raman bands 865 cm^{-1} and 1082 cm^{-1} , significant differences in ρ values were observed for crystalline (0.80 ± 0.07 , 0.89 ± 0.06 respectively) and amorphous samples (0.44 ± 0.07 , 0.51 ± 0.10).

The depolarisations ratios obtained for crystalline and amorphous lactose are not as one would expect; the Raman bands in the crystalline sample are significantly depolarised, while those in the amorphous sample are polarised. There are two possible explanations: firstly, α -lactose has low symmetry meaning it is quite complex, with 129 Raman-active vibrational groups, and second, the ability of α -lactose to optically rotate the plane of polarised light could have the effect of depolarising the bands in the crystalline sample by rotating the incident light. Despite these unpredicted results, RS was demonstrated as a potential technique in determining the crystallinity of lactose powders.

Poster 22
Score

The Characterisation of Leachates Derived from Thermally Altered Plant Matter

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Bushfires are a menace to people, animals, forests and property as well as the economy. After bushfire events, residues including char, ash and chemically diverse humic substances persist in affected topsoils and inevitably enter waterways after precipitation. This study investigated the chemical structure of leachates derived from fire residues in an attempt to elucidate humic functionality in aqueous systems. Plant matter from five different species – *Eucalyptus sideroxylon*, *Pinus pinaceae*, *Isolepis nodosa*, *Acacia pycnantha* and *Cassinia arcuata* – was thermally altered at 150 °C, 300 °C and 400 °C under oxidising and reducing conditions. The leaching of humic compounds from fire residues into water was conducted over 96 hours. During the leaching period solution concentrations of humic was measured using High Performance Liquid Chromatography, and the chemistry of the leachates characterised using Attenuated Total Reflectance Fourier Transform Infrared spectroscopy and UV spectroscopy. The nature of the leached humic material depended on the originating species and burning conditions. Humic materials dissolved from the residues of the Australian native species (*Eucalyptus sideroxylon*, *Acacia pycnantha* and *Cassinia arcuata*) were generally more aromatic and conjugated than the materials leached from *Pinus pinaceae*, *Isolepis nodosa*. Leachates became more alkaline and inorganic in character as burning temperature increased. Results show that water conditions following a fire will be affected by the nature of the material burnt and the burning temperature.

Poster 23
Score

Probing Membrane Rafts Using Surface-Selective Spectroscopy

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One of the major functions performed by biological membranes is signal transduction. In signal transduction and immune response, a key role is played by the conformation and oligomerisation of biological macromolecules at the cell membrane. Perturbations to protein-protein interactions can cause abnormalities in signalling networks and can lead to diseases such as cancer. It has been suggested that within the cell membrane, cholesterol and sphingolipids spontaneously associate with one another to form platforms for the segregation of trans-membrane proteins and that these segregated domains mediate signalling by altering protein-protein interactions and protein conformations.

The main aim of this study is to investigate the segregation and conformation of proteins upon adsorption to the cell membrane using time-resolved evanescent wave-induced fluorescence spectroscopy (TREWIFS). TREWIFS is an excitation technique that is based upon total internal reflection at an interface. The evanescent wave resultant from total internal reflection propagates finitely into the medium of interest (proportional to the angle of incidence and refractive index of the medium). This makes TREWIFS a surface-specific technique as well as one that enables depth profiling through altering the angle of incidence. Physiological systems are very complex and the biophysics of such systems is not fully understood. Thus, a single-component supported lipid bilayer is prepared as a 'membrane mimic'; the platform for adsorption of a short-chain peptide. This allows a simplified system (that retains some of the characteristics of physiological systems) to be investigated.

The outcome of this study is important in understanding the signalling networks in cell systems and potential for the development of cancer and other diseases. Such systems have not been greatly explored as a whole and through the use of TREWIFS, conformational information that has been previously unobtainable can be observed.

Poster 24
Score

Dynamic Wetting of Chemically Heterogeneous Surfaces

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The wetting of solid surfaces is central to many processes, both natural and man-made. As the wetting of surfaces and coating processes involve the flow of fluid over the solid, the contact angle is often a dynamic quantity. It depends on the speed at which the three phase line advances or recedes. A major limitation in the current theories of dynamic contact angle is that they consider the wetting of surfaces which are smooth and homogeneous. In practical situations this is rarely the case. Solid surfaces are normally heterogeneous.

The objectives of this work are to investigate the influence of chemical heterogeneity on dynamic wetting and to develop a predictive model. Key information on the velocity dependence of the dynamic contact angle on heterogeneous surfaces will be acquired. Initially the influence of a single heterogeneous patch will be investigated. Then the wetting behaviour of regular arrays and randomly distributed defects will be examined. The work will be important to the coating industry as it will give an insight to the velocity dependence of the dynamic contact angle on heterogeneous surfaces, relating the chemical identity of the heterogeneities, as well as their size and distribution, to the velocity of wetting.

Poster 25
Score

Nanolithography and Protein Patterning of Low-Fouling Plasma Polymer Multi-Layer Coatings

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The patterned immobilisation of proteins on surfaces has widespread applications ranging from fundamental studies in cell biology to the development of high-throughput 'biochip' and 'bioarray' platforms. The goal is to control bioreactions and cell attachment, generate miniaturised arrays and patterns of proteins for use in immunoassays, protein screening and numerous other applications.

A variety of techniques have been employed for the controlled patterning of proteins including ink-jet printing, microcontact printing, electron, photo and ion-beam lithography and microfluidic channel networks. These techniques however do not allow for the accurate sub-micrometer patterning of proteins on surfaces. Scanning probe microscopy allows for the generation of patterns on the nanometer scale due to its very high spatial resolution.

In the present work a technique is introduced to produce nanometer-sized protein patterns. The method involves the generation of multi-layer plasma polymer (pp) films consisting of a protein fouling heptylamine (HA) pp base surface and a low-fouling (DG) pp top surface. The DG pp surface is then selectively removed through the use of atomic force microscopy (AFM) nanolithography. This allows the subsequent selective immobilisation of proteins from solution with nanometre scale spatial resolution. The resulting templates and protein patterns were characterised using AFM, X-Ray Photoelectron Spectroscopy (XPS), time-of-flight Secondary Ion Mass Spectroscopy (ToF-SIMS) and Fluorescence Microscopy (FM).

Poster 26
Score

Comprehensive Dewaterability Characterisation of Incompressible Materials

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Accurate characterisation of the quantities governing solid-liquid separation is critical to the success of any attempt to employ theoretical tools for design or optimisation of dewatering operations. Depending on the physical characteristics of the solid-liquid system in question, such as the compressibility of the solid network formed, different characterisation challenges exist. During a case study on the pressure and vacuum filtration of iron ore, which forms dense, incompressible sediments, a number of challenges were encountered. This article details the strategies employed in refining and validating existing dewaterability characterisation techniques that had been previously developed for flocculated, compressible networks, so they could be used on incompressible materials for the first time.

The dewaterability characteristics of a solid-liquid system can be defined in terms of compressive yield stress, $P_y(\phi)$ and hindered settling function, $R(\phi)$. There are many experimental approaches available for dewaterability characterisation at high and low solids volume fractions. In this study, stepped pressure filtration and settling test techniques were employed for high and low solids volume fraction respectively. However, as the use of stepped pressure filtration for $R(\phi)$ determination at high solids concentrations was not viable for iron ore due to its quick settleability, a modified single pressure permeation test, based on a traditional Darcian permeability test, was developed.

The data set from the filtration tests and from a single transient settling test was then used as input for the proprietary software package, P527 – BSAMS. The BSAMS software was originally developed to determine the gel point, compressive yield stress and hindered settling of flocculated or coagulated systems from a combination of transient settling and filtration testing. However, given the untested nature of BSAMS for incompressible systems, an alternative approach was then adopted to independently determine gel point, compressive yield stress and hindered settling function for low solids volume fraction from a set of batch settling tests. The data generated using the alternative approach indicated that the iron ore fines exhibited a weak level of structure at lower solids concentrations which rearranges easily to form a dense bed with low levels of applied pressure. There was a significant difference observed between the hindered settling function determined independently by BSAMS and transient batch settling test. To ascertain which of the hindered settling function data sets is the correct one, simulations of experimental filtration tests are currently underway.

Poster 27
Score

Polymer Adsorption on Heterogeneous Surfaces

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The collection of mineral particles in flotation relies on the bubble-particle attachment process. Polymeric depressants reduce gangue mineral flotation by increasing the bubble-particle induction time, through an alteration of wettability, for successful bubble-particle attachment. Induction time is the amount of time it takes for rupture of the intervening water layer and formation of a stable three-phase contact. The formation of a thick, hydrated, hydrophilic polymer layer on a gangue mineral surface increases the induction time to a point beyond the average contact time between bubbles and particles in a flotation cell.

For composite particles, with surfaces that have exposed valuable and gangue mineral phases, or so called "pure" particles with surface regions that are oxidised or covered metal ion hydrolysis, products are problematic in this regard for thin film rupture can be rapid, and a stable three-phase contact line easily formed. In some cases the presence of heterogeneities can retard the formation of a three-phase contact line, depending on the size and the distribution of the heterogeneity.

The aim of this project is to study the effect of surface heterogeneity, i.e. real surfaces, on layer thickness and hydrophobicity of an adsorbed polymer in an effort to ensure that effective depressants can be developed for heterogeneous/composite surfaces.

The surface modification will include several major steps:

1. A silicon wafer will be covered with layer of gold.
2. The surfactant will be adsorbed on the gold surface using 2 different methods: SAM and LB-monolayer techniques:
 - a. Surfactant with a thiol group at the one end and with methyl groups ($-\text{CH}_3$) at the other the end) for a hydrophobic effect will be adsorbed;
 - b. Surfactant with a thiol group at the one end and with a carboxylic group at the other end for a hydrophilic effect;
 - c. A mixture of both surfactants (with various concentration ratios) will be used also for producing a "patched" surface with differences in wetting properties.
 - d. The hydrophobic / hydrophilic properties of the surface will be determined by Sessile drop measurements.
3. The surface then will be placed in a solution of polyacrylamide (with hydroxide groups substitutions) to investigate the adsorption of this polymer. The main goal is to model a "real particle" in a flotation process. This particle has both hydrophilic and hydrophobic sections on the surface and we will try to predict its behaviour.

The adsorption of the polymer will be investigated using Atomic Force Microscopy, Infrared microscopy and adsorption curves.

The wetting properties of the modelled surface will be measured by the sessile drop technique.

Poster 28
Score

Synthesis of Phosphonate Copolymers as Titania Pigment Dispersants

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Titania pigment has a wide range of applications such as paints, plastics, paper making, cosmetics and pharmaceuticals. Throughout titania pigment processing dispersion is important to ensure discrete pigment particles for application of inorganic coatings. The raw pigment is slurried and coated with thin layers of alumina, or silica followed by alumina, to improve pigment gloss and degradation resistance.

Polyphosphates are commonly used industrially to provide electrostatic stabilisation during the inorganic oxide coatings applications. Polyphosphates however show instability under processing conditions of high temperature and acidic pH, leading to a loss of dispersion stability and higher aggregation levels in the aqueous pigment slurry. Any new dispersant needs to be stable across a pH range of 3-11 and between 30-100 °C to withstand the processing conditions for silicate and aluminate deposition. Phosphonates offer greater thermal and pH stability than phosphates due to the presence of the P-C bond. Consequently they can be considered as a potential replacement for the polyphosphates currently used.

In the present work, carboxylate-phosphonate copolymers have been synthesised by two different methods: free radical polymerisation in the presence of sodium persulfate and grafting phosphonates groups onto a functional polymer, polyethylenimine. The synthesised copolymers were analysed by NMR, FTIR and GPC. A range of polymers varying in carboxylate-phosphonate copolymer ratios were synthesised by free radical polymerisation however ratio control was difficult. Initial characterisation has shown the presence of unreacted starting reagent despite precipitation or dialysis. Ionic interaction between polymer and starting reagents may be causing purification difficulties.

Poster 29
Score

New Emulsifying Agents for Food Applications

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Emulsions and emulsifying agents are important food additives and can be applied to various types of commercial products for the benefit of consumers. Proteins are naturally occurring surfactants and as such are widely used as emulsifying agents. However, changes in conformation with heating, pH and the presence of organic solvents make proteins unsuitable for use in certain situations. For some years now, it has been well established that the conjugation of proteins and polysaccharides results in surfactants with improved functional properties.

The main aim of this project was to synthesise and investigate the emulsifying properties of sodium caseinate (protein)-dextran (polysaccharide) conjugates derived by the Maillard reaction. Other objectives included the characterisation of the starting materials and conjugates, as well as analysing their adsorption at the air/water and oil/water interfaces. Three dextrans with molecular weights of; 10k (D10), 35k (D35) and 65k (D65) were used.

Conjugates were prepared by the solid phase Maillard reaction (condensation reaction between a primary amine of protein with a reducing sugar) between a freeze dried solution of sodium caseinate (NaC) and dextran at 65 °C and 70% relative humidity. The degree of conjugation of the dextrans to sodium caseinate was determined by analysis for the unreacted amine groups sodium caseinate using a colorimetric assay with *o*-phthaldialdehyde. This method was effective and the results revealed that in the NaC-D10 conjugate, an average of three molecules of dextran reacted with each molecule of NaC. An average of two D65 molecules reacted with each molecule of NaC and one molecule of D35 reacted with each NaC molecule.

The surface/interfacial tensions of the three conjugate solutions were measured to investigate the degree of adsorption of the conjugates at the air/water and oil(canola oil)/water interface using the pendant drop technique. As expected the conjugates were more surface active than sodium caseinate. The emulsifying properties of the conjugates were tested by making oil in water emulsions and determining the approximate particle size and creaming rate. The results showed that for a given surfactant load the size of the emulsion droplets differed with NaC<conjugate D10<conjugate D65. The improved emulsifying properties observed for the sodium caseinate-dextran conjugates show that these conjugates make promising approaches for developing new emulsifying agents.

Poster 30
Score

Thermally Chitosan/Orthophosphate Gelling System

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Directed drug and vaccine delivery has a number of significant advantages over general administration. Controlled delivery allows reduced levels of drug to be administered for similar efficacy. In summary, controlled delivery has both improved patient outcomes and significant economic benefits in reduced drug requirements.

Several different methods have been researched to control directed delivery. A thermally gelling biopolymer system such as chitosan linked with orthophosphate is found to be liquid at room temperature and gelled at body temperature. The molar ratio of chitosan to orthophosphate significantly affects gelling temperature of the system. The lower the ratio, the lower the gelling temperature.

Different molecular weights of chitosan macromolecules also influence the gelling temperature of the cross-linking system. Medium and high molecular weight chitosan exhibits higher gelling temperature than low molecular weight chitosan. However, among low molecular weight chitosan solutions, the lower the molecular weight, the higher the gelling temperature.

The outcome of this study is crucial in optimising the chitosan gelling system which will be applied as a delivery system for drugs and vaccines.

Poster 31
Score

Experimental Studies of the Dynamic and Static Mechanical Response of Single Polymers

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The atomic force microscope (AFM) has become a common tool for investigation of the mechanical response from single polymers. By attaching one end of a polymer to a substrate and the other end to the tip of an AFM-cantilever a Force vs. distance curve can be obtained. Here we have expanded the setup used in the common polymer stretching experiments. By oscillating the substrate by a fixed frequency and amplitude while stretching the polymer a dynamic response from the polymer can be measured in addition to the normal static response. While this is preliminary studies we believe that this new approach can provide novel knowledge of single polymer mechanics.

Poster 32
Score

Molecular Spacers in Powder Coatings

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Powder coating processes (an alternative to solvent based paints) are currently wasteful due to fine particle agglomeration, reducing the fluidisation properties of the powder. Agglomeration tends to be determined by the interparticle interactions, that is, at small interparticle separations. Spacer material can be used to limit the interparticle attraction. For example, low density alumina is used in the powder coating industry with limited effect, as it is not bound to the powder surface.

The aim of this study is to bond various stabilisers to the surface of fine (<5 micron) powder coating particles and investigate the effects these stabilisers have on interparticle agglomeration. Stabilisers of various molecular size were selected to separate particles by various lengths. Stabilisers were successfully bound to the surface of the fine powder coating particles. X-ray photoelectron spectroscopy was used to characterise the surface of uncoated powder coating particles and coated particles.

Bound stabilisers of molecular lengths below 1 nm had little effect on reducing interparticle agglomeration. Stabilisers of greater molecular length reduced interparticle agglomeration, enabling the fluidisation of previously unfluidisable powder coatings.

Poster 33
Score

Dairy Sludge Dewatering: A Novel Approach

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The drive by the dairy industry to employ environmentally and financially sustainable methods of sludge treatment has been the focus of this novel research into dairy sludge dewatering. The aim of this work has been to develop an understanding of the factors that influence the rate and extent of dairy sludge dewatering with a view to developing a knowledge-base to drive decisions relating to the treatment of dairy sludges within the future.

Methods developed by The University of Melbourne to classify the rate and extent of dewatering of biological sludges in terms of the hindered settling function, $R(\phi)$, and compressive yield stress or compressibility, $P_y(\phi)$, (de Kretser *et al.* 2001) were shown to be appropriate for the characterisation of dairy sludge dewatering. The hindered settling function and compressive yield stress of a number of aged and non-aged dairy sludges from aerated lagoons and evaporation basins at plants in Australia and New Zealand was determined. Initial results have suggested that aged dairy sludges are more compressible and exhibit a lower hindered settling function, and therefore a higher permeability, than non-aged dairy sludges. These results provide valuable information about the conditions under which optimum dairy sludge dewatering can be achieved.

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Poster 34
Score

Preparation of Porous Au/TiO₂ Nanocomposite Using an Agarose Gel Template

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Environmental pollution is a global concern, and diverse approaches are being investigated to resolve these issues. TiO₂-based photocatalyst materials are widely researched as titania is non-toxic, readily available and inexpensive. However, the relatively low photocatalytic activity, which may be caused by a high rate of recombination between electron and hole pairs and the requirement of high energy UV radiation to induce the reaction, has yet to be overcome. Hence the ability to either decrease the recombination rate or change the band-gap of titania to allow photoactivity on irradiation with visible light is attracting more and more attention. Recent studies have shown that gold ion doping or gold nanoparticle deposition into TiO₂ is a promising approach leading to such improvements^{1,2}.

The templating technique has been demonstrated to be an effective method to prepare porous materials. The combination of controlled porosity and gold doping to produce porous Au/TiO₂ is a promising approach to further increase the photocatalytic activity due to a higher guest molecule diffusion rate in the porous channels. The objective of this study is to synthesize porous Au/TiO₂ nanocomposite materials with high photoactivity by using agarose gel as a template coupled with the sol-gel method. The effect of gold introduced at various times during the synthesis, the gold concentration and the reduction method on the properties of the materials are being investigated.

The templating technique produced homogeneously porous Au/TiO₂ materials. Analysis using X-ray diffraction determined the synthesised materials to be crystalline with the anatase phase. Comparison between the control sample (TiO₂) and the gold doped materials (Au/TiO₂) showed significant colour differences due to the successful incorporation of the gold species. The samples have been studied using scanning electron microscopy and transmission electron microscopy to determine the stability of the porous network and the size of the particles with the variation in synthesis routes.

The significance of this work is that it provides a novel method to fabricate porous Au/TiO₂ composite materials which have the potential to enhance the diffusion rate for the probe molecule to access the active sites of the catalysts during photocatalytic applications. A specific photocatalytic reaction to ascertain the diffusion improvement is to be conducted in the future.

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2. M I Arabatzis, T Stergiopoulos, D Andreeva, S Kitova, S G Neophytides and P J Falaras, *Catalysis* 220: 127 (2003).

Poster 35
Score

Cadmium Chalcogenide Quantum Dot Surface Chemistry

Aidan Young¹, James McQuillan¹, and David Green²

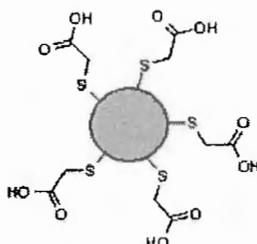
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Quantum dots are crystalline inorganic fluorophore particles (typically 2-10 nm in diameter) with applications in biological imaging and analysis. Cadmium chalcogenides, CdS, CdSe and CdTe, are often studied. Quantum dots as fluorophores have significant advantages over conventional dyes. The emission spectrum is very narrow (FWHM < 50 nm) allowing simultaneous analysis of multiple fluorophores. The emission wavelength is tuneable from the near UV to near IR regions, by altering the size and composition of the inorganic core during synthesis. The excitation spectrum is very broad allowing multiple fluorophores to be excited by a single wavelength. Surface capping ligands are used to alter the nanocrystal solubility in differing solvents. Surface capped quantum dots are prone to degradation in solution with the weakest point usually being the interaction between the inorganic core surface atoms and capping ligand functional group. The nanocrystal stability in solution is dependent on this interaction.

This research investigates the surface chemistry of cadmium chalcogenides. Surface ligand exchange reactions upon thin films are observed *in situ* with attenuated total reflection IR (ATR-IR) spectroscopy and photoluminescence spectrophotometry. Initial studies are being applied to CdS nanocrystals, an easily prepared and well studied compound. These methodologies will be adapted to CdSe nanocrystals.



Two ligands commonly employed with cadmium chalcogenides are mercaptoacetic acid (HSCH₂COOH) and dihydrolipoic acid (HS(CH₂)₂CHSH(CH₂)₄CO₂H). These ligands bind to cadmium chalcogenides via the thiol functional group, leaving the carboxylic acid exposed to the surface for further reaction. DHLA having chelating thiol groups bind cadmium chalcogenides stronger than MAA. The binding ability of these two ligands is being studied and compared, and any decomposition products investigated. Surface carbonate ligands appear to be removed upon binding of DHLA, while MAA binding produces no observed loss. This evidence suggests different surface binding sites for the two ligands.

Poster 36
Score

Mixed Micelle Formation in Polyethylene Oxide/Dodecyl Sulfate Solutions

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Poly(ethylene oxide) (PEO) dissolved in water associates with anionic dodecyl sulfate to form PEO-DS⁻ aggregates which can be described as mixed micelles. For such a mixed micelle, the polymer is wrapped around the surfactant micelle, and many surfactant monomers are complexed with the polymer.

From the structure of the PEO-DS⁻ mixed micelle, we suggest that different counterions and different PEO monomers may affect mixed micelle structure.

We used PEO with different molecular weight to investigate its effect on the critical micelle concentration of lithium and sodium dodecyl sulfate, and the Krafft temperature of potassium dodecyl sulfate.

Poster 37
Score

Sonochemical Cross-Linking of Proteins in Aqueous Solutions

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Proteinaceous microspheres have a wide range of applications that includes micro-encapsulation of dyes, flavours and fragrances, as drug-delivery systems and ultrasound contrast agents.¹ It has been reported that the cross-linkage between protein molecules can be induced by acoustic cavitation-induced physical and chemical processes that include the involvement of highly reactive radicals.² This study involves the use of sonochemical cross-linking between protein molecules for synthesizing proteinaceous microspheres that can be used for encapsulating fluorescent molecules and as ultrasound contrast agents.

A 20 kHz ultrasound generator coupled with a horn-type transducer is used for the sonication of aqueous solutions containing dispersed proteins such as bovine serum albumin (BSA). BSA microspheres, produced after 3-10 minutes of sonication, are filtered and dried. The conversion % of protein to microspheres is calculated gravimetrically.

The results obtained to date indicate that the sonication of an aqueous solution containing dispersed proteins (e.g., BSA) results in the formation of microspheres with diameters in the size range, 1-5 micrometre, as determined by SEM and dynamic light-scattering techniques. Confocal microscopy has also been used to characterise these microspheres. The conversion % of protein to microspheres increases with an increase in the ultrasonic power. Our preliminary study has also shown that aqueous solutions containing fluorescent solutes such as fluorescein can be encapsulated within these microspheres.

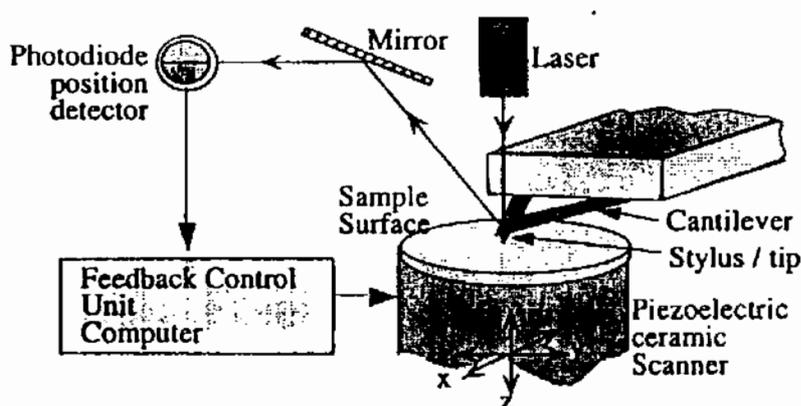
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Poster 38
Score

Experimental Techniques

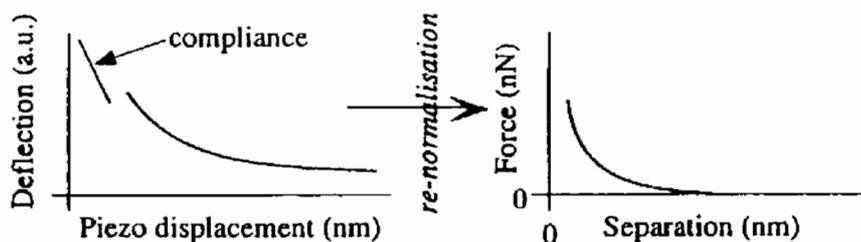
(Atomic) Force Microscopy

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, and 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 $O(\text{pN} - \mu\text{N})$, distance $O(\text{\AA} - \mu\text{m})$ }. Tip composition and geometry may be varied.

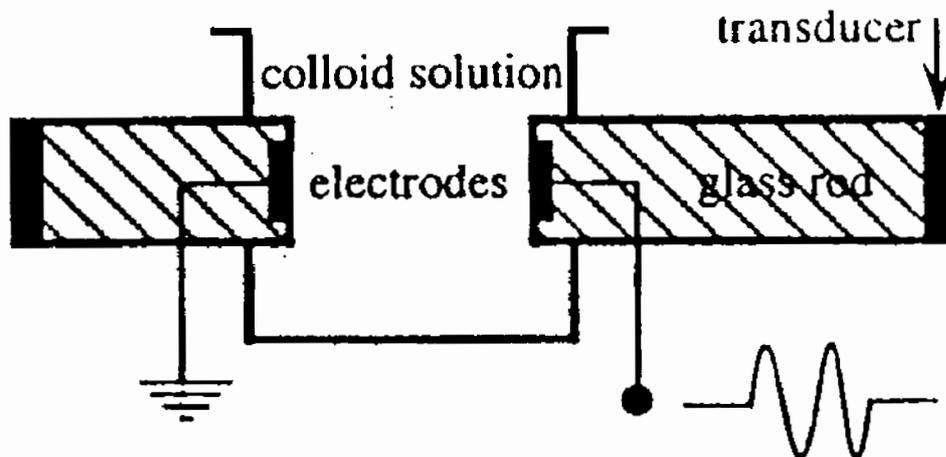


Suggested Reading

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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.

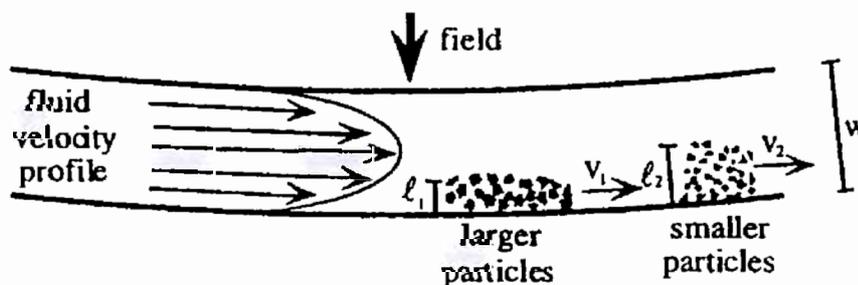
The dynamic mobility is a complex quantity equal in magnitude to the ratio of the particle velocity divided by the applied field. It is complex because there is a phase lag between driving frequency and the response of the particles to that field. As the applied field tends to zero the mobility becomes 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^{-11} 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

R W O'Brien, D W Cannon and W N Rowlands, *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.

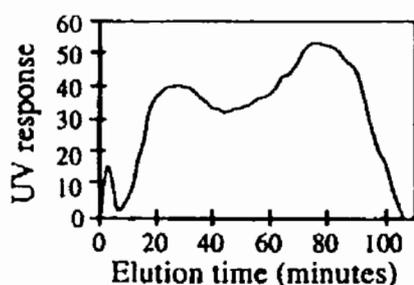


A schematic diagram of a sedimentation FFF channel.

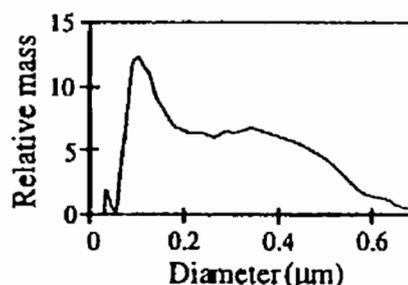
The data obtained is called a fractogram. The elution time can be converted to particle diameter using the equation;

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

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

J C Giddings, 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

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M C Fuerstenau, J D Miller and M C Kuhn, *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

$$|g(\tau)| = \exp(-\Gamma \tau)$$

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

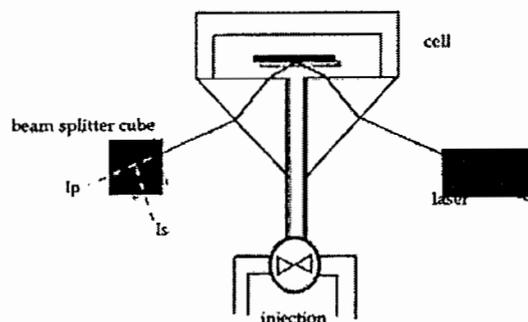
$$\frac{Hc}{R(\theta, c)} = \frac{1}{M_w} \left[1 + \frac{r_g^2 K^2}{3} \right] + 2A_2 c$$

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

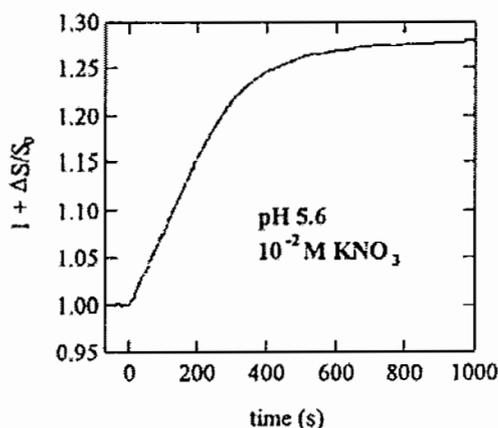
Reflectometry

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 ($\Delta S/S_0$) 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 polymer 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 confirmation 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

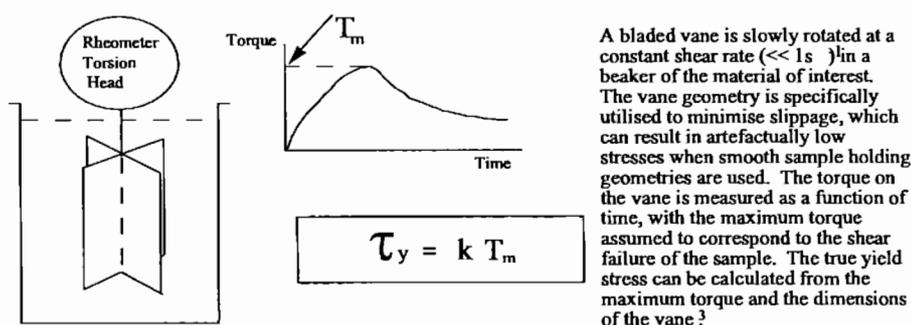
J C Dijt, M A Chohen Stuart, J E Hofman and G J Fler, *Colloids and Surfaces* 51: 141 (1990).

Summary provided by Rob Hayes

Concentric Cylinder 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 measurable shear rates (10^{-6} to 10^4 s^{-1}) and dynamic stresses or strains. Cone and plate is the preferred 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-structure¹. 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.



Schematic of the Vane technique for yield value determination

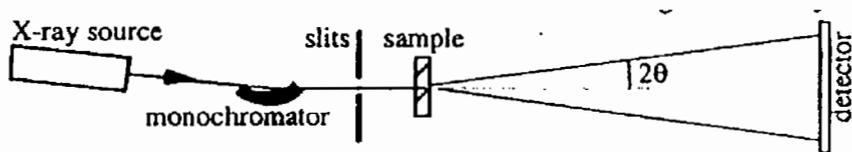
The viscoelastic characteristics of colloidal systems are also characterised by concentric cylinder rheometry, through measurement of the response to application of a sinusoidal stress or strain. G' , the storage or elastic modulus and G'' , the loss or viscous modulus, are determined from the stress-strain 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 system¹.

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3. Q D Nguyen and D V Boger, J. Rheol. 27: 321 (1985).

Summary provided by Clive Prestidge

Small Angle X-Ray Scattering

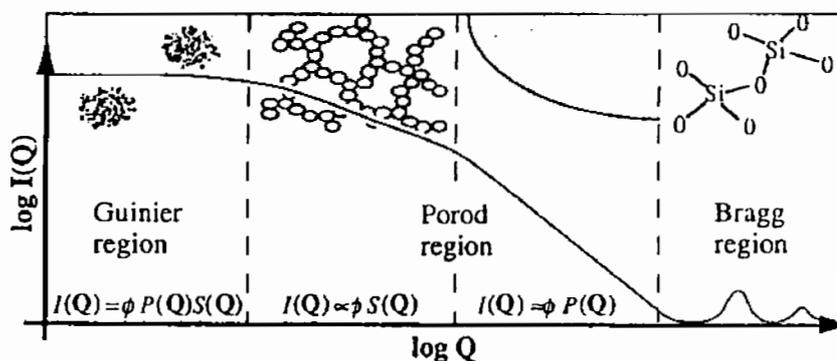
Small angle X-ray scattering allows the physical characteristics - dimensions, surface roughness and spatial arrangement - of particles (\AA 10 - 1000 \AA) in solution to be studied. In practice a collimated beam of monochromatic X-rays is passed through the sample and the intensity of scattering measured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



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, ρ_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, ρ 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, $(\rho_1 - \rho_2)$, where ρ_1 and ρ_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 $(\rho_1 - \rho_2)^2$ 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.

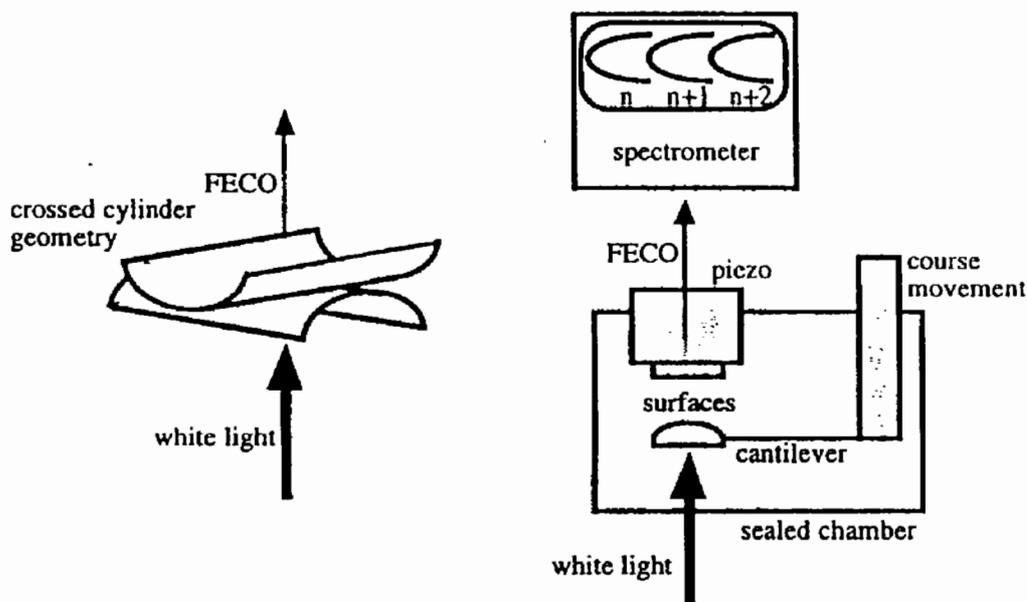
Suggested Reading

O Glatter and O Kratky, (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 ($O(\mu\text{m})$) 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 $O(0.1\mu\text{N}-\text{mN})$, distance $O(\text{\AA}-\mu\text{m})$ }.

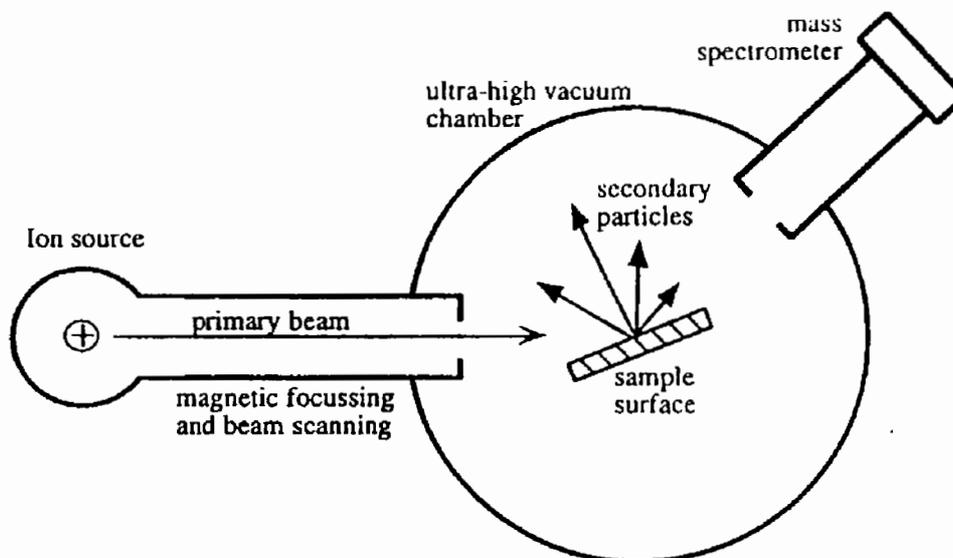
The crossed cylinder geometry approximates well as a sphere, with a radius equal to the geometric mean curvature of the two cylinders, interacting with a plane. Surfaces are restricted to those that can easily form transparent, thin smooth films, e.g. silica, sapphire, mica. Alternatively the interferometer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

Suggested Reading

J N Israelachvili, *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.

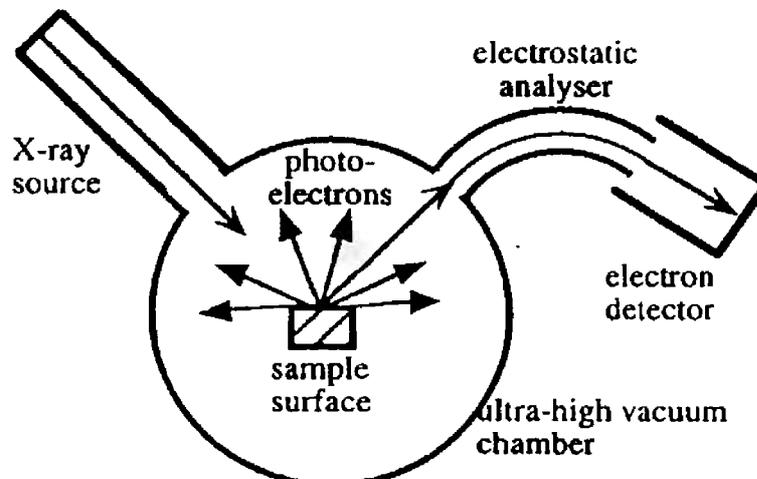
Mass spectroscopy not only provides isotopic discrimination, but both negative and positive species can also be analysed.

Suggested Reading

A Benninghoven, F G Rüdener and H W Werner, *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, $h\nu$ 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

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

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4:00-6:00pm

WINE TASTING

7:00pm-late

CONFERENCE DINNER

Friday 10/2/06

7:00-9:00am

BREAKFAST

10:00am

**BUS DEPARTS
LEAVE FOR HOME**

Amendment

Liquid Crystal Dispersions for Agricultural Application – Phase Behaviour Studies using Phytantriol

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²ANSTO, Lucas Heights, NSW, Australia

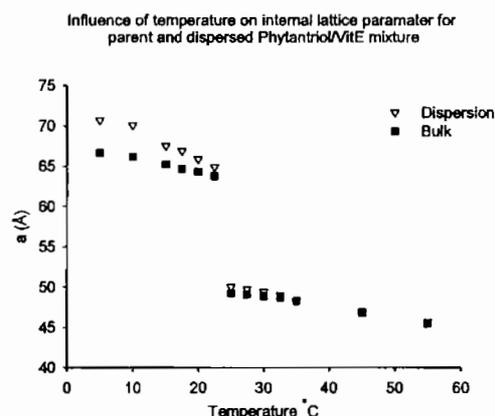
yao-da.dong@vcp.monash.edu.au

Certain amphiphilic polar lipids, when placed in water, spontaneously form thermodynamically stable lipid nanostructures differing in geometric structure, such as the reversed cubic and reversed hexagonal phases. Recent studies have shown that the liquid crystal phases can often be dispersed into nanoparticles with addition of stabilizer whilst retaining their internal 'parent' phase structure (termed Cubosomes and Hexosomes respectively). We are interested in the use of these materials as agricultural delivery systems, which may provide slow release with minimal wash-off in rain. Thus we have an interest in the phase structure of these materials in the nanoparticle form, and have conducted some preliminary studies into the structure of these particles with a view to studying their interaction at surfaces. In this study, we have utilized small angle X-ray scattering to compare the internal structure of dispersed and non-dispersed liquid crystalline systems prepared using GMO and PHYT, the temperature dependence of these structures, and the influence of polymer used to stabilize Cubosomes.



The addition of stabilizer (Poloxamer 407), to Cubosomes made from GMO, is known to induce an increase in lattice spacing at low concentration and conversion from cubic Pn3m to cubic Im3m at higher concentration. In contrast, we have found that Cubosomes made from phytantriol retained the Pn3m structure with minimal change in lattice spacing. Phytantriol cubic phase has significantly smaller lattice spacing than that of glycerol monooleate and we would hypothesise that this inhibits the partition of Poloxamer 407 into the internal cubic nanostructure thereby preventing the phase change.

In these studies we also found that PHYT parent cubic phase in excess water was persisted from 25 to >65 °C. This differs from the reported phase diagram for PHYT which demonstrated conversion of reversed cubic phase to reversed hexagonal at 44 °C and then to reversed micelle phase above 60 °C. We hypothesise that differences may be attributed to the purity of PHYT used, which was supported by the finding that the addition of a very low quantity of Vitamin E to PHYT significantly lowered the cubic to reversed hexagonal phase conversion temperature. The phase structure of the dispersed α -tocopherol/PHYT mixture in excess water was shown by SAXS to be identical to the non-dispersed parent phase, again in contrast to the GMO system.



- Gustafsson, LjusbergWahren, Almgren, and Larsson, "Cubic lipid-water phase dispersed into submicron particles", *Langmuir* 12(20): 4611-4613 (1996).

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 Score

Amendment

Surfactant Self-Assembly in Room-Temperature Ionic Liquids

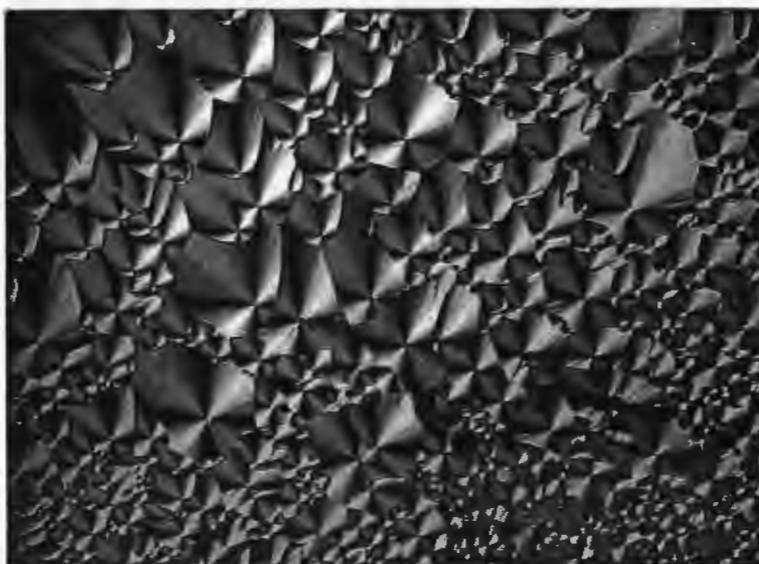
Jeannette McAlpine and Gregory Warr
School of Chemistry, The University of Sydney, NSW 2006, Australia

j.mcalpine@chem.usyd.edu.au

Over the past 12 months, the formation of lyotropic liquid crystals in a hydrogen-bonding ionic liquid has been unambiguously demonstrated.¹ Here we report mesophase formation by polyoxyethylene non-ionic surfactants in room-temperature ionic liquids (RTILs) incapable of supporting a three-dimensional hydrogen-bonding network.

Novel RTILs comprising thiocyanate anions and alkyl and alkanol ammonium cations were synthesised to provide a series of solvents with systematic variations in molecular geometries and hydrogen-bonding capabilities. Polarising optical microscopy was used to examine the self-assembly behaviour of polyoxyethylene glycol esters (C_nE_m , $n = 12-18$, $m = 3-8$) in these solvents; phase compositions were determined by FTIR microscopy.

Mesophase formation was observed for each surfactant and was similar in extent to that reported for the corresponding aqueous system. These results indicate that hydrogen bonding may not be a prerequisite for amphiphilic self-assembly. It is proposed that solvophobic interactions analogous to those that drive aggregation in hydrogen-bonding solvents may be present in systems where solvent structure arises from formation of an electrostatic network.



H₁ phase of C₁₆E₅ in ethylmethylammonium thiocyanate at 18 °C

References

1. M U Araos and G G Warr, Phys. Chem. B 109: 14275-14277 (2005).

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Amendment

Ruthenium Tris (2,2'-Bipyridine) Loaded Nafion/Polypyrrole Composites for Electrochemiluminescent Detection

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The use of electrochemiluminescence (ECL) has gained importance in recent years as an analysis technique for biological and biochemical applications. The immobilisation of the luminescent reagent on an electrode surface would have a number of benefits for analytical systems such as simplicity and enhanced sensitivity. However, many immobilisation strategies previously investigated have suffered from compromised stability.

By pre-concentrating the highly luminescent species Ruthenium tris(2,2'-bipyridine) ($\text{Ru}(\text{bpy})_3$) and pyrrole monomer at an electrode surface within a nafion membrane and then initiating an electropolymerisation reaction, we have formed an ECL sensor which displays good electrochemical stability and displays intense emission in the presence of certain target analytes. Using these Nafion / Polypyrrole composite electrodes, ECL detection of oxalate and tertiary amines has been demonstrated, indicating potential use for biochemical sensing applications including DNA detection.

Both electrochemical and surface characterisations of the sensor have been undertaken. Cyclic voltammetry with *in situ* monitoring of the light emission signal were used to optimise the response. The chemical and elemental composition of the sensing layers was determined using X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

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Score